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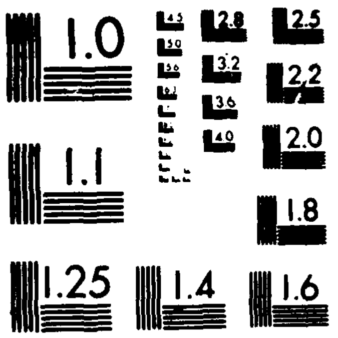

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VOLATILE ORGANIC CARBON EMISSIONS PHASE II

C. A. Jake
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Radford, Virginia 24141-0298

Final Report
February 1987

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Engineering studies evaluated bisulfite (HSO_3^-) absorbent solutions in a bench-scale absorption unit for the control of volatile organic compounds (VOCs) emitted from the manufacture of multi-base propellant at Radford Army Ammunition Plant. An optimization study showed that a dual-column absorption system is required for the removal of solvent vapors: a recycle column containing 15 wt % HSO_3^- absorbent solution and a single-pass column using plant process water. The recycle column concentrated acetone to 1.6 wt % in the absorber bottoms, resulting in 40-85% solvent recovery by distillation; the single-pass column failed to concentrate ethanol sufficiently (i.e., 0.3 wt %) for recovery. The 15 wt % HSO_3^- absorbent solution also destroyed both neat and vaporous nitroglycerin.

Economic analyses of the proposed process designs for the multi-base propellant mixing process and forced air drying operations indicated HSO_3 absorbent systems to be uneconomical.

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Sulfuric acid (H_2SO_4)
Membrane technology
Glycols
Union Carbide's PURASIV HR solvent recovery process

19. Therefore, alternative VOC abatement systems were cursorily evaluated, including glycols and sulfuric acid as absorbents, membrane technology, Ceilcote's VOC control system, and Union Carbide's PURASIV HR solvent recovery process.

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INTRODUCTION

In the production of multi-base propellants at Radford Army Ammunition Plant (RAAP), volatile organic compounds (VOCs) are emitted from the manufacturing processes. A reduction in VOC emissions is necessary based on the requirements cited in the consolidated Virginia - U.S. Environmental Protection Agency (EPA) permit granted to RAAP for the construction and operation of the continuous automated multi-base line (CAMBL) propellant manufacturing facility.[1] This permit controls VOC emissions by limiting the production of multi-base propellants from both the Green Line operations (batch propellant manufacturing facilities) and CAMBL facilities; the permit also contains a condition that RAAP shall investigate methods of controlling VOC emissions from the plant and shall report yearly on the results of these investigations. Furthermore, RAAP is currently operating under waiver of another EPA regulation prohibiting the discharge of VOCs into the atmosphere unless the organic content has been reduced by 85%.[2] This waiver was granted because no safe, economical technology presently exists for the abatement of RAAP's VOC emissions; this project was initiated in order to achieve compliance in the event that this additional EPA regulation is imposed.

Phase I of this project assessed state-of-the-art emission control technology and its applicability to the abatement of VOC emissions in multi-base propellant manufacturing processes.[3] This engineering study conducted an emission survey of multi-base propellant manufacturing operations at RAAP. The VOCs emitted from multi-base operations include ethanol (alcohol), acetone, diethyl ether (ether), nitroglycerin (NG), and other organic compounds. The survey of the Green Line operations during production of M30 propellant formulation showed solvent losses of 37% in the mixing operations and 47% in the forced air drying (FAD) operations based on propellant analyses. Therefore, recovery of these solvent losses would permit approximately 85% VOC reduction required by EPA.

Previous Process Engineering (PE) studies at RAAP addressed the treatment of VOC emissions from the multi-base propellant manufacturing facilities. One study concluded that the acetone and alcohol in the FAD exhaust air were effectively removed for treatment in the biological treatment facility by using a continuous addition of fresh water in a three-sieve plate scrubber.[4] A second study was successful in treating FAD exhaust by NG destruction in a prototype caustic scrubber, followed by water absorption of the solvent vapors.[5] This system used large quantities of water to achieve 85% removal of organics but failed to concentrate the solvents sufficiently in the absorber bottoms (effluent) for economic recovery by distillation. It was, therefore, concluded that the pollution abatement system should not be installed and that studies should continue to improve the efficiency and to reduce the operating costs of the pollution abatement system.

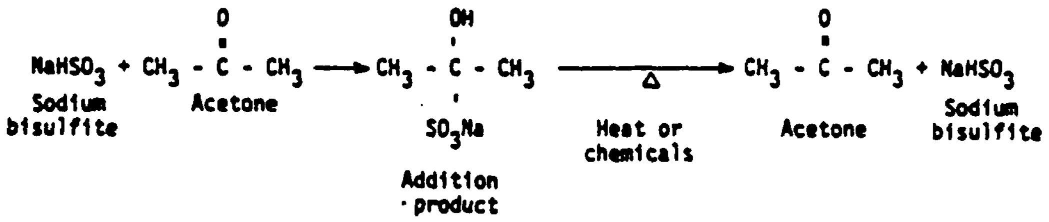
Another PE study evaluated the use of surfactants to enhance the removal of the solvent vapors.[6] This enhanced absorbent system successfully removed the solvent vapors from the exhaust air stream and met all pollution abatement standards; however, the cost of facilitization was excessive in that the solvent recovery aspect of the system proved to be uneconomical. An improved system for solvent recovery in both the Green Lines and FADs is therefore required for economical pollution abatement in the manufacture of multi-base propellants.

Literature and vendor reviews of state-of-the-art technologies summarized in the Phase I study of this project and laboratory-scale absorption studies showed compounds that generate bisulfite ions (HSO_3^-) should prove to be the best absorbents. This project (Phase II) evaluated these HSO_3^- absorbent solutions in the bench-scale absorption unit used during the Phase I engineering studies, including optimization, solvent recovery studies, and NG effects. The optimization study included a review of previous work using HSO_3^- compounds as absorbents to obtain parameters for additional evaluation. The solvent recovery study was a series of absorption/distillation tests conducted to determine design criteria information for a pilot plant to recover VOCs and recycle the absorbent solution. The NG effects study consisted of testing various quantities of NG expected from the multi-base propellant drying operations in HSO_3^- absorbent solutions to determine if the presence of NG as a liquid and vapor interferes with absorbent solution reuse.

Five additional evaluation studies were performed to assess alternate methods of VOC treatment. These special studies included using glycols and sulfuric acid (H_2SO_4) as absorbents, Union Carbide's PURASIV HR and Ceilcote's solvent recovery systems, and membrane technology. A detailed economic study was conducted for a VOC treatment system using HSO_3^-; a cursory study comparing the HSO_3^- system with the most promising methods assessed in the special studies was conducted.

OPTIMIZATION STUDY OF BISULFITE (HSO_3^-) ABSORBENT SOLUTIONS

The Phase I engineering studies showed that compounds which generate HSO_3^- were the best absorbents tested. The mechanism of absorption is sodium bisulfite ($NaHSO_3$) combining with acetone to form a solid, water-soluble crystalline compound known as addition product. The application of heat or chemicals to the addition product reverses the reaction to release acetone and HSO_3^-:



$$\mathrm{NaHSO_3} + \mathrm{CH_3}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3} \longrightarrow \mathrm{CH_3}-\underset{\mathrm{SO_3Na}}{\underset{|}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_3} \xrightarrow[\Delta]{} \mathrm{CH_3}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3} + \mathrm{NaHSO_3}$$

When used in a 3:1 recycle mode, >96% ethanol and 100% acetone were removed from the recycle absorber column inlet gas stream, resulting in 0.51 wt % total solvents in the absorbent.

In order to increase the concentration of solvents in the HSO_3^- absorbent solutions, water quality, recycle and feed rates, and HSO_3^- concentration in the absorbents were evaluated. Compounds that generate HSO_3^- for the absorption of solvent vapors are oxidized from HSO_3^- to sulfate ion (SO_4^{2-}) due to the air in the recycle column inlet gas stream. Oxidation can be controlled by using inert gas as the solvent carrier gas or by adding antioxidants to the HSO_3^- absorbents. Since an inert gas atmosphere for solvent recovery is not available to all RAAP manufacturing areas, an evaluation of solution parameters that affect oxidation of HSO_3^- was conducted.

Furthermore, review of the literature indicated that an increase in both solvent absorption and absorbent reuse could possibly be accomplished at neutral pH; therefore, tests were conducted to optimize the pH level of the HSO_3^- absorbent solutions.

A schematic diagram of the 4-in. diameter bench-scale absorber unit used in both phases of this project is shown in figure 1. During tests, air at ambient temperature is pulled through a cyclone scrubber and a demister column to assure uniform flow and humidity. The air is pulled through the blower and preheated to 38°C (100°F) prior to entering the recycle column. The solvent vapors are introduced into the gas stream by bubbling part of the blower exhaust through a pre-weighed liquid solution of acetone and ethanol and subsequently admitting the vapors generated into the recycle column inlet gas stream. Gases are exhausted from the recycle column at a rate of 9.2 cfm.

Gas and recycled absorbent solution samples were collected every 30 min and 60 min, respectively. Gas samples were taken at the inlet and exit ports of the recycle column by using 100-mg coconut shell charcoal tubes at a sampling rate of 0.5 L/min. The inlet gas was sampled for 2 min and the exit gas was sampled for 6 min. Absorbent solution samples were collected in 1-mL gas chromatographic (GC) sampling vials. All samples were analyzed by GC in accordance with Hercules Methods and tests.

Evaluation of Absorbent Solution Parameters

The concern with absorbent solutions containing HSO_3^- is the oxidation of HSO_3^- to SO_4^{2-} due to the oxygen in the air of the recycle column inlet gas stream. The loss of HSO_3^- results in decreased absorptive efficiency of the absorbent solution for reuse (i.e., recycle). The quality of water used in preparing the HSO_3^- absorbent solution affects the oxidation potential in that less HSO_3^- is lost when softened or chemically treated water is used. This reduction is due to the removal or chelation of the metal ions in the water which catalyze the oxidation reaction.

Water Quality

Four 3:1 recycle/feed rate bench-scale absorber tests were completed with HSO_3^- absorbent solutions. Absorbent solutions of 5 wt % sodium sulfite (Na_2SO_3) at neutral pH (pH of 7) were tested at lower recycle and feed rates than previously reported in the Phase I engineering studies. Each 5 wt % Na_2SO_3 absorbent solution was prepared in a different quality of water to determine the effects of water quality on the oxidation potential of HSO_3^-. The waters selected for testing were plant process water, distilled water, softened water, and chemically treated plant process water containing 5 wt % ethylenediaminetetraacetic acid (EDTA), disodium salt, which is an antioxidant that forms chelates with metal ions in the plant process water.

Test conditions and results together with a baseline water test are summarized in table 1. The 5 wt % Na_2SO_3 absorbent solutions absorbed 79 to 85+% total solvents from the recycle column inlet gas stream whereas plant process water absorbed 51% total solvents. Results reported in the Phase I engineering studies showed that identical absorbent solutions absorbed 98+% total solvents and plant process water absorbed 82% total solvents from the recycle column inlet gas stream. These differences are due to the changes in the recycle and feed rates. It should be noted that the feed rate was 200 mL/min and the recycle rate was 600 mL/min in the Phase I engineering studies whereas the feed rate initially used in this project was 50 mL/min and the recycle rate was 150 mL/min. The lowered feed rates decreased the amounts of solvents absorbed; however, decreasing the feed rates increased the average solvent concentrations in the absorbent solutions by 3.5 to 5 times. The variations of average solvent concentrations in the absorbents follow the trend of lower solvent concentration in the recycle column inlet gas stream, i.e., lower solvent concentrations are obtained in the absorbents.

The effect of water quality is further demonstrated in table 2. The results show less $NaHSO_3$ loss when softened or chemically treated (EDTA) plant process water is used in the 5 wt % Na_2SO_3 absorbent solutions. This is due to the removal or chelation of the metal ions in the water which catalyze the oxidation reaction. The higher amounts of $NaHSO_3$ loss for absorbent solutions prepared with plant process water or tap distilled water (metal distillation equipment) are due to the greater amount of metal ions present.

Comparison of the amount of $NaHSO_3$ lost to sodium sulfate (Na_2SO_4) formed for each of the four 5 wt % Na_2SO_3 absorbent solutions in table 2 indicates that either the acetic acid, acetone, or ethanol interferes with the analytical tests. However, calculations to determine the expected amount of Na_2SO_4 formed in the test solutions were based on the analytical results of $NaHSO_3$ lost since acetic acid, acetone, and ethanol exert minimal interference in this analytical determination. These calculations indicated that softened water or chemically treated (EDTA) plant process water forms less Na_2SO_4.

A review of the plant process water analyses showed 160 mg/L metals present in the water. The amount of EDTA required to chelate 340 mg/L metal as calcium carbonate ($CaCO_3$) is 1 g/L of water; therefore, approximately 0.5-g EDTA/L of water is required to chelate the metals present in the HSO_3^- absorbent solutions (i.e., 0.05 wt % EDTA). This reduces the EDTA chemical demand by 100 times (5 wt % to 0.05 wt % EDTA), resulting in less EDTA usage and improved economics.

Neutralized 5 wt % Na_2SO_3 in distilled water, softened water or 5 wt % EDTA in plant process water absorbed 82 to 85% total solvents from the recycle column inlet gas stream compared to 51% absorbed with plant process water without EDTA (table 1). The 82 to 85% total solvent absorption is approaching the EPA requirement of 85% solvent removal. The 5 wt % Na_2SO_3 absorbent solutions contained an average of 1.04 wt % and 0.98 wt % total solvent concentration in the softened water and EDTA-treated plant process water, respectively, compared to 0.5 wt % total solvent concentration in plant process water. Decreasing the absorbent feed rate also increased the total solvent concentration in the recycle column bottoms. To recover the solvents economically by distillation, 1.4 wt % total solvent concentration is required in the recycle column bottoms. Analytical determinations of HSO_3^- loss as $NaHSO_3$ showed less reduction in HSO_3^- content in the 5 wt % Na_2SO_3/5 wt % EDTA-treated plant process water than other 5 wt % Na_2SO_3 absorbent solutions prepared with different qualities of water.

Recycle and Feed Rate

A review of the literature indicated that a pH of 5 is required for maximum HSO_3^- concentration in the Na_2SO_3 absorbent solutions (fig. 2).[7] The water quality bench-scale absorber tests using 5 wt % Na_2SO_3 absorbent solutions to generate HSO_3^- were conducted at pH 7 which kept the sulfur (S IV) species in equilibrium and may have reduced absorptive efficiency. Therefore, one 10:1 recycle-to-feed bench-scale absorber test was conducted using 5 wt % Na_2SO_3/0.05 wt % EDTA at pH 5. This selected 10:1 recycle-to-feed ratio should improve the absorption of solvent vapors by providing a greater concentration of HSO_3^- (more HSO_3^- solution is recycled; therefore, more HSO_3^- ions are available for solvent absorption). The decreased feed rate should increase the total solvent concentration in the absorber bottoms to possibly attain economic recovery.

Test conditions and results are summarized in table 3. A total solvent concentration of 1.7 wt % was obtained in the recycle column bottoms by decreasing the feed rate and increasing the recycle rate. However, total solvent absorption was only 66.1%. The 1.7 wt % total solvent concentration in the recycle column bottoms met the engineering estimate of 1.4 wt % total solvent concentration required for economic solvent recovery by distillation. However, the percentage of total solvents absorbed from the recycle column gas inlet stream did not meet the EPA requirement of 85% solvent removal.

HSO_3^- Absorbent Solution Concentration

The results of the water quality and recycle/feed rate bench-scale absorber tests indicated that a dual-column system would be required to meet the EPA and economic solvent recovery requirements since only 66.1% total solvent absorption occured in the previous test due to acetone vapors being absorbed by the HSO_3^- and ethanol vapors being exhausted. The bench-scale absorber unit was modified such that the recycle column was used for the absorption of acetone vapors and a single-pass column using plant process water was added for the absorption of ethanol vapors. A schematic diagram of the bench-scale absorber unit is shown in figure 3. During the initial tests, air at ambient temperature is pulled through a cyclone scrubber and a demister column to assure uniform flow and humidity. The air is then preheated to 38°C (100°F) prior to entering the recycle column. The solvent vapors are introduced into the gas stream by bubbling part of the blower exhaust through a pre-weighed liquid solution of acetone and ethanol and subsequently admitting the vapors generated into the recycle column inlet gas stream. The acetone-free gas is exhausted from the recycle column and enters the single-pass column for the counter-current absorption of ethanol vapors. Gases are exhausted from the single-pass column at a rate of 9.2 cfm. A series of tests were conducted, using this dual-column bench-scale absorber unit to determine the optimal HSO_3^- absorption solution composition at two different recycle rates. The first set of tests were conducted with low and high concentrations of HSO_3^- absorbent solutions to determine the effect of HSO_3^- concentration on solvent absorption.

Comparison of 5 wt % Na_2SO_3/0.05 wt % EDTA and 15 wt % Na_2SO_3/0.05 wt % EDTA. Four recycle efficiency tests for determining the absorption rate of acetone were completed. The tests were conducted as a closed system, i.e., fresh absorbent solution was not introduced into the recycle column and the recycled absorbent solution was not removed from the column bottoms except for sampling. Gas samples were collected every 30 min and recycled absorbent solution samples were collected at either 10- or 20-min intervals.

In the two tests using 5 wt % Na_2SO_3/0.05 wt % EDTA at pH 5, the absorbent solutions were recycled for 3 h at 300 mL/min for one test and 1,000 mL/min for the other test. The results are shown in figure 4. After 1 h of operation, the concentration of acetone in the absorbent solution plateaued with the 1,000 mL/min recycled absorbent solution containing 0.4 wt % more acetone than the 300 mL/min recycled absorbent solution. After 2.5 h of operation, an increase of acetone concentration was observed in the absorbent solutions for both tests, indicating that the system probably did not achieve saturation. The ethanol concentration in both absorbent solutions increased to 0.2 wt %.

Two additional tests were conducted using 15 wt % Na_2SO_3/0.05 wt % EDTA at pH 5. Absorbent solutions were recycled for 6 h at 300 mL/min in one test and 1,000 mL/min in the other test. The results are shown in figure 5. Between 80 and 260 min of operation, the

300 mL/min recycled absorbent solution contained 0.6 to 0.8 wt % more acetone than the 1,000 mL/min recycled absorbent solution. Both absorbent solutions continued to absorb acetone beyond 260-min until the tests were terminated. (The system possibly did not achieve saturation.) The ethanol concentration in both absorbent solutions did not exceed 0.2 wt %.

The 5 wt % Na_2SO_3/0.05 wt % EDTA absorbent solutions evaluated earlier did not absorb greater amounts of acetone than the 15 wt % Na_2SO_3/0.05 wt % EDTA absorbent solutions because of the decreased amount of HSO_3^- present for acetone absorption. In general, when the recycle rate of the absorbent solution is increased, more HSO_3^- is available for solvent absorption per unit volume of gas stream to be treated; when the recycle rate of the absorbent solution is decreased, greater contact time of HSO_3^- is provided (at the expense of decreasing the amount of available HSO_3^-) to treat the same unit volume of gas stream. The 1,000 mL/min 5 wt % Na_2SO_3/0.05 wt % EDTA recycled absorbent solution absorbed more acetone than the 300 mL/min 5 wt % Na_2SO_3/0.05 wt % EDTA recycled absorbent solution because the greater recycle rate provided more HSO_3^- available per unit time for acetone absorption. The 300 mL/min 15 wt % Na_2SO_3/0.05 wt % EDTA recycled absorbent solution absorbed more acetone than the 1,000 mL/min 15 wt % Na_2SO_3/0.05 wt % EDTA recycled absorbent solution because the decreased recycle rate provided longer contact time for absorption to occur.

The above series of tests showed that the highest concentrations of HSO_3^- absorbed more acetone. Further comparisons of the effect of HSO_3^- concentrations for acetone absorption were therefore conducted.

<u>Comparison of 20 wt % Na_2SO_3/0.05 wt % EDTA and 20 wt % $Na_2S_2O_5$/0.05 wt % EDTA</u>. Two additional dual-column bench-scale absorber tests were completed. Acidified 20 wt % Na_2SO_3/0.05 wt % EDTA was used for the first test and 20 wt % sodium metabisulfite ($Na_2S_2O_5$)/0.05 wt % EDTA for the other test. The $Na_2S_2O_5$ solution has a pH of approximately 5 and therefore does not require acidification in generating HSO_3^- ions. Plant process water was the single-pass column absorbent solution in both tests. The recycle rates were identical in both tests; the plant process water rates were varied in both tests. The test conditions and results are summarized in table 4.

The results show 20 wt % $Na_2S_2O_5$/0.05 wt % EDTA absorbent solution to be a better absorbent for acetone than acidified 20 wt % Na_2SO_3/0.05 wt % EDTA when the average acetone concentration in the inlet gas and the recycle rates of the absorbent solutions were identical. The ethanol concentrations in the single-pass column absorbent solution (i.e., plant process water) were the same for both tests. These concentrations were expected since the amount of ethanol in the single-pass column inlet gas stream was doubled from test 1 to test 2 with the flow rate also doubled.

A review of the $Na_2S_2O_5$ absorbent solution coordination chemistry confirmed that sulfur dioxide (SO_2) gas can be present and evolve from the solution. To alleviate the SO_2 emissions, Na_2SO_3 was added to the $Na_2S_2O_5$ absorbent solution for SO_2 absorption and further tests performed. Details of the coordination chemistry are presented in a subsequent section (Coordination Chemistry by Ion Chromatography).

Comparison of 15 wt % $Na_2S_2O_5$/0.05 wt % EDTA and 15 wt % $Na_2S_2O_5$/6.5 wt %Na_2SO_3/0.05 wt % EDTA. Two additional tests using the dual-column bench-scale absorber unit were conducted using absorbent solutions that were 15 wt % $Na_2S_2O_5$/0.05 wt % EDTA for the first test and 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA for the other test. These tests were designed to test the effects of gaseous SO_2 in solution. As in the two previous tests, plant process water was the single-pass column absorbent solution in both tests and both the feed and recycle rates of the HSO_3^- absorbent solutions were identical. Test conditions and results are summarized in table 5. The results show 85% and 81% total solvents were absorbed for tests 1 and 2, respectively.

The test 1 recycle column absorbent solution (15 wt % $Na_2S_2O_5$/0.05 wt % EDTA) contained 0.85 wt % solvents in the recycle column bottoms and 0.19 wt % solvents in the single-pass column bottoms. This was due to the test being stopped after 2 h of operation since SO_2 was emitted in the absorber off-gas, thereby not permitting steady-state operation. Test 2 used Na_2SO_3 in the recycle column absorbent solution to absorb any SO_2 formed. The absorbent solution (15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA) contained 1.4 wt % solvents in the recycle column bottoms and 0.14 wt % solvents in the single-pass column bottoms. The percentage of inlet gas solvent absorbed increased as operating time increased; however, the efficiency of the single-pass column decreased with increased operating time as ethanol was exhausted from the recycle column absorbent solution.

Operating Temperature

Four additional bench-scale absorption tests were conducted in the dual-column bench-scale unit to evaluate the effect of temperature on solvent absorption (table 6). The recycled HSO_3^- absorbent solutions were 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA; plant process water (both ambient and chilled) was the single-pass column absorbent solution. Tests 1 and 2 had solvent vapors generated by bubbling a specified air flow through a known solution of liquid solvents. Tests 3 and 4 had solvent vapors generated by vaporizing a specified rate of a known solution of liquid solvents. This technique was used to investigate if a more constant solvent solution could be obtained. Tests 1 and 2 had 1,500 mL/min HSO_3^- absorbent solution recycled with a feed rate of 100 mL/min in the recycle column whereas tests 3 and 4 had 300 mL/min and 50 mL/min, respectively. All tests had 100 mL/min of plant process water fed into the single-pass column with tests 2 and 4 waters being chilled.

More acetone was absorbed in the test 2 recycle column bottoms in the HSO_3^- absorbent solution whereas test 1 absorbed more ethanol in the single-pass column bottoms in water. It was expected to have more ethanol in the test 2 single-pass absorber column bottoms since the water was chilled. Neither test 1 nor 2 absorbed 1 wt % total solvents in the recycle absorber column bottoms; on the other hand, even less solvents were absorbed in the bottoms in tests 3 and 4. Apparently the manner in which the solvents were vaporized for tests 3 and 4 caused less absorption. No conclusive reasons for this anomaly were found. Mass balances on all tests indicated that either sample acquisition, sample preparation, or sample analysis was in gross error. Trend analyses of gas and absorbent solution samples also showed upsets in the system, indicating that steady-state conditions in the tests were not achieved.

Based on discussions with experts in gas sampling and analyses (EPA and Research Triangle), there are apparently no specified EPA methods or standards for gas sampling which are directly applicable to RAAP's VOC exhaust streams. Previous results of gas vs liquor sample analyses indicate more accuracy in liquor analyses. Two tests were therefore initiated to determine where discrepancies in gas and liquor sampling and analyses occur. To determine if the HSO_3^- absorbent solutions were interfering in GC analyses of the solvents, known concentrations of solvent mixtures were prepared in HSO_3^- absorbent solutions and water. These mixtures spanned a large solvent concentration range to determine if solvent concentration also affects the analyses. The results (table 7) show there is a slight discrepancy between the expected concentration of solvents vs the GC analyses; however these discrepancies are minimal and indicate there are no interferences in the liquor analyses.

2^5 Fractional Factorial (1/2 Replicate) Experiment Design

The experimental design of the optimization study is a fractional factorial experiment in which several factors are controlled to investigate their effects at each of two or more levels.[8] These factors were selected based on the results of the earlier evaluations of absorbent solution concentrations, recycle and feed rates, and operating temperatures. The plan consists of taking an observation at each one of all possible combinations that can be formed for the different levels of the factors. The analysis of factorial experiments yields the main effects of a given factor and the presence of interactions. Furthermore, the use of planned grouping (i.e., blocked factorial) improves the precision of estimation of experimental error and allows estimation of the main effects free of block differences.

The 2^5 fractional factorial (1/2 replicate) experimental design for the optimization study is listed in table 8. The Yates' method for obtaining estimates of main effects and interactions for two-level factorials was used in accordance with the Army Material Command AMCP-706 Series.[8] The experiment was conducted as a fractional factorial (1/2 replicate) to reduce the number of tests from thirty-two to sixteen. The sixteen tests were those treatment combinations listed for block 1 (the treatment combinations for observation). It should be noted that the factors (i.e., A, B, C, D, and E) will be confounded (will fail to be discerned) with block effects; in this case the ABCDE interaction is confounded with block effects.

The dual-column bench-scale absorber unit was used to conduct the 2^5 fractional factorial (1/2 replicate) experiment. The recycle column absorbent solutions were 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA and 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA. Plant process water (ambient and chilled) was the single-pass column absorbent solution. Both low and high recycle rates (i.e., 300 and 1500 mL/min) and feed rates (i.e., 25 and 100 mL/min) were evaluated in the recycle column whereas only low and high feed rates (i.e., 80 and 130 mL/min) were evaluated in the single-pass column. The results of the sixteen individual tests conducted in the 2^5 fractional factorial (1/2 replicate) experiment are presented in table 9.

Tests 1 and 2 were conducted under the same conditions for debugging purposes. The percentages of inlet gas solvents absorbed for tests 1 and 2 were 79 and 90, respectively, with the solvent concentration being greater for test 1 than test 2. This discrepancy is due two factors. Problems were encountered in delivering the absorbent solution feed for test 1 resulting in low amounts of solution fed. The decreased absorbent solution feed rate resulted in a higher solvent concentration in the absorbent solution and less recovery of the inlet gas solvents due to the solvents being more readily exhausted with increasing solvent concentration in the absorbent' solution. The other factor for this discrepancy occurred in test 2. The solvent concentrations in the absorbent solution for test 2 suddenly decreased after 2 h of operation. This decrease is not fully understood since no major upsets occurred during this test. This decrease is possibly the result of salts in the absorbent solutions accumulating in the automatic sample injection syringe in the GC thereby causing low analytical analyses of the absorbent solutions. Figures 6 and 7 show the solvent concentration in the absorbent solutions for test 1. Figures 8 and 9 present the solvent concentration in the absorbent solutions for test 2.

The first test conducted in the 2^5 fractional factorial (1/2 replicate) experiment was the bcde interaction. The results show 95% of the inlet gas solvents were absorbed with 0.73 wt % and 0.12 wt % solvent concentration in the absorbent solutions for the recycle and single-pass columns, respectively. Figures 10 and 11 show that the solvent concentrations in the absorbent solutions for this test also decreased suddenly after 3 h of operation. Again, this decrease is not fully understood since no major upsets occurred in the system; however, salts in the absorbent solutions apparently interfered with the analytical analyses.

The abcd and abce interactions resulted in 86% and 91% solvent removal, respectively, which meet the EPA requirement of 85% solvent removal. However, the engineering estimate of 1.4 wt % total solvent concentration in the recycle column bottoms for economic recovery was not achieved by either set of interactions. The ad and (1) interactions did concentrate the solvents in the recycle column to 1.88 wt % and 2.0 wt %, respectively, meeting the engineering economic recovery requirement.

The de and be interactions resulted in 85% and 93% solvent removal, respectively, which also meet the EPA requirement of 85% solvent removal. The engineering estimate of 1.4 wt % total solvent concentration in the recycle column bottoms for economic recovery was achieved by the de interaction but not by the be interaction. The ab interaction also failed to achieve the engineering estimate of 1.4 wt % total solvent concentration in the recycle column bottoms. The ce, cd, and ae interactions did concentrate the solvents in the recycle column bottoms to 2.2 wt %, 3.1 wt %, and 4.0 wt %, respectively, meeting the engineering economic recovery requirement.

The bd, acde, abde, and bc interactions resulted in >85% solvent removal, meeting the EPA requirement of 85% solvent removal. The ac interaction failed to meet the >85% solvent removal EPA requirement. The engineering estimate of 1.4 wt % total solvent concentration in the absorber bottoms for economic recovery was achieved by the acde and ac interactions. The only interactions that meet both the EPA and engineering estimate requirements were the de and acde interactions shown in table 10. The ce interaction was the next best in meeting these requirements.

2^5 Fractional Factorial (1/2 replicate) Experiment Analysis

The 2^5 fractional factorial (1/2 replicate) experimental design for the optimization study is listed in table 8. The Yates' methods for obtaining estimates of main effects and interactions for two-level factorials was used.[8]

The first step in the Yates' procedure is to prepare a table with n+2 columns, where n is the number of factors in the factorial experiment. For the fractional factorial experiments, n is replaced by n' where n' = n-b, with b determining the fractional replicate tested. For this particular experiment, five factors (n=5) were studied with one-half replication (b=1) having sixteen observations. Therefore, tables having six columns (n'+2) were generated. The first column contains the treatment combinations listed in a prescribed standardized order. The second column contains the measured response for the corresponding treatment combination listed in column 1. Columns 3 through 6 contain the systematic procedure of sums and differences between consecutive pairs of data. The entries in column 6 correspond to the ordered effects (g) listed in an additional column, column 7, as the estimated effects of the treatment combinations listed in column 1 for the fractional factorial (1/2 replicate) experiment. Tables 11, 12, and 13 contain the results obtained by using the Yates' method of analysis when the responses are percentage of total solvent removed from the recycle column inlet gas stream, weight percent of solvents concentrated in the recycle absorber column bottoms, and weight percent of solvents concentrated in the single-pass column bottoms, respectively.

The second step in the Yates' method test for significance of main effects of the evaluated factors and interactions is to choose a level of significance, α , and compute the main effect(s) or interaction(s), w. For this particular fractional factorial experiment, the significance of any main effect was determined based on the second-order interactions. These interactions were used as an independent estimate of error since no experimental data were available for estimating purposes. The results of main effects for the responses (individual results presented in tables 11, 12, and 13) are summarized in table 14. These results show the recycle and single-pass column absorbent solution feed rates affect the percentage of solvent removal from the inlet gas streams. The results also show that the recycle column feed rates affect the solvent concentration in the recycle bottoms and the single-pass column bottoms. The solvent concentration in the single-pass absorber column bottoms is also affected by the percentage of HSO_3^- in the recycle column and the single-pass column feed rates.

SOLVENT RECOVERY STUDY OF HSO_3^- ABSORBENT SOLUTIONS

Solvent recovery studies were conducted using 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA (i.e., 5 wt % HSO_3^-) and 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA (i.e., 15 wt % HSO_3^-) absorbent solutions. Five bench-scale absorption/solvent recovery by distillation evaluations on the same (i.e., recirculated) 5 wt % HSO_3^- absorbent solution were completed. Additional efforts to increase the solvent concentration in the recycle column bottoms for solvent recovery using 5 wt % HSO_3^- absorbent solutions were unsuccessful. Six similar evaluations using the 15 wt % HSO_3^- absorbent solution were, on the other hand, successful.

Evaluation of 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA Absorbent Solution

The dual-column bench-scale absorber unit was used for the 5 wt % HSO_3^- absorbent solution evaluations. Plant process water was the single-pass column absorbent. The test parameters selected were those of the de interaction of the fractional factorial (1/2 replicate) experiment which met the EPA requirement of 85% solvent removal and the engineering estimate of 1.4 wt % total solvent concentration in the absorber bottoms. These parameters included 5 wt % HSO_3^- absorbent solution fed into the recycle column at 25 mL/min and recycled at 300 mL/min. The ambient temperature plant process water was fed into the single-pass column at 130 mL/min. Operating times were 4 h instead of 6 h as for the fractional factorial (1/2 replicate) experiment.

The 5 wt % HSO_3^- absorbent solution from the bottoms of the recycle column was batch distilled using a 1-in. diameter Snyder distillation column. The column contained twelve sections, each of which contains a floating ball valve. Rising vapors lift the valves off the seats, allowing condensate to flow down. At the same time, condensate washes the vapors of the heavier water fractions back into the distilling pot. The distilling column was operated in a 3:1 reflux mode, allowing the acetone and ethanol solvent vapors to be enriched as they were condensed as overhead product. The temperature of the distilling pot was 100°C (212°F). The overhead was collected between 56°C (133°F) and 78°C (172°F), the boiling points of acetone and ethanol, respectively.

The test results (table 15) show the EPA VOC removal requirement was met in trial 3 only. When the system had constant absorbent solution feed, steady-state was usually accomplished in 2 h; however, shorter operating times affected system stabilization. The engineering estimate was met in all five trials. The percentage of total solvents recovered by distillation ranged from 40 to 60% due to the low concentration of solvents in the recycle absorber bottoms. The percentage of $Na_2S_2O_5$ decreased with each trial as the percentage of SO_4^{2-} increased.

To assure that steady-state conditions and system stabilization were met, a sixth trial was conducted as described above. This test was conducted for 16 h. The total amount of solvents removed from the recycle column inlet gas stream was 88%, resulting in 2.36 wt % total solvent concentration in the recycle bottoms. The percentage of $Na_2S_2O_5$ loss was 2%. The percentage of solvent recovery by distillation was 40% with the remainder in the 5 wt % HSO_3^- absorbent solution.

To improve upon the percentage of solvent recovered by distillation, two additional trials were conducted. Two liters of 5 wt % HSO_3^- absorbent solution were recirculated in the recycle column at 300 mL/min for each test. One test recirculated the HSO_3^- absorbent solution with no makeup for evaporative losses while the other test used plant process water as makeup in the HSO_3^- absorbent solution. Tests were monitored with an organic vapor analyzer (OVA) to determine total solvent concentrations in the inlet and exit recycle column gas streams. When 75% of the solvents in the inlet gas stream broke through into the exit gas stream of the recycle column, the trials were stopped. The trial with no water makeup ran 4 h while the trial with water makeup ran 3.5 h. The concentrations of the solvents in the recycle bottoms were 3.94% and 2.67% for the trials with no water makeup and water makeup, respectively. The evaporative losses of water from the first trial increased the $Na_2S_2O_5$ content from 5.0 wt % to 9.3 wt % whereas the water makeup in the second trial resulted in the $Na_2S_2O_5$ content decreasing from 4.2 wt % to 3.2 wt %. The increase in solvent concentration in the recycle bottoms resulted in the 83% and 66% solvent recovery by distillation for the trial with no water makeup and the trial with water makeup, respectively.

These above trials indicated that increasing HSO_3^- content increases solvent removal by absorption from the recycle inlet gas stream, thereby increasing the quantity of solvents available for recovery by distillation. According to the results of the fractional factorial (1/2 replicate) experiment, HSO_3^- concentration did not influence the solvent concentration in the recycle column bottoms but slightly influenced the solvent concentration in single-pass column bottoms. Since these findings were based on indiscernable second-order interactions and not the main effects, trials were conducted using 15 wt % HSO_3^- absorbent solutions.

Evaluation of 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA Absorbent Solution

The dual-column bench-scale absorber system was also used for the 15 wt % HSO_3^- absorbent solution evaluations. The 15 wt % HSO_3^- solution was chosen for evaluation since the previous tests had indicated that increasing HSO_3^- content increases solvent removal from the recycle column inlet gas stream which in turn enhances solvent recovery by distillation. The trial parameters were identical to those used in the 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA absorbent solution evaluations, i.e., the de interaction of the fractional factorial (1/2 replicate) experiment with the exception that the operating times ranged from 4.5 to 6.5 h. The results of the six trials are summarized in table 16.

Trial 1 utilized 2 L of 15 wt % HSO_3^- absorbent solution recirculated in the recycle column at 300 mL/min. Plant process water was added as makeup for evaporative losses. The solvent concentration in the recycle column bottoms was 3.39 wt % which resulted in 86% solvent recovery by distillation. The percentage of $Na_2S_2O_5$ loss was 3%. The single-pass column was not in operation during this trial; therefore, total solvents removed from inlet gas stream was not calculated.

Five additional trials using this same absorbent solution were completed. The results showed 96% of the solvents from the recycle column inlet gas stream were removed yielding 4.5 wt % total solvents in the recycle column bottoms for trial 2. The results of trials 3 through 6 show that the EPA requirement was not met. The results also show that, as the $Na_2S_2O_5$ solution is recycled, SO_4^{2-} concentration increases due to oxidation of $Na_2S_2O_5$.

Figures 12 and 13 show the relationship of $Na_2S_2O_5$ and SO_4^{2-} concentration trends before absorption, after absorption, and after distillation testing, respectively, for each trial. As acetone reacts with HSO_3^- during absorption, the concentration of $Na_2S_2O_5$ decreases (fig. 12). After the acetone is distilled from the HSO_3^- absorbent solution, the $Na_2S_2O_5$ concentration increases but does not return to the original concentration for the start of the trial (fig. 12). At the end of trial 6, no $Na_2S_2O_5$ was present after absorption and distillation showing that the absorbent solution was spent (fig. 12). The SO_4^{2-} concentration in the absorbent solution increased throughout testing (fig. 13) due to oxidation of $Na_2S_2O_5$.

EFFECTS OF NITROGLYCERIN (NG) ON HSO_3^- ABSORBENT SOLUTIONS

A review of the literature showed NG vapors were successfully removed in three different ways. One technique for removing NG vapors used a sieve plate column with recirculated water as the absorbent medium and a reservoir of dibutylphthalate (DBP) to act as an inert diluent in the bottom of the column to absorb and desensitize any NG which precipitated from the absorbent water.[4] A second method evaluated was an adsorption system using a styrene-divinylbenzene copolymer resin that effectively adsorbed the NG vapors and allowed the solvent vapors to pass free of any NG contamination.[9] Another method was passing the FAD exhaust air through a caustic absorber containing six sieve plates which successfully removed 99% of the NG from the air.[5]

Based on the literature review and the VOC emission survey conducted in the Phase I engineering studies, the maximal NG concentration that could be removed by the bench-scale absorber unit was calculated. For this NG concentration, the effect of HSO_3^- absorbent solutions on NG was studied.

NG Calculations

Calculations were performed for the maximal NG concentration expected to be considered for the NG effects study. The main assumption for the calculations is that the majority of the NG is lost as VOC when a FAD is on cycle. The basis for these calculations is the existing FADs which use an air flow of 5,500 cfm per bay. The propellant considered in the calculations is M30, a major RAAP production item.

Two sets of calculations were conducted to determine the quantity of NG to be expected in the FAD exhaust air. If 2 lb of NG is added per mix for line loss, the expected concentration of NG in the FAD exhaust is 4 to 5 ppm. Figure 14 shows 2 to 3 ppm is exhausted from a FAD bay drying M30 propellant.[5] If line loss is 1 wt % NG, which occurs with certain M30 propellant formulations, the expected concentration of NG in the FAD exhaust is 14 ppm. Using the worst case of 14 ppm NG exhausted from a FAD and scaling down to the bench-scale absorber unit, the maximal amount of NG expected to be absorbed by an absorbent solution feed rate of 100 mL/min is 850 mg/L.

The theoretical solubility of NG in water is around 1,800 to 2,000 mg/L. Since most M30 propellants exhaust 2 to 3 ppm NG while drying, the representative quantity of NG absorbed in the absorbent solutions would be 350 mg/L NG.

NG Effects

Based on the above discussion, NG effects were studied with neat NG being added to the HSO_3^- absorbent solutions and NG vapors being absorbed into HSO_3^- absorbent solutions.

Liquid NG Effects

The effect of HSO_3^- absorbent solutions on neat NG was studied with absorbent solutions containing an initial concentration of 350 mg/L NG. In the initial study, liquid chromatographic (LC) analyses of NG in the HSO_3^- absorbent solutions showed NG decomposition in the 15 wt % HSO_3^- absorbent solution but not in the 5 wt % HSO_3^- solution. After one week, the NG in the 15 wt % HSO_3^- solution was reduced to only 14 mg/L NG in one sample and no NG was detected in the two other samples. The 5 wt % HSO_3^- absorbent solution contained 250 mg/L NG. Inspection of the 5 wt % HSO_3^- absorbent solution showed NG droplets in the bottom of the samples which could explain these low results. These results, after one week, are summarized below:

Sample	(mg/L)
NG in water	334
NG in 15 wt % HSO_3^- absorbent solution	14
NG in 5 wt % HSO_3^- absorbent solution	247

Based on the LC analytical results, the 15 wt % HSO_3^- absorbent solution might be more desirable for controlling NG even though the 5 wt % HSO_3^- absorbent solution was selected as a good solvent absorbent for economic reasons. The fractional factorial (1/2 replicate) experiment showed there was no significant difference in solvent absorption capabilities between the 5 wt % and 15 wt % HSO_3^- absorbent solutions. (Fresh HSO_3^- absorbent solution was used for each trial of the experiment.) Therefore, either concentration could be used for solvent absorption.

A second study to further delineate the effect of HSO_3^- absorbent solutions on liquid NG was conducted. Absorbent solutions containing an initial concentration of 350 mg/L NG were monitored over time by LC. NG decomposition occurred in the 15 wt % HSO_3^- absorbent solution but not in the 5 wt % HSO_3^- absorbent solution in the first set of tests. A review of the data coupled with additional testing showed the soluble NG in the 5 wt % HSO_3^- absorbent solution was slowly decomposed to dinitroglycerin (DNG) in one week. The insoluble NG in the 5 wt % HSO_3^- absorbent solution remained as NG droplets in the bottom of the samples. When methanol was added to the NG in the 5 wt % HSO_3^- absorbent solution, the NG was solubilized and decomposition to DNG began to occur. Test results are in table 17.

No NG or DNG was detected in the 15 wt % HSO_3^- absorbent solution after one day (table 17). Droplets were observed in the second testing of NG decomposition in the 15 wt % HSO_3^- absorbent solution whereas no droplets were observed in the first test. Ambient temperature differences are believed to be the cause of droplet formation. When these droplets were solubilized by the addition of methanol to the 15 wt % HSO_3^- absorbent solution and analyzed by LC, no NG or DNG were detected after approximately 20 min, indicating that the nitrate esters were decomposed.

Vapor NG Effects

A 4.5-h laboratory-scale study was completed to determine the effect of HSO_3^- absorbent solution on NG vapors. The 15 wt % HSO_3^- absorbent solution was selected since NG decomposition had occurred in absorbent solutions containing an initial concentration of 350 mg/L NG. Solvent vapors were generated by bubbling 0.4 L/min air through a solution of ethanol and acetone in water. This gas stream was preheated to 30°C (86°F) and entered a gas washing bottle containing heated N-5 propellant to generate NG vapors. The solvent/NG gas stream was introduced into a 15 wt % HSO_3^- absorbent solution which was contained in a second gas washing bottle. Figure 15 shows the laboratory-scale unit used for this study.

Samples of the gas washing bottle inlet and exit gas streams were analyzed by GC for ethanol, acetone, and NG concentrations. Figures 16 and 17 show the inlet and exit gas streams' NG and solvent concentrations, respectively. The percentage of NG absorbed was 99+%. All of this NG was destroyed in the 15 wt % HSO_3^- absorbent solution according to LC analyses. Decomposition of NG to DNG was not observed since neither component was detected. The percentage of acetone absorbed was 97+% with most of the ethanol being exhausted (i.e., 65% as shown in fig. 17]. This resulted in 1.2 wt % total solvent concentration in the gas washing bottle bottoms.

PROCESS DESCRIPTION OF HSO_3^- ABSORPTION SYSTEMS

Information from the optimization, solvent recovery, and NG effects studies directed the selection of the HSO_3^- system processing equipment for VOC recovery/reuse and abatement. Preliminary design considerations and criteria, including general safety guidelines (appendix A), of conceptual designs for the pilot-scale mixing operation and FAD exhausts were developed.

Preliminary Design Considerations

Several concerns in the process design were given consideration. These concerns are the treatment of Na_2SO_4 that is formed in the HSO_3^- absorbent solution and the disposal of the residual solvents in the single-pass column bottoms.

Disposal of Residual Solvents

A biological treatment facility for treating the solvent residuals obtained from the single-pass absorber column was selected as part of the preliminary design for the FADs. However, the fugitive emission of solvent vapors from the absorber stream would be expected to be significant, i.e., a large percentage of the solvent would be lost to the atmosphere on pumping and circulation of the water in the biological treatment equalization basin.[5] Other methods of potential treatment of the low solvent concentrations in the absorber bottoms were, therefore, investigated. These methods are activated carbon (AC) and carbonaceous absorbents for solvent recovery.

The adsorption of solvents from simulated green propellant manufacturing wastewater onto AC has been tested.[14] The simulated wastewater contained 950 mg/L ethanol, 303 mg/L acetone, and 293 mg/L diethyl ether. This wastewater was processed through a 400-cc AC column at an average flow rate of 16.8 mL/min (2.1 gal./min/ft^3 of AC). During this test, 25 L of wastewater was processed with effluent samples collected every 1 L for analyses. Results of this test are presented in table 18. The results show that ethanol, acetone, and diethyl ether can be removed from wastewater by AC adsorption. However, the capacity of AC for adsorbing the solvents is small whereas the required capacity for solvent recovery by AC is 55 to 70 wt %. This study did not address the presence of NG and NG incompatibility with AC; however, an earlier study on carbonaceous adsorbents concluded that a total systems safety risk analysis would be required before additional testing with NG and other nitrate esters can be performed (appendix B).[15]

Coordination Chemistry Monitored by Ion Chromatography

Coordination chemistry of the HSO_3^- solutions was completed in which standardization curves were generated according to Hercules test methods as is done for other chromatographic evaluations, e.g., GC and LC. These curves were for % Na_2SO_4 vs % $Na_2S_2O_5$ made-up, % total solids vs % $Na_2S_2O_5$ made-up, pH vs % $Na_2S_2O_5$ made-up, % total solids vs % $Na_2S_2O_5$ titrated by iodine, and % $Na_2S_2O_5$ titrated by iodine vs % $Na_2S_2O_5$ made-up. These solutions were evaluated in the RAAP laboratory by a Dionex 2000i series ion chromatograph (IC). The Dionex 2000i series IC was evaluated as a potential analytical tool to determine its capabilities for analyzing HSO_3^- absorber solutions used for the absorption of acetone and ethanol vapors in the bench-scale absorber unit.

IC is the separation of ionic species using the appropriate chromatographic conditions and the detection of these separated species via the appropriate detection scheme. The basic principles of IC and a flow diagram showing the IC operation is presented in figure 18. An example of an anion standard chromatogram including analytical conditions is shown in figure 19. The purpose of the IC evaluation is to quickly assess the concentration of SO_4^{2-} accumulation in the HSO_3^- absorbent solutions and obtain a profile of the more stable sulfur oxide species present in the solution. The capability of monitoring SO_4^{2-} determines when the absorbent solution is spent and cannot be recycled in the absorption process. A profile of the more stable sulfur oxides (i.e., SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_5^{2-}$) will aid in determining the availability of HSO_3^- present in the absorbent solution for reuse.

Data reduction of absorbent solution IC chromatograms used in bench-scale absorption testing for solvent recovery and standard solutions of HSO_3^- showed SO_4^{2-} was readily separated from the sulfur oxides present in the solutions. The IC anion standard and operating conditions are shown in figure 20.

Initial HSO_3^- absorber solutions used Na_2SO_3 to generate HSO_3^- when neutralized to a pH of 6 to 7. Unneutralized solutions of Na_2SO_3 are shown in figures 21 and 22. The ICs of the solutions show that 1.5% of the 6.5 wt % HSO_3^- solution (fig. 21) and 5.6% of the 15 wt % HSO_3^- solution (fig. 22) consists of SO_3^{2-} and SO_4^{2-} anions. The other sulfur oxides and HSO_3^- were not detected under the IC operating conditions.

Past absorber tests with HSO_3^- showed $Na_2S_2O_5$ to be a better absorbent than neutralized Na_2SO_3. Additional bench-scale testing with $Na_2S_2O_5$ absorbent solutions also showed that Na_2SO_3 is required in the $Na_2S_2O_5$ solutions to absorb any SO_2 emitted in the absorber off-gas. Therefore, a 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3 solution was analyzed by IC (fig. 23). The analysis showed 6.7% SO_4^{2-} was present in this absorbent solution with no sulfur oxides present. Past absorber tests also showed that the addition of EDTA, an antioxidant, inhibits the oxidation of HSO_3^-. A 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA solution was analyzed by IC (fig. 24). This analysis shows 3.4% SO_4^{2-} and 6% SO_3^- present with no other sulfur oxides present. This analysis also indicates that the addition of EDTA reduces sulfur oxide oxidation by approximately one half (6.5% SO_4^{2-} compared to 3.4% SO_4^{2-} in figures 23 and 24, respectively).

Analyses of absorbent solutions used in a bench-scale test were conducted on the 15 wt % HSO_3^- absorbent solution and plant process water before and after the test trial. The before and after analyses of 15 wt % HSO_3^- absorbent solution in plant process water are shown in figures 25 and 26, respectively. An increase in SO_4^{2-} from 1.8% to 2.5% was observed with a decrease in SO_3^{2-} from 5.9 to 5.1% in figures 31 and 32, respectively. No other sulfur oxide species were detected. The before and after analyses of plant process water used in the single-pass absorber column are shown in figures 27 and 28, respectively. The SO_4^{2-} increased from 17 mg/L to 140 mg/L in figures 27 and 28, respectively. This increase is due to a portion of the HSO_3^- solution being carried into the single-pass absorption column.

The IC is capable of determining the concentration of SO_4^{2-} present in HSO_3^- absorbent solutions. However, determining the presence of HSO_3^- and sulfur oxides other than SO_3^{2-} requires additional IC capabilities. $Na_2S_2O_5$, when added to water, acts as $NaHSO_3$ as shown in the following reaction: $Na_2S_2O_5 + H_2O \longrightarrow 2NaHSO_3$. However, solutions of $NaHSO_3$ appear to have four species of the thionate-thionite ion ($S_2O_5^-$) shown in figure 29. At low concentrations, the tautomers (A) and (B) exist. When the concentrations increase, the tautomers interact by hydrogen bonding to form (C) which is in equilibrium with the disulfite ion (D) as shown in figure 29. These tautomers require different IC conditions to establish their presence (SO_3^{2-} and SO_4^{2-} are determined using the IC conditions in figures 20 through 28). The tautomer conditions, including dithionate and tetrathionate analyses, are shown in figure 30.

The IC evaluation showed that concentrations of SO_4^{2-} can be rapidly determined to establish SO_4^{2-} accumulation in HSO_3^- absorbent solutions. The HSO_3^- needs to be determined using the IC column and conditions presented for the thionate-thionite tautomers shown in figure 30. It is concluded that the IC is capable of monitoring SO_4^{2-} to determine when the absorbent solution is spent and cannot be recycled in the absorption process. Also, a profile of the more stable sulfur oxides as thionate-thionite tautomers can be established to determine the availability of HSO_3^- present in the solution for absorption reuse.

Sodium Sulfate (Na_2SO_4) Treatment

The treatment of Na_2SO_4 that is formed in HSO_3^- absorbent solutions by oxidation may be effected in three ways: removal by purge crystallization, the formation of calcium sulfate ($CaSO_4$) for reuse, or Na_2SO_4 reduction in a multiple-hearth furnace (MHF).

Removal of Na_2SO_4 from the HSO_3^- absorbent by the purge crystallization method used in the Wellman-Lord SO_2 recovery system could produce a potentially marketable by-product.[10] The purge crystallization method uses high temperature separation of the sulfate (HTSS). Previously, a low temperature sulfate separation (LTSS) system precipitated Na_2SO_4 from the solution by cooling in a chiller-crystallizer. Advantages of the HTSS process are simplicity, savings in annual energy and operation costs, and few equipment requirements. A disadvantage is the production of a less pure Na_2SO_4 product.

Na_2SO_4 can be converted to $CaSO_4$. Decomposing $CaSO_4$ for reuse in H_2SO_4 manufacture and lime generation has been studied. A final report describes the current status and design criteria for $CaSO_4$ reuse.[11] However, a literature review did not reveal a simplistic technology for converting Na_2SO_4 to $CaSO_4$.

The reduction of Na_2SO_4 in furnaces having a reducing atmosphere for process reuse is documented by the papermill industry.[12,13] One of these processes, the Sulfite Recovery Process (SRP), was selected and modified for future Na_2SO_3 recovery/reuse in the RAAP trinitrotoluene (TNT) purification process.[13] During part of the RAAP SRP operation, excess Na_2SO_4 is converted to hydrogen sulfide (H_2S) and sodium sulfide (Na_2S) in a MHF having a reducing atmosphere. The H_2S is then oxidized to SO_2 in an afterburner and subsequently removed via a Na_2SO_3 solution forming $NaHSO_3$. The $NaHSO_3$ is further processed to Na_2SO_3 in the ash precipitation step of the process. The minor amount of Na_2S from the reducing zone of the MHF is oxidized to Na_2SO_4 which becomes a minor impurity in the ultimate Na_2SO_3 product formed in the ash precipitation step.

Preliminary Design Criteria

Two conceptual designs were developed for solvent recovery of acetone and ethanol emissions from the mix operation in the Green Line multi-base propellant manufacturing area during the Phase I engineering studies. Previous M30 propellant analyses showed 37% of the processing solvents are lost in the mixing operation. Based on the propellant analyses, this is the point of greatest loss in the Green Line area. The designs included an absorber or a condenser in each of the individual mixer bays. Of these mixer designs, the absorber design was selected for solvent recovery using the HSO_3^- system.

Two conceptual designs were also developed for solvent recovery of acetone and ethanol from the FAD exhausts during the Phase I engineering studies. Analyses of M30 propellant showed that 47% of the processing solvents are lost in the drying operation. The designs, which include absorption of the solvent vapors from the FAD exhaust followed by distillation for solvent recovery, were modified for the HSO_3^- system.

Mixer Design

The conceptual absorber design selected for solvent recovery from a mixer bay is shown in figure 31. The concept is based on solvent recovery during the mix dry-down cycle. The propellants are generally oversolvated to obtain proper mixing. In order to achieve the consistency necessary for press extrusion, heat is applied to the mixer shell to remove the bulk of the solvents during the mix dry-down cycle. The inert gas stream used to remove the solvents from the mix is diverted to a recycle absorber containing a liquid absorbent. The absorbent would remove the solvent vapors and the absorber off-gas will be exhausted to the atmosphere through the existing ventilation system in the mixer bay. The absorber bottoms containing the spent absorbent and recovered solvents would then be transported to a central reclamation area for solvent recovery and absorbent regeneration.

The proposed conceptual placement of the solvent recovery units in the individual mixer bays for a typical mix house is shown in figure 32. Mixer design criteria information are listed in table 19. The size of each individual absorber column required for solvent absorption was based on engineering calculations of the inert gas used during a mixer dry-down cycle and information obtained from bench-scale testing (appendix C). The conceptual mixer absorber design for solvent recovery consists of a recycle column 10-ft high by 0.75 ft in diameter containing eighteen theoretical stages of Koch-Sulzer polypropylene-polyacrylonitrile packing. The 15 wt% HSO_3^- absorbent solution recycle-to-feed ratio of 12:1 is 1.4 to 0.1 L/min to treat 35 standard cfm of solvent-laden inert gas.

Forced Air Dry (FAD) Design

The conceptual FAD design consists of a dual-column system for solvent absorption, two distillation towers for solvent recovery, and an abatement facility for treating residual solvents. The FAD design criteria information are listed in table 20. The two columns for solvent absorption are a recycle absorber and a single-pass absorber. The recycle column requires a 12:1 recycle-to-feed ratio using 15 wt % HSO_3^- absorbent solution to treat a liquid-to-gas ratio (L/G) of 1.28 to absorb acetone. The single-pass column for removing ethanol with plant process water requires an L/G ratio of 0.46. The solvent recovery unit consists of two distillation towers for the separation of the solvents from the HSO_3^- absorbent solution. The abatement facility is a biological treatment facility for treating the solvent residuals obtained from the single-pass column.

FAD Solvent Absorption System. Individual solvent absorption units are proposed to be placed on each individual FAD bay resulting in 80 units required (i.e., 4 bays/FAD building, 20 FAD buildings total). The absorption units were modeled by the Flowtran system, a proprietary system of digital computer programs which provide a generalized approach in simulating the steady-state operation of a process by a mathematical model. The simulation of the prototype absorbers assumed a 6 in. height-equivalent-theoretical-plate (HETP) involving nine theoretical stages of Koch-Sulzer packing for the maximum flow of components expected. Figure 33 depicts the flowsheet simulation. The overall results showed 2 ppm acetone and 0 ppm ethanol in the off-gas. This Flowtran model of the prototype absorbers is in agreement with the actual data obtained for the off-gas from pilot plant test trials (3.9 ppm acetone, 4.1 ppm ethanol).[3,5,6] Since Flowtran will not model chemical reactions occurring in absorption units, the use of water as the absorbing liquid was therefore utilized in the solvent absorption design with compensations made for the 15 wt % HSO_3^- absorbent solution. The compensation calculations for the HSO_3^- absorbent solution show 9 ppm acetone and 150 ppm ethanol in the single-pass prototype absorber off-gas.

The flow rates of acetone and ethanol in the FAD exhaust for the Flowtran model were 8.47 lb/h and 10.60 lb/h, respectively. This equates to 688 ppm acetone and 1,102 ppm ethanol, which is the largest amount of solvent vapors exiting the FAD bay during the first 18 h of operation (fig. 34). The Flowtran analyses were performed for the maximum concentration of solvents: the Flowtran system is not capable of adjusting to the decreasing concentration of solvents. Flowtran analyses were also performed at half the concentration of solvent vapors, with the results agreeing with the actual data obtained from pilot plant test trials.[3,5,6]

The following prototype absorber models are proposed. The recycle absorber column will use a 12:1 recycle-to-feed ratio of 15 wt % HSO_3^- absorbent solution. The recycled absorbent will enter the fourth theoretical plate and the feed will enter the ninth plate. The recycle absorber column is to recover 60% of the solvents (i.e., 100% acetone and

20% ethanol) with a solvent concentration of 1.6 wt % in the bottoms for recovery by distillation. The recycle column will be 19-ft high by 2.2 ft in diameter. The single-pass absorber column will utilize plant process water as the absorbent to remove 33% of the solvents as ethanol resulting in 0.25 wt % solvent concentration in the absorber bottoms. The single-pass absorber bottoms are to be treated in a biological treatment facility. The single-pass column will be 19 ft high by 2.0 ft in diameter.

FAD Distillation System. The development of preliminary design criteria for distilling the recycle column bottoms are based on the percentage of solvents recovered by distilling the 15 wt % HSO_3^- absorbent solution that was reused five times and information obtained from the Flowtran simulation.[3,5,6] The bench-scale tests showed that 40 to 85% of the solvents absorbed in the 15 wt % HSO_3^- absorbent solution could be recovered by distillation (table 16). However, the total number of times (i.e., 6) that the 15 wt % HSO_3^- absorbent solution was used showed that after the third usage additional makeup is required to effectively absorb acetone for recovery by distillation. After the HSO_3^- absorbent solution is spent due to SO_4^{2-} accumulation, this solution could be environmentally discharged without violating the RAAP SO_4^{2-} discharge requirements. The Flowtran modeling of distilling the recycle column bottoms could not be accomplished directly since chemical reactions could not be utilized in the recycle absorber model. However, previous Flowtran results are described.[6] This Flowtran model would improve the lesser percentage of solvents recovered by distillation demonstrated in the bench-scale solvent recovery studies. The preliminary design criteria information for the proposed distillation system is in table 21. It should be noted that this design is over-sized for the recycle column bottoms since the model utilized the physical properties of water absorption and not the physical properties of HSO_3^- absorbent solutions. The physical properties are different due to chemical reactions occurring in the HSO_3^- absorbent solution.

The distillation process obtained from the Flowtran analyses consisted of two distillation columns, each sized to accommodate the bottoms from twenty FAD absorbers. The absorber bottoms are fed to the first column from which acetone and the ethanol-water azeotrope are taken overhead and solvent-free water discharged from the base. The overhead is then fed to the second column from which acetone (maximum ethanol content of 0.06 wt %) is produced as an overhead product, with ethanol (maximum 0.3 wt % acetone and 8.9 wt % water) being produced as bottoms. The actual flow of the components obtained from the Flowtran absorber models and bench-scale data are also shown in figure 35.

The first distillation column contained thirty-six sieve trays with downcomers having a tray efficiency of 48% and a reflux ratio of 10:1. The column height was 72.5 ft. The column diameter required was dependent upon the vapor rate and was estimated to be 2 ft. Thus, a 2-ft diameter column has sufficient capacity to accommodate the solvent from twenty operating FAD's when the dryers are exhausting maximum solvent concentration for 2 h. When the dryers are exhausting the average solvent concentration for 17 h, the turn-down ratio is not affected and the 2 ft-diameter column can be used.

FAD Biological Treatment Facility. The biological treatment facility to treat the bottoms of the single-pass absorber column was sized to accommodate the bottoms from twenty absorbers. The amount of chemical oxygen demand (COD) determines the size of the biological treatment facility. Therefore, to treat 7.2 lb/h of ethanol, the COD would be 18 lb/h for each FAD. For a FAD system containing twenty units, the facility would treat 18 lb/h x 24 h x 20 FAD units = 8,640 lb COD/day. To treat 8,640 lb COD/day would require an additional twelve 25-ft rotating biological contactors (RBC). This is the same size plant previously reported in the modernized FAD studies.[5] Figure 36 shows the facility size and costs that were reported in the modernized FAD studies to treat 9,312 lb COD/day; identical facilities are required to treat 8,640 lb COD/day from the single-pass absorber columns.

PROCESS ECONOMICS OF HSO_3^- ABSORBENT SYSTEMS

The economic analyses were performed for the installation of HSO_3^- absorbent systems on the mixer bays and on the FAD bays. These solvent recovery systems meet the Virginia Air Quality Standards of 85% solvent removal and the 1.4 wt % solvents in the recycle absorber column bottoms necessary for economic recovery by distillation. The official inflation factors used for Production Support and Equipment Replacement (PS&ER) projects [AMSMC-BP(R)] were utilized in generating rough order of magnitude (ROM) costs in CY86 dollars. The ROM estimate does include the Corps of Engineering costs.

Mixer Absorption Equipment

An economic analysis of installing and operating thirty-six mixer absorbers (12 bays/mixer building, 3 buildings) with ambient temperature 15 wt % HSO_3^- absorbent solution in a 12:1 recycle-to-feed rate was performed. Appendix D contains the ROM estimate and complete cost analysis.

The column shell costs were estimated for three 4-ft sections of 316 stainless steel as described by Hall, Matley, and McNaughton.[16] The packing costs were obtained from previous Flowtran analysis. The installed costs were estimated by the Lang method mentioned by Hall, Matley, and McNaughton.[16] These costs were for CY82 and were updated using the PS&ER inflationary factors.

The operating costs were based on one operator per shift with maintenance occurring every two weeks. The chemical costs of the 15 wt % HSO_3^- absorbent solution considered solution usage of three times before makeup is required or the solution is spent.[17,18] The assumption of 5-min dry-down cycles per mix was made. The average number of mixes per shift, based on the Green Line emission survey described in the Phase I engineering studies, is 30. Utility costs were calculated for the absorber recycle pump and absorber feed pump.[19] Solvent savings assume a minimum of 1.6 wt % total solvents in the absorber bottoms which can be recovered at the proposed FAD distillation site.

The ROM estimate (appendix D) for the installation of 36 mixer absorbers per 3 mixer buildings was $5,592,000 (CY86 dollars). Operating costs for the facilities would be $69,300 per year.

FAD Solvent Absorption, Distillation, and Treatment Facilities

Economic analyses were performed for the installation and operation of eighty recycle absorbers (i.e., four bays/FAD building, twenty FAD buildings total) and eighty single-pass absorbers for the solvent absorption system, a distillation system to recover the solvents from twenty FAD recycle absorbers, and a biological treatment facility to treat the residual solvents from twenty single-pass absorbers.

FAD Solvent Absorption System

An economic analysis of installing and operating eighty recycle absorbers with ambient temperature 15 wt % HSO_3^- absorbent solution and eighty single-pass absorbers with ambient temperature plant process water was completed. The 15 wt % HSO_3^- absorbent solution is 12:1 recycle-to-feed ratio for the recycle absorber to treat a L/G of 1.28 to absorb acetone. The single-pass absorber will treat a L/G of 0.46. Appendix D contains the ROM estimate and complete cost analysis.

The recycle and single-pass column shells and packing costs (capital costs) and installed costs of the dual-column absorption process were obtained from Flowtran analyses.[6]

The operating, maintenance, and utility costs were based on actual field data obtained from the modernized FAD study.[5] These costs were based on CY83 rates and were inflated to CY86 rates. The chemical costs of the 15 wt % HSO_3^- absorbent solution considered solution usage of three times before makeup is required or the solution is spent. The assumptions of 8.5 lb/h acetone and 2.1 lb/h ethanol are recoverable in the recycle absorber and that 7.2 lb/h ethanol is removed by the single-pass absorber were made (refer to process description section and fig. 33). These assumptions result in 1.6 wt % solvents concentrated in the recycle absorber bottoms.

The ROM estimate (appendix D) for installing eighty solvent absorption units per 20 FAD buildings was $24,452,700. Operating costs for the solvent absorption units would be $3,186,200.

FAD Distillation System

The existing distillation facilities at RAAP that were utilized in the manufacture of diethyl ether were not investigated for the distillation of the bottoms from the proposed FAD recycle absorbers. The material of construction of these facilities is copper which will erode in the presence of the HSO_3^- absorbent solution. However, an economic analysis for distilling the absorber bottoms from the Flowtran recycle model was conducted. This analysis is for the distillation system described in the process description section of this report. The economics are presented in appendix D.

The column shells and packing costs (capital costs) and installed costs were obtained from Flowtran analyses. The condensers, reboilers, and utility costs were also obtained from Flowtran analyses.

In order to estimate distillation costs for recovering acetone and alcohol from the exhaust of 20 FAD buildings assuming 50% downtime, one system containing two 2-ft columns is required based on the vapor rate and turn-down ratios.

The ROM estimate for installing one distillation system to accommodate the bottoms from eighty FAD recycle absorbers was $4,223,000. Operating costs for the facilities would be $1,092,240 per year. Annual savings of $166,690 would result from the recovery of solvents. Therefore, the net operating costs would be $925,550.

FAD Biological Treatment Facility

The biological treatment facility to treat the bottoms of the single-pass absorber column was sized to accommodate twenty absorbers. The plant size is twelve new 25-ft RBCs. This is the same size plant previously reported in the modernized FAD studies.[5] Figure 36 shows the costs in FY82 dollars. This cost would be $7,813,000 in FY86 dollars.

Operating costs require 25 man shifts per week resulting in $232,860. Maintenance cost would be $18,000.[5] Chemical costs would be $21,640.[5] Electrical costs would be $24,000.[5] This results in an annual operating cost of $296,500 (FY86 dollars).

Summary of Process Economics

The HSO_3^- solvent recovery systems designed for intallation on the mixer bays and on the FAD buildings were analyzed for process economics as applied to RAAP's production facilities. The following summarizes the economic analyses of the HSO_3^- solvent recovery systems which will meet the Virginia Air Quality Standards of 85% solvent removal:

Installation location	Facilities costs (ROM $)	Annual operating costs (ROM $)
Mixer process		
36 mixer absorbers	5,592,000	69,300
FAD process		
80 recycle absorbers	24,452,700	3,186,200
80 single-pass absorbers		
Distillation system	4,223,000	1,092,240

Installation location	Facilities costs (ROM $)	Annual operating costs (ROM $)
Biological treatment	7,813,000	296,500
Recovered solvents	-	-166,690*
Total	42,080,700	4,477,500

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*Value of recovered solvents.

SPECIAL STUDIES

The solvent recovery/reuse deficiencies of the HSO_3^- absorbent system are two-fold. First, the recycle absorber column removes acetone but not ethanol for recovery/reuse. Second, the single-pass absorber column removes ethanol but not sufficiently for recovery/reuse. The economic deficiencies of the HSO_3^- absorbent system are four-fold. First, two columns instead of one are required for solvent absorption. Second, the recovery of acetone from the recycle column by distillation in RAAP's existing ether manufacturing facility may not be suitable due to HSO_3^- eroding the copper in the towers. Third, the costs of chemicals to prepare HSO_3^- absorbent solution are excessively high. Fourth, the costs of additional facilities for ethanol treatment would also be prohibitive. Due to these required improvement for the HSO_3^- absorbent system, five separate cursory studies were conducted in order to define possible alternatives to the HSO_3^- absorbent system.

Glycols as Absorbents

Previous laboratory studies (Phase I engineering studies) indicated that diethylene glycol (DEG) and triethylene glycol (TEG) were borderline absorbents. The dual-column bench-scale absorber unit was used to evaluate DEG and TEG absorptive capabilities for acetone and ethanol vapors. Both the recycle and single-pass columns used the same glycol as the absorbent in each test to obtain recycle and single-pass column absorption information on each glycol.

Test conditions and results are summarized in table 22. The results show that the DEG absorbent solution absorbed 80.5% of the total solvents indicating DEG could possibly be used to meet the EPA requirement of 85% solvent removal. However, the DEG total solvent concentration of 0.21 wt % does not meet the economic recovery requirement of 1.4 wt %. The results for TEG absorbent solution show TEG is a poor absorbent since none of the solvents were absorbed. The row labeled "Inlet gas solvent absorbed (%)" in table 21 shows <-100%, indicating that all solvents were exhausted in the absorber off-gas after a small level of solvents from the absorber inlet gas stream was concentrated in the TEG absorbent solution. The TEG total solvent concentration of 0.22 wt % is therefore based on the maximum amount of solvents that were absorbed by TEG before being exhausted; the TEG total solvent concentration does not meet the economic recovery requirement.

Union Carbide PURASIV HR Solvent Recovery System

Union Carbide's PURASIV HR solvent recovery system utilizes the unique physical properties of beaded activated carbon (AC) to perform a continuous, indirectly heated solvent recovery via carbon adsorption. Figure 37 contains Union Carbide's description of the system.

The AC adsorption system provides an efficient method of removing small quantities of organic solvents from gas streams. However, its use for solvent recovery from multi-base propellant manufacturing operations has been rejected in the past due to the incompatibility of NG with AC. The earlier systems were fixed-bed batch systems, incorporating long contact times between the NG and AC and regeneration of the carbon bed. The PURASIV HR solvent recovery system is a fluidized bed operation that presents several advantages, e.g., short contact time, short regeneration process, and inert atmosphere, etc.

A Preliminary Hazards Analysis (PHA) determined that the proposed concept for using the PURASIV HR fluidized carbon bed solvent recovery system is not safe for solvent recovery from solvent vapor/air mixtures laden with NG as described in appendix E.

Membrane Technology

A membrane process for the recovery of solvents from gas streams was developed by Membrane Technology and Research, Inc. [(MTR), Menlo Park, CA]. The proposed process and process description is shown in Figure 38. An abbreviated compilation of membrane terminology is presented in table 23. The field unit is a 100-ft^2 membrane area unit of spiral-wound membranes that treats 100 standard cfm of feed. The membranes have an active layer of silicone rubber supported on a polysulfone compound. The average solvent concentration in the treated gas streams was 0.5% [5,000 ppm (v/v)] of chlorinated hydrocarbons. This average solvent concentration in the gas streams is also the average concentration of solvents that are emitted as VOCs from the multi-base propellant manufacturing operations at RAAP. Furthermore, two of the solvents screened by MTR are acetone and ethanol, solvents which are emitted at RAAP.

Two membrane systems were screened in MTR's laboratory for the recovery of 1,500 ppm acetone vapors, the most difficult solvent to be recovered with membranes. Experimental testing of a 4-μ thick silicone rubber membrane module (2,000 cm^2 active membrane) was conducted. The feed contained 1,500 ppm acetone in nitrogen (N_2). The pressure drop between the feed and residue was 0.8 psi. The permeate pressure was 17.9 mmHg (vacuum). These conditions resulted in a permeate concentration of 8.0% acetone when the residue stream was recycled into the feed stream. The separation factor (β) was 53.3 and the selectivity factor (α) was >52.2. The membrane flex (J) for this small laboratory-scale unit was 1.22 $L/m^2 \cdot d$.

Another membrane module underwent experimental testing. This module was a composite spiral-wound membrane consisting of three membrane layers: silicone rubber, Kraton, and silicone rubber. The membranes were 4-μ thick having 2,300 cm^2 of active membrane. The feed for this test contained 1,400 ppm acetone in N_2. The pressure drop between the feed and residue was 0.9 psi. The permeate pressure was 14.3 mmHg (vacuum). The residue stream was recycled into the feed stream resulting in a permeate concentration of 14% acetone. The β was 100 and the α was >98. The J was only 0.36 $L/m^2 \cdot d$.

The NG compatibility testing of the spiral-wound membrane supplied by MTR produced a pressure of 191 mmHg with HEN-12 propellant. Any substance is considered incompatible if a pressure of 200+ mmHg is obtained; the spiral-wound membrane is therefore borderline in this test. The basic membrane material was subjected to NG compatibility testing to determine if other components in the spiral-wrapping of the membrane caused the high results. The NG compatibility testing of the basic membrane material detected 0 mmHg with HEN-12 propellant; the basic membrane is therefore compatible with NG. The NG absorptivity on the basic membrane was 76.19% absorbed (4.89 mg/cm^2). NG absorptivity is conducted with neat NG to allow maximal absorption. If this technology were further evaluated for the recovery of solvent vapors from gas streams, the presence of low NG vapor concentrations would require Hazards Analysis investigation.

Ceilcote Solvent Recovery System

The Ceilcote solvent recovery system [The Ceilcote Company (Berea, OH)] is a continuous, closed-loop absorption process for removal of VOCs. The absorbent fluid for the VOCs is a proprietary high-boiling point organic liquid. This fluid is inexpensive and does not deteriorate with age or use. Furthermore, due to the fluid's high boiling point and low vapor pressure, small amounts are required for makeup to the system. The principle of operation is described in figure 39.

A proposal for the recovery of VOC from one FAD bay was prepared by Ceilcote. Part of the proposal is contained in appendix F. The equipment cost for one solvent recovery unit is $195,000. The operating cost is $4.45/h for electrical usage or $2.10/h for steam usage for heating. However, the system uses high-pressure (400-lb) steam which is not available in the FAD area. Also, the total plant does not have the steam capacity to support this type of system. In addition, the NG vapors may be condensed on the internal condenser; therefore, the process may not meet safety requirements.

Sulfuric Acid as a Potential Absorbent

A cursory literature search to determine a more effective absorbent than water for ethanol absorption resulted in H_2SO_4 being identified as an absorbent for combined vapors of ethanol and diethyl ether from air.[20] Ormandy also described a process for the recovery of acetone from air by using chilled H_2SO_4 as an absorbent.[21]

H_2SO_4 was first used for the absorption and recovery of ethanol and diethyl ether vapors in the manufacture of artificial silk by the Chardonnet process. The technology was then applied in the manufacture of propellant in Germany and Austria before and during World War I.[22] The methods of solvent absorption were passing the solvent-laden air up through tanks that were cooled from the outside by spraying with water and by counter-current absorption in the lead towers.[22] The solvents were distilled at 120°C (248°F) for recovery resulting in partial conversion of ethanol to diethyl ether and low solvent yields.[20,22] These disadvantages plus the corrosive nature of H_2SO_4 rendered the process to be discontinued after World War I.

Figure 40 contains the conceptual design described by Ormandy in 1929, for recovering acetone vapors in H_2SO_4.[20,21] Three major changes in Ormandy's design make the use of H_2SO_4 a possible absorbent candidate. One change is the temperature requirement of the acid to be 5 to 25°C (41 to 77°F) to avoid solvent decomposition. A second change is using 76% H_2SO_4 for handling purposes and also avoid solvent decomposition. A third change is the addition of dilution water to the bubbler bottoms prior to solvent recovery by distillation to further reduce solvent decomposition.

A cursory study performed in the RAAP laboratory using a gas washing bottle showed cold [8°C (46°F)] 95% H_2SO_4 to be an excellent solvent absorbent. Treatment of a gas stream containing approximately 1,000 ppm each of acetone and ethanol vapors with 100 mL of acid was compared to past laboratory results using the same gas stream as follows:

Absorbent	Breakthrough time (min)	Absorber inlet gas removed (%)
100 mL cold H_2SO_4 (95%)	320	100.00
100 mL 10 wt % HSO_3^-	150	88.0
100 mL water	34	86.3

Breakthrough time in the above data is defined as the length of time before solvents were detected in the exit gas stream.

A second laboratory study consisted of bubbling air through a 100-g solution of 10 wt % ethanol, 10 wt % acetone, and 80 wt % H_2SO_4 (95%) at ambient temperature for 165 min in a gas washing bottle to determine if the solvents would strip from the acid. Laboratory analyses of the exit gas stream and of the solution showed no solvents were lost, indicating H_2SO_4 retains solvents extremely well.

Four additional laboratory-scale absorber studies were conducted with the gas washing bottle using 95% H_2SO_4 (100 g). The results of these studies are shown in table 24. The first trial used H_2SO_4 at ambient temperature since no solvents were detected in the exit gas stream when chilled H_2SO_4 was utilized. This trial (trial 1) was stopped after 17 h of operation resulting in no solvents detected in the exit gas stream. The initial absorber inlet gas concentration was increased from ppm concentrations to percentage concentrations for the second trial (trial 2) to determine if solvent breakthrough would occur at a faster rate. The results showed solvent breakthrough did occur at a faster rate than in trial 1. Even though the breakthrough time was 4 h, it is 2.5 times greater than the 10 wt % HSO_3^- absorbent showing H_2SO_4 to be a better absorbent even when treating high concentrations of solvent vapors. Trial 3 was a duplicate of trial 2 with lower solvent concentrations in the inlet gas stream. This reduced inlet gas stream concentration allowed for an additional 2.5 h of operation before solvent breakthrough occurred. Trial 4 utilized cold H_2SO_4 to treat high solvent concentrations from the inlet gas stream to determine if chilling the acid would increase the operating time. The results show that chilling the acid did not influence operating time for the laboratory test conditions.

The above cursory laboratory studies show H_2SO_4 to be the best absorbent screened to date for solvent absorption. A review of the literature states H_2SO_4 absorbs acetone, ethanol, and diethyl ether (approximately 20 wt %).[20,21,22] This absorptive capability would allow a recovery system to consist of a single column for solvent absorption. Facilities operated at RAAP are the oleum manufacturing plant where H_2SO_4 regeneration (SAR) occurs and the nitric acid (HNO_3)/H_2SO_4 concentrators (NAC/SAC) where weak H_2SO_4(73%) is converted to strong H_2SO_4(95%). The existing ether manufacturing facilities, where ethanol is converted to diethyl ether (under proper conditions) in the H_2SO_4, are also available at RAAP for stripping the VOC from the acid and recovery by distillation in the rectification equipment.

The presence of NG vapors poses minimal problems since NG is destroyed by concentrated H_2SO_4 under controlled conditions. Nitric oxide (NO_x), which is formed when NG is destroyed, is absorbed by the H_2SO_4. During solvent absorption in H_2SO_4, the main side-reaction of concern is ethanol conversion to diethyl ether which only occurs under proper conditions. For this reaction, no peroxide formation would likely occur. The advantages and disadvantages of using H_2SO_4 as an absorbent are summarized in table 25.

One of the advantages listed in table 25 is total abatement system costs. The capital costs are less for the H_2SO_4 system than for the HSO_3^- system since a single column is required for the solvent absorption process for each FAD bay. The H_2SO_4 for absorption can be obtained from the NAC/SAC or SAR. Solvent recovery could be accomplished by distillation in the existing ether manufacturing plant. If solvent recovery is not desired, the absorbed solvents could be a fuel supplement in the existing SAR.

CONCLUSIONS

1. The bisulfite (HSO_3^-) absorption solution can effectively remove the volatile organic compounds (VOC) from the exhaust air to meet the Virginia Air Quality Standards.

2. Nitroglycerin (NG) decomposition occurred in the 15 wt % HSO_3^- absorbent solution but not in the 5 wt % HSO_3^- absorbent solution.

3. In order to attain sufficient accumulation of acetone in the recycle absorber column for economic recovery, the HSO_3^- absorbent solution must be recycled; however, no effective recovery technology has been developed for economical recovery of ethanol.

4. The conceptual forced air dry (FAD) design of the HSO_3^- absorption system consists of a dual-column system for solvent absorption, two distillation towers for solvent recovery, and an abatement facility for treating residual solvents.

5. The economic deficiencies of the HSO_3^- absorbent system are four-fold. First, two columns instead of one are required for solvent absorption. Second, the recovery of acetone from the recycle column by distillation in Radford Army Ammunition Plant's (RAAP's) existing ether manufacturing facility may not be suitable due to HSO_3^- eroding the copper in the towers. Third, the costs of chemicals to prepare HSO_3^- absorbent solution are excessively high. Fourth, the costs of additional facilities for ethanol treatment would also be prohibitive.

6. The conceptual HSO_3^- absorber design selected for solvent recovery from a mixer bay consists of a recycle absorber column 10-ft high by 0.75 ft in diameter containing eighteen theoretical stages.

7. Bench-scale testing of glycols as absorbents showed them to be poor absorbents.

8. A Preliminary Hazards Analysis determined that the proposed concept for using the PURASIV HR fluidized carbon bed solvent recovery system is not safe for solvent recovery from solvent vapor/air mixtures laden with NG.

9. A membrane process for the recovery of solvents from gas streams developed by Membrane Technology and Research, Inc., was screened in their laboratory for the recovery of 1,500 ppm acetone vapors. The cursory results showed acetone vapors could be concentrated to 8% and 14% for additional solvent recovery treatment.

10. The theoretical calculations of the Ceilcote solvent recovery system based on their laboratory-scale evaluations showed the system to economically remove the VOC to meet the Virginia Air Quality Standards; however, the system will likely not meet safety or steam availability requirements.

11. A cursory study performed in the RAAP laboratory showed cold [8°C (46°F)] 95% sulfuric acid (H_2SO_4) to be an excellent absorbent.

RECOMMENDATIONS

1. Continue to investigate innovative approaches to VOC recovery or abatement in RAAP's propellant manufacturing areas.

2. Conduct a more thorough engineering study on the Ceilcote solvent recovery system as related to hazards analysis and steam requirements.

3. Conduct comprehensive studies on the H_2SO_4 absorption system and perform an economic analysis on the design found most applicable to the Green Line and FAD areas.

4. Implement an economical system to meet the 85% VOC reduction criteria.

Table 1. Water quality bench-scale recycle absorber tests

Scrubbing solution	pH		Avg solvent conc in inlet gas (ppm)		Avg solvent conc in exit gas (ppm)		Inlet gas solvent absorbed (%)			Avg absorbent solvent conc (wt %)		
	Initial	Final	Acetone	Ethanol	Acetone	Ethanol	Total	Acetone	Ethanol	Total	Acetone	Ethanol
5 wt % Na_2SO_3 in plant process water	7.0*	7.3	1,280	1,119	298	207	79.1	76.7	81.5	0.93	0.66	0.27
5 wt % Na_2SO_3 in distilled water	7.0*	7.0	790	784	111	182	85.6	94.6	76.9	0.73	0.52	0.22
5 wt % Na_2SO_3 in softened water	7.3*	7.6	1,430	1,419	272	239	82.1	81.0	83.2	1.04	0.72	0.31
5 wt % Na_2SO_3/ 5 wt % EDTA in plant process water	7.0	7.6	1,267	1,199	155	212	85.1	87.8	82.3	0.98	0.73	0.24
Plant process water	8.5	8.0	1,283	1,435	907	389	51.1	29.3	72.9	0.50	0.14	0.37

Test conditions:

Absorbent solutions at ambient temperature.
pH adjusted with acetic acid noted with (*).
Inlet gas temperature: 38°C (100°F).
Average air flow of exit gas: 262 L/min (9.2 cfm).
Average absorbent flows: 50 mL/min feed; 150 mL/min recycle.
Test time: 6.5 h.

Table 2. $NaHSO_3/Na_2SO_4$ comparison in neutralized Na_2SO_3 absorbent solutions

	Analytical determination							
	Reactive compound, $NaHSO_3$			Inactive compound, Na_2SO_4				
	Blank (g)	Test solution (g)	Loss (g)	Blank (g)	Test solution (g)	Formed (g)	Expected Na_2SO_4 formed in test solution[a] (g)	Na_2SO_4 difference[b] (%)
5 wt % Na_2SO_3 in plant process water	4.90	2.10	2.80	1.83	1.56	-0.27	3.82	-107.1
5 wt % Na_2SO_3 in distilled water	4.27	1.32	2.95	1.11	3.48	2.37[c]	4.03	-41.2
5 wt % Na_2SO_3 in softened water	3.35	2.80	0.55	1.24	1.09	-0.15	0.75	120.0
5 wt % Na_2SO_3/ 5 wt % EDTA in plant process water	3.86	3.73	0.16	0.35	0.16	-0.19	0.22	-186.4

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[a] Calculations based on analytical determination of $NaHSO_3$ loss.

[b] $$Na_2SO_4 \text{ \% difference} = \frac{Na_2SO_4 \text{ formed (g)} - Na_2SO_4 \text{ expected (g)}}{Na_2SO_4 \text{ expected (g)}} \times 100.$$

[c] High value may be due to ions from distillation equipment piping.

Table 3. Bench-scale 10:1 recycle-to-feed absorber test using 5 wt % Na_2SO_3/0.05 wt % EDTA in plant process water

pH	
Initial	5.1
Final	5.5
Avg solvent conc in inlet gas (ppm)	
Acetone	842
Ethanol	858
Avg solvent conc in exit gas (ppm)	
Acetone	195
Ethanol	383
Inlet gas solvent absorbed (%)	
Total solvent	66.1
Acetone	76.8
Ethanol	55.4
Avg absorbent solvent conc (wt %)	
Total solvent	1.7
Acetone	1.5
Ethanol	0.2
Test conditions	
Absorbent solution temperature	Ambient
Acid for pH adjustment	Acetic
Inlet gas temperature	38°C (100°F)
Avg air flow of exit gas	262 L/min (9.2 cfm)
Avg absorbent flows	
Feed (mL/min)	30
Recycle (mL/min)	300
Test time (h)	6.5

Table 4. Dual-column bench-scale absorber recycle and feed rate tests using 20 wt % Na_2SO_3/0.05 wt % EDTA and 20 wt % $Na_2S_2O_5$/0.05 wt % EDTA in plant process water

	Test 1		Test 2	
	Recycle column	Single-pass column	Recycle column	Single-pass column
	20 wt % Na_2SO_3/0.05 wt % EDTA in plant process water	plant process water	20 wt % $Na_2S_2O_5$/ 0.05 wt % EDTA in plant process water	plant process water
pH				
Initial	5.4	-	3.8	-
Final	5.5	-	6.0	-
Avg solvent conc in inlet gas (ppm)				
Acetone	391	167	403	125
Ethanol	445	324	860	630
Avg solvent conc in exit gas (ppm)				
Acetone	167	132	125	52
Ethanol	324	214	630	260
Inlet gas solvent absorbed (%)				
Total solvent (both columns)[a]	59.1		78.5	
Acetone	57.3	21.0	69.0	58.4
Ethanol	27.2	34.0	26.7	58.7
Absorbent solvent concentration (wt %)[b]				
Total solvent	1.91	0.14	3.86	0.13
Acetone	1.79	0.04	3.70	0.02
Ethanol	0.12	0.10	0.16	0.11
Test Conditions:				
Absorbent solution temperature	ambient	ambient	ambient	ambient
Acid for pH adjustment	adipic	-	-	-
Inlet gas temperature	49°C (120°F)	27°C (80°F)	49°C	27°C
Avg air flow of exit gas	262 L/min (9.2 cfm)	262 L/min	262 L/min	262 L/min
Avg absorbent flows (mL/min)	500	55	500	110
Test time for both columns (h)	6.5		5	

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[a] % absorbed by dual-column system.
[b] At end of test.

Table 5. Dual-column bench-scale absorber recycle and feed rate tests using 15 wt % $Na_2S_2O_5$/0.05 wt % EDTA and 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA in plant process water

	Test 1		Test 2	
	Recycle column	Single-pass column	Recycle column	Single-pass column
	15 wt % $Na_2S_2O_5$/ 0.05 wt % EDTA	Plant process water	15 wt % $Na_2S_2O_5$/ 6.5 wt % Na_2SO_3/ 0.05 wt % EDTA	Plant process water
Avg solvent conc in inlet gas (ppm)				
Acetone	630	194	356	–[c]
Ethanol	1,654	913	799	435
Avg solvent conc in exit gas (ppm)				
Acetone	194	74	–[c]	59
Ethanol	913	301	435	174
Inlet gas solvent absorbed (%)				
Total solvent (both columns)[a]	85.1		80.8	
Acetone	69.2	61.9	90.4	–[c]
Ethanol	44.8	67.0	45.6	60.0
Absorbent solvent concentration (wt %)[b]				
Total solvent	0.85	0.19	1.4	0.14
Acetone	0.67	0.01	1.1	0.01
Ethanol	0.18	0.18	0.3	0.13
Test conditions:				
Absorbent solution temperature	ambient	ambient	ambient	ambient
Inlet gas temperature	49°C (120°F)	27°C (80°F)	49°C	27°C
Avg air flow of exit gas	262 L/min (9.2 cfm)	262 L/min	262 L/min	262 L/min
Avg absorbent flows (ml/min)	1,500	100	1,500	100
Test time for both columns (h)	2		5	

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[a] [illegible] absorbed by dual-column system.
[b] At end of test.
[c] Incomplete data.

Table 6. Dual-column bench-scale absorber temperature tests using 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA in plant process water (ambient and chilled)

Columns	Test 1[c]		Test 2[c]		Test 3[h]		Test 4[h]	
	Recycle	Single-pass	Recycle	Single-pass	Recycle	Single-pass	Recycle	Single-pass
Absorbent	HSO_3^-[d]	Water[g]	HSO_3^-	Water[g]	HSO_3^-	Water[g]	HSO_3^-	Water[g]
Avg solvent conc in inlet gas (ppm)								
Acetone	-(1,000)[e,f]	-[e]	1,196 (756)	82	270 (668)	6	272 (756)	6
Ethanol	-(1,000)[e,f]	-[e]	1,625 (1,076)	677	206 (1,067)	87	210 (1,155)	78
Avg solvent conc in exit gas (ppm)								
Acetone	-[e]	-[e]	82	27	6	5	6	4
Ethanol	-[e]	-[e]	677	135	87	49	78	34
Inlet gas solvent absorbed (%)								
Total solvent[a]	-[e]		94.3		88.7		92.0	
Acetone	-[e]	-[e]	93.1	67.1	98.8	16.7	97.8	33.3
Ethanol	-[e]	-[e]	58.3	80.1	57.8	43.7	61.2	56.4
Absorbent solvent conc (wt %)[b]								
Total solvent	0.50	0.25	0.94	0.21	0.23	0.034	0.23	0.043
Acetone	0.40	0.05	0.74	0.00	0.20	0.004	0.20	0.003
Ethanol	0.10	0.20	0.20	0.21	0.03	0.030	0.03	0.040
Test conditions:								
Absorbent temperature (°C)	ambient	ambient	ambient 1 (34°F)	18	18	20 (68°F)	2 (36°F)	
Inlet gas temperature (°C)	38 (100°F)	21 (70°F)	38	18 (65°F)	43 (110°F)	23 (74°F)	46 (115°F)	20
Avg air flow of exist gas (l/min)	262 (9.2 cfm)		262				262	
Avg absorbent feed flows (ml/min)	100	100	100	100	50	100	50	100
Avg absorbent recycle flows (mL/min)	1,500	-	1,500	-	300	-	300	-
Test time (h)	6		6		6		6.25	

---

[a] . absorbed by dual-column system.
[b] At steady-state condition.
[c] Solvent vapors generated by vaporizing a known solution of liquid solvent.
[d] 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA.
[e] Inconclusive data due to gross discrepancies in sampling and data analyses.
[f] Calculated solvent concentration.
[g] Plant process water.
[h] Solvent vapors generated by vaporizing a known solution of liquid solvent at a specific rate.

Table 7. Test for HSO_3^- interference in absorbent solution analyses

Sample no.	Sample composition	Expected (ppm)		GC results (ppm)	
		Ethanol	Acetone	Ethanol	Acetone
1	10 mL ethanol + 10 mL acetone diluted to 1,000 mL in water[a]	9,781	9,659	8,092	8,127
2	500 mL of sample 1 diluted to 1,000 mL in water[a]	4,891	4,830	3,918	3,903
3	500 mL of sample 2 diluted to 1,000 mL in water[a]	2,445	2,415	1,817	1,794
4	500 mL of sample 3 diluted to 1,000 mL in water[a]	1,222	1,208	950	938
5	10 mL ethanol + 10 mL acetone diluted to 1,000 mL in HSO_3^- solution[b]	8,177	8,075	8,198	8,030
6	500 mL of sample 5 diluted to 1,000 mL in HSO_3^- solution[b]	4,089	4,037	3,946	3,918
7	500 mL of sample 6 diluted to 1,000 mL in HSO_3^- solution[b]	2,044	2,019	2,017	1,994
8	500 mL of sample 7 diluted to 1,000 mL in HSO_3^- solution[b]	1,022	1,009	938	927

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[a] Plant process water.
[b] 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA.

Table 8. Fractional factorial (1/2 replicate) experiment design

Factors	Description	Levels
A	HSO_3^- absorbent solutions	A_0 = 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA A_1 = 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA
B	Recycle absorber column feed rates	B_0 = low (25 mL/min) B_1 = high (100 mL/min)
C	Recycle absorber column rates	C_0 = low (300 mL/min) C_1 = high (1,500 mL/min)
D	Single-pass absorber column feed temperatures	D_0 = ambient* D_1 = chilled*
E	Single-pass absorber column feed rates	E_0 = low (80 mL/min) E_1 = high (130 mL/min)

NOTE: The following figure illustrates the five factors (A,B,C,D, and E) to be evaluated. The thirty-two possible experimental conditions (full factorial experiment) are presented by the 32 cells; the sixteen experimental conditions which were evaluated are underscored and are designated Block 1 (i.e., ABCDE interaction confounded with block effects):

		A_0				A_1			
		B_0		B_1		B_0		B_1	
		C_0	C_1	C_0	C_1	C_0	C_1	C_0	C_1
D_0	E_0	(1)	c	b	bc	a	ac	ab	abc
	E_1	e	ce	be	bce	ae	ace	abe	abce
D_1	E_0	d	cd	bd	bcd	ad	acd	abd	abcd
	E_1	de	cde	bde	bcde	ade	acde	abde	abcde

---

*Refer to table 9 for temperatures of individual trials.

Table 9. Dual-column bench-scale absorber 2^5 fractional factorial (1/2 replicate) experiment results

	Test 1[c]		Test 2[c]		bcde interaction[c]	
Columns	Recycle	SP[g]	Recycle	SP[g]	Recycle	SP[g]
Absorbent	HSO_3^-[d]	Water[e]	HSO_3^-[d]	Water[e]	HSO_3^-[f]	Water[e]
Avg solvent conc in inlet gas (ppm)						
Acetone	498	108	673	33	330	10
Ethanol	703	520	757	380	326	118
Avg solvent conc in exit gas (ppm)						
Acetone	108	63	33	26	10	6
Ethanol	520	186	380	115	118	30
Inlet gas solvent absorbed (%)						
Total solvent[d]	79		90		95	
Acetone	78	42	95	21	97	40
Ethanol	26	64	50	70	64	75
Absorbent solvent conc (wt %)[b]						
Total solvent	2.26	0.24	1.26	0.21	0.73	0.12
Acetone	2.12	0.05	1.13	0.02	0.53	0.01
Ethanol	0.14	0.19	0.13	0.19	0.20	0.11
Test conditions:						
Absorbent temperature (°C)	23	19	21	23	21	23
Inlet gas temperature (°C)	53	27	51	22	49	22
Avg air flow of exit gas (L/min)	262		262		262	
Avg absorbent feed flows (ml/min)	25	80	25	80	100	130
Avg absorbent recycle flows (ml/min)	300		300		1500	
Test time (h)	6		6		6	

Table 9. (cont)

Columns	ad interaction^c		(1) interaction^c		abcd interaction^c		abce interaction^c	
	Recycle	SP^g	Recycle	SP^g	Recycle	SP^g	Recycle	SP^g
Absorbent	HSO_3^-^{d}	Water^e	HSO_3^-^{f}	Water^e	HSO_3^-^{d}	Water^e	HSO_3^-^{d}	Water^e
Avg solvent conc in inlet gas (ppm)								
Acetone	764	67	734	91	709	13	621	22
Ethanol	1131	590	1040	457	1051	418	888	442
Avg solvent conc in exit gas (ppm)								
Acetone	67	61	91	71	13	12	22	9
Ethanol	590	307	457	233	418	232	442	121
Inlet gas solvent absorbed (%)								
Total solvent^a	81		83		86		91	
Acetone	91	9	88	22	98	8	96	59
Ethanol	48	48	56	49	60	44	50	73
Absorbent solvent conc (wt %)^b								
Total solvent	1.81	0.36	1.97	0.32	0.65	0.26	0.67	0.14
Acetone	1.64	0.03	1.54	0.03	0.51	0.01	0.54	0.01
Ethanol	0.17	0.33	0.43	0.29	0.14	0.25	0.13	0.13
Test conditions:								
Absorbent temperature (°C)	22	22	18	3	21	3	23	3
Inlet gas temperature (°C)	51	22	47	18	51	21	53	24
Avg air flow of exit gas (l/min)	262		262		262		262	
Avg absorbent feed flows (ml/min)	25	80	25	80	100	80	100	130
Avg absorbent recycle flows (ml/min)	300		300		1500		1500	
Test time (h)	6		6		6		6	

Table 9. (cont)

Columns	de interaction[c]		ce interaction[c]		be interaction[c]	
	Recycle	SP[g]	Recycle	SP[g]	Recycle	SP[g]
Absorbent	HSO_3^-[f]	Water[e]	HSO_3^-[f]	Water[e]	HSO_3^-[f]	Water[e]
Avg solvent conc in inlet gas (ppm)						
Acetone	961	65	883	66	850	34
Ethanol	1387	779	1208	65	1215	452
Avg solvent conc in exit gas (ppm)						
Acetone	65	41	66	68	34	25
Ethanol	779	310	652	266	452	118
Inlet gas solvent absorbed (%)						
Total solvent[a]	85		84		93	
Acetone	93	37	93	0	96	26
Ethanol	44	60	46	59	63	74
Absorbent solvent conc (wt %)[b]						
Total solvent	2.57	0.16	2.16	0.19	1.24	0.15
Acetone	2.14	0.01	1.87	0.03	0.97	0.01
Ethanol	0.43	0.15	0.29	0.16	0.27	0.14
Test conditions:						
Absorbent temperature (°C)	21	21	23	5	18	7
Inlet gas temperature (°C)	54	22	57	29	52	36
Avg air flow of exit gas (L/min)	262		262		262	
Avg absorbent feed flows (mL/min)	25	130	25	130	100	130
Avg absorbent recycle flows (mL/min)	300		300		300	
Test time (h)	6		6		6	

Table 9. (cont)

	ab interaction[c]		cd interaction[c]		ae interaction[c]	
Columns	Recycle	SP[g]	Recycle	SP[g]	Recycle	SP[g]
Absorbent	HSO_3^-[d]	Water[e]	HSO_3^-[f]	Water[e]	HSO_3^-[d]	Water[e]
Avg solvent conc in inlet gas (ppm)						
Acetone	684	27	611	138	615	82
Ethanol	1114	619	799	566	817	427
Avg solvent conc in exit gas (ppm)						
Acetone	27	21	138	121	82	85
Ethanol	619	322	566	232	427	221
Inlet gas solvent absorbed (%)						
Total solvent[a]	81		75		79	
Acetone	96	22	77	12	87	0
Ethanol	44	48	29	59	48	48
Absorbent solvent conc (wt %)[b]						
Total solvent	1.17	0.28	3.05	0.28	4.02	0.28
Acetone	1.00	0.03	2.69	0.23	3.86	0.04
Ethanol	0.17	0.25	0.36	0.05	0.16	0.24
Test conditions:						
Absorbent temperature (°C)	21	8	13	13	17	7
Inlet gas temperature (°C)	53	38	47	34	50	37
Avg air flow of exit gas (L/min)	262		262		262	
Avg absorbent feed flows (mL/min)	100	80	25	80	25	130
Avg absorbent recycle flows (mL/min)	300		1500		300	
Test time (h)	6		6		6	

Table 9. (cont)

Columns	bd interaction[c]		acde interaction[c]		abde interaction[c]	
	Recycle	SP[g]	Recycle	SP[g]	Recycle	SP[g]
Absorbent	HSO_3^-[f]	Water[e]	HSO_3^-[d]	Water[e]	HSO_3^-[d]	Water[e]
Avg solvent conc in inlet gas (ppm)						
Acetone	629	13	627	69	672	16
Ethanol	719	220	984	614	886	439
Avg solvent conc in exit gas (ppm)						
Acetone	13	11	69	38	16	12
Ethanol	220	105	614	186	439	149
Inlet gas solvent absorbed (%)						
Total solvent[a]	91		86		90	
Acetone	98	15	89	45	98	25
Ethanol	69	52	38	70	50	66
Absorbent solvent conc (wt %)[b]						
Total solvent	0.78	0.13	2.14	0.23	0.87	0.13
Acetone	0.58	0.01	1.99	0.03	0.69	0.01
Ethanol	0.20	0.12	0.15	0.20	0.18	0.12
Test conditions:						
Absorbent temperature (°C)	21	20	21	21	17	17
Inlet gas temperature (°C)	53	38	53	39	48	34
Avg air flow of exit gas (L/min)	262		262		262	
Avg absorbent feed flows (mL/min)	100	80	25	130	100	130
Avg absorbent recycle flows (mL/min)	300		1500		300	
Test time (h)	6		6		6	

Table 9. (cont)

	bc interaction[c]		ac interaction[c]	
Columns	Recycle	SP[g]	Recycle	SP[g]
Absorbent	HSO_3^-[f]	Water[e]	HSO_3^-[d]	Water[e]
Avg solvent conc in inlet gas (ppm)				
Acetone	671	13	471	45
Ethanol	851	305	704	568
Avg solvent conc in exit gas (ppm)				
Acetone	13	10	45	37
Ethanol	305	121	568	240
Inlet gas solvent absorbed (%)				
Total solvent[a]	91		76	
Acetone	98	23	90	19
Ethanol	64	60	18	58
Absorbent solvent conc (wt %)[b]				
Total solvent	0.87	0.146	2.00	0.26
Acetone	0.62	0.006	1.86	0.23
Ethanol	0.25	0.14	0.14	0.03
Test conditions:				
Absorbent temperature (°C)	17	7	18	7
Inlet gas temperature (°C)	48	33	52	36
Avg air flow of exit gas (L/min)	262		262	
Avg absorbent feed flows (mL/min)	100	80	25	80
Avg absorbent recycle flows (mL/min)	1500		1500	
Test time (h)	6		6	

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[a] % absorbed by dual column system.

[b] At steady-state condition.

[c] Solvent vapors generated by vaporizing a known solution of liquid solvent at a specific rate.

[d] 15 wt % $Na_2S_2O_5$ + 6.5 wt % Na_2SO_3 + 0.05 wt % EDTA.

[e] Plant process water.

[f] 5 wt % $Na_2S_2O_5$ + 2.5 wt % Na_2SO_3 + 0.05 wt % EDTA.

[g] Single-pass absorber column.

Table 10. Summary of results for the 2^5 fractional factorial (1/2 replicate) experiment

Tests conducted in randomized order[a]	Test parameters/conditions varied: HSO_3 absorbent[b] 5 wt %	HSO_3 absorbent[b] 15 wt %	Recycle column feed (mL/min) 25	Recycle column feed (mL/min) 100	Recycle column recycle rate (mL/min) 300	Recycle column recycle rate (mL/min) 1500	Single-pass column absorbent temperature Chilled	Single-pass column absorbent temperature Ambient	Single-pass column feed (mL/min) 80[c]	Single-pass column feed (mL/min) 130	Test results: Inlet gas solvent absorbed (total %)[d]	Absorbent solvent conc (wt %)[e] Recycle column	Absorbent solvent conc (wt %)[e] Single-pass
Test bcde	X			X		X		X		X	95	0.73	0.12
Test abcd		X		X		X		X	X		86	0.58	0.25
Test abce		X		X		X	X			X	91	0.64	0.13
Test ad		X	X		X			X	X		81	1.91	0.36
Test (1)	X		X		X		X		X		83	1.96	0.30
Test de	X		X		X			X		X	85	2.57	0.16
Test be	X			X	X		X			X	93	1.24	0.15
Test ab		X		X	X		X		X		81	1.17	0.28
Test ce	X		X			X	X			X	84	2.16	0.19
Test cd	X		X			X		X	X		75	3.05	0.28
Test ae		X	X		X		X			X	79	4.02	0.28
Test bd	X			X	X			X	X		91	0.78	0.13
Test acde		X	X			X		X		X	86	2.14	0.23
Test abde		X		X	X			X		X	90	0.87	0.13
Test bc	X			X		X	X		X		91	0.87	0.15
Test ac		X	X			X	X		X		76	2.00	0.26

---

[a] Tests for 2^5 fractional factorial (1/2 replicate) experiment.

[b] 5 wt % HSO_3^- solution = 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA.
15 wt % HSO_3^- solution = 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA.

[c] Minimum flow rate to wet column packing.

[d] Averaged data.

[e] Composite samples.

Table 11. Analysis of percentage solvent removal from absorber inlet gas by Yates' method

Col. 1 Treatment combination	Col. 2 Response [solvent removal (%)]	Col. 3	Col. 4	Col. 5	Col. 6 q	Col. 7 Estimated effect
bcde	95	11	3	16	-5	-AE
abcd	86	-9	-20	-23	-39	-E
abce	91	181	2	-17	-7	-DE
ad	81	-12	22	-5	21	AD
(1)	83	162	336	678	1,367	T
de	85	-4	12	6	11	D
be	93	160	347	-24	69	B
ab	81	182	342	-3	-17	AB
ce	84	166	-16	34	1	C
cd	75	-4	-8	10	-11	CD
ae	79	174	342	689	-27	A
bd	91	-8	15	8	1	BD
acde	86	-1	8	5	-1	-BE
abde	90	0	20	7	-17	-CE
bc	91	161	-5	0	15	BC
ac	76	181	-8	35	15	AC
Total	1,367					
Sum of squares	117,343				1,877,488	

Table 12. Analysis of weight percent solvent in recycle column absorber bottoms by Yates' method

Col. 1 Treatment combination	Col. 2 Response [absorbent solvent conc. (wt %)]	Col. 3	Col. 4	Col. 5	Col. 6 g	Col. 7 Estimated effect
bcde	0.73	-0.91	0.75	2.06	-1.97	-AE
abcd	0.58	-0.15	0.76	0.01	-2.05	-E
abce	0.64	1.31	-1.06	1.51	2.07	-DE
ad	1.91	-0.07	-2.65	0.37	-3.23	AD
(1)	1.96	5.98	8.39	14.06	26.69	T
de	2.57	2.06	-3.57	-2.72	-1.43	D
be	1.24	4.16	6.13	1.60	-12.93	B
ab	1.17	1.51	6.50	-1.63	-0.69	AB
ce	2.16	4.48	1.99	-6.22	-2.35	C
cd	3.05	-0.66	-2.13	0.92	3.09	CD
ae	4.02	2.41	5.67	12.63	-0.03	A
bd	0.78	-0.16	-2.83	-2.38	-0.49	BD
acde	2.14	0.09	-0.07	-1.05	1.89	-BE
abde	0.87	-0.23	-3.88	-0.49	3.71	-CE
bc	0.87	5.19	-0.57	-2.20	-0.13	BC
ac	2.00	1.65	-0.39	-6.71	-2.87	AC
Total	26.69					
Sum of squares	59.1103				945.7648	

Table 13. Analysis of weight percent solvent in single-pass column absorber bottoms by Yates' method

Col. 1 Treatment combination	Col. 2 Response [absorbent solvent conc. (wt %)]	Col. 3	Col. 4	Col. 5	Col. 6 g	Col. 7 Estimated effect
bcde	0.12	-0.05	-0.20	-0.24	0.14	-AE
abcd	0.25	0.13	0.18	0.38	0.62	-E
abce	0.13	0.37	0.08	-0.02	0.14	-DE
ad	0.36	0.13	-0.17	0.10	0.12	AD
(1)	0.30	0.58	1.01	1.74	3.40	T
de	0.16	-0.02	-0.15	-0.28	-0.08	D
be	0.15	0.45	0.78	0.16	-0.72	B
ab	0.28	0.28	0.88	0.28	0.04	AB
ce	0.19	0.52	0.11	-0.32	-0.18	C
cd	0.28	0.20	0.15	-0.02	0.38	CD
ae	0.28	0.43	0.73	1.66	0.44	A
bd	0.13	0.07	-0.26	-0.06	-0.08	BD
acde	0.23	0.00	-0.09	0.12	-0.06	-BE
abde	0.13	-0.02	-0.14	-0.12	-0.08	-CE
bc	0.15	0.51	0.20	0.06	0.10	BC
ac	0.26	0.26	0.05	-0.40	-0.18	AC
Total	3.40					
Sum of squares	0.8096				12.9536	

Table 14. Testing for significance of main effects by Yates' method

	Solvent removal from inlet absorber gas stream (%)	Recycle column absorbent solvent concentration (wt %)	Single-pass column absorbent solvent concentration (wt %)
Level of significance, α	0.05	0.05	0.05
Estimate of experimental error, sum of g^2 of two factors	1,666	54.453	0.2584
Standard deviation estimate, s^2 [a]	10.4125	0.3403	0.001615
$t_{0.975,10}$ [b]	2.228	2.228	2.228
Main effect, w[c]	28.76	5.20	0.3
Effects different from zero $\lvert\text{effect}\rvert > w$ from tables 11, 12, and 13	B and -E	B	A, B, and -E

---

[a] s^2 = sum of $g^2/2^{n'}V$ where $n'=4$ and V (degrees of freedom) = 10.

[b] $t_{1-(\alpha/2),V}$ where t is obtained from a distribution of percentiles using s^2 as the estimate of the standard deviation.

[c] $w = (2^{n'})^{1/2}\, t_{1-(\alpha/2)}\, s$.

Table 15. 5 wt % $Na_2S_2O_5$/2.5 wt % Na_2SO_3/0.05 wt % EDTA reuse absorption/distillation tests

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Total solvents removed from inlet gas stream (%)	78	82	90	54	70
Total solvent concentration in recycle absorbent solution (wt %)	1.43	1.56	1.80	1.74	1.36
Total solvent in recycle absorbent solution (g)	140	159	146	169	119
Total solvent recovered by distillation from recycle absorbent solution (g)	70	70	81	68	73
Total solvent recovered by distillation from recycle absorbent (%)	50	44	55	40	61
$Na_2S_2O_5$ (wt %)	5.51	4.82	4.46	3.77	2.97
SO_4^{2-} (wt %)	1.56	2.74	2.91	3.56	4.48
Operating time (h)	4.0	4.0	4.0	4.0	4.0

Table 16. 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA reuse absorption/distillation tests

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6
Total solvents removed from inlet gas stream (%)	-[a]	96	79	67	69	64
Total solvent concentration in recycle absorbent solution (wt %)	3.39	4.46	4.29	3.64	3.20	0.90
Total solvent in recycle absorbent solution (g)	71	92	107	89	72	21
Total solvent recovered by distillation from recyle absorbent solution (g)	61	58	44	63	48	7
Total solvent recovered by distillation from recyle absorbent solution (%)	86	63	41[b]	70	67	33
$Na_2S_2O_5$ (wt %)	17.73	14.87	10.35[b]	14.62	12.32	5.66
SO_4^{2-} (wt %)	1.24	2.80	3.93	3.73	4.83	5.33
Operating time (h)	6.5	4.5	5.5	6.0	6.0	6.0

---

[a] Gas samples were not collected for this trial.

[b] Low result likely due to an analytical error.

Table 17. Effect of HSO_3^- absorbent solutions on neat NG

Day	NG in water (mg/L)		NG in 15 wt % HSO_3^- absorbent solution (mg/L)		NG in 5 wt % HSO_3^- absorbent solution (mg/L)	
	NG	DNG	NG	DNG	NG	DNG
1	357	ND[a]	5	ND	253	ND
2	348	ND	ND	ND	152	ND
3	354	ND	ND	ND	132	202
8	376	ND	ND	ND	55	229
9	359	ND	ND	ND	52	219
10	-[b]	-	-	-	31	204

---

[a] ND = Not detected.

[b] - = Sample was not analyzed.

NOTE: NG droplets were present in the 15 wt % and 5 wt % HSO_3^- absorbent solutions for day 1. Methanol addition on day 2 solubilized the NG droplets in these samples.

Table 18. Activated carbon adsorption of organic solvents from wastewater[a,b]

	Breakthrough bed volume[c]	Individual solvents adsorbed			Total solvents adsorbed at time of individual breakthrough		
		(kg/m³ carbon)[d]	(lb/ft³ carbon)	(wt %)[e]	(kg/m³ carbon)	(lb/ft³ carbon)	(wt %)
Ethanol	14	13.14	0.82	3.15	21.31	1.33	5.12
Acetone	57	16.98	1.06	4.08	46.62	2.91	11.19
Diethyl ether	62	17.78	1.11	4.27	49.50	3.09	11.88

---

[a] Ref 14.

[b] Wastewater influent concentration, ppm (mg/L)
Ethanol = 950
Acetone = 303
Diethyl ether = 293.

[c] One (1) bed vol = 400 cc carbon.

[d] One cubic meter (1-m^3) carbon = 416.52 lb.

[e] Required wt % for solvent recovery is 55 to 70 wt % on activated carbon.

Table 19. Mixer design criteria

Parameter	Description
NG constraints	15 wt % HSO_3^- absorbent solution destroys NG vapors
Solvents in gas stream	Recover 85% of solvents emitted in the following concentrations: Ethanol $\leq$ 900 ppm Acetone $\leq$ 450 ppm Ether $\leq$ 200 ppm (HSO_3^- absorbent solution requires hazards analysis)
Flow of gas stream (inert gas for dry-down cycle)	1,000 standard cfm (calculations in appendix C)
Inert gas temperature	50°C (122°F)
Operating pressure	Atmospheric
Absorbent	15 wt % HSO_3^- absorbent solution
Absorbent recycle-to-feed rate	12:1
Liquid-to-gas ratio (liquid downflow, gas upflow, wt/wt)	1.32
Materials specifications	Presence of NG vapors restricts materials of construction and must be in accordance to Hercules Incorporated Standards 5CS-2A1 and 5CS-3T3
Safety considerations	Complete hazards analysis of selected technology must be performed

Table 20. FAD design criteria

Parameters	Description
NG constraints	15 wt % HSO_3^- absorbent solution destroys NG vapors
Solvents in gas stream	Recover 85% of solvents emitted in the following concentrations: 1,200 standard L/min for modernized FAD 4,300 standard L/min for regular FAD
Gas temperature	60°C (140°F)
Operating pressure	Atmospheric
Absorbent	15 wt % HSO_3^- absorbent solution in recycle column for acetone absorption Plant process water in single-pass column for ethanol absorption
Recycled absorbent recycle-to-feed rate	12:1
Liquid-to-gas ratio (liquid downflow, gas upflow, wt/wt)	1.28 for recycle column 0.46 for single-pass column
Materials specifications	Presence of NG vapors restricts materials of construction and must be in accordance to Hercules Incorporated Standards 5CS-2A1 and 5CS-3T3
Safety considerations	Complete hazards analysis of selected technology must be performed

Table 21. Pilot plant design parameters for distillation process

Parameter	Conditions
Solvents in absorber bottoms to be distilled, wt %	0.89 to 1.70
First distillation column containing sieve trays with downcomers	36 trays with absorber bottoms entering theoretical stage 22
Operating temperature of first column	16 - 102°C (60 - 215°F)
Operating pressure of first column	18.8 - 29.7 psia
Overhead product of first column	Acetone and ethanol-water azeotrope
Bottoms product of first column	Water
Second distillation column containing sieve trays with downcomers	49 trays with first column overhead entering theoretical stage 8
Operating temperature of second column	51 - 79°C (123 - 175°F)
Operating pressure of second column	14.8 - 29.7 psia
Overhead product of second column	Acetone (maximum ethanol content of 0.06 wt %)
Bottoms product of second column	Ethanol (maximum 0.3 wt % acetone and 8.9 wt % water)

Table 22. Dual-column bench-scale absorber tests of glycols

	DEG test		TEG test	
	Recycle column	Single-pass column	Recycle column	Single-pass column
	100% DEG	100% DEG	100% TEG	100% TEG
Avg solvent conc in inlet gas (ppm)				
Acetone	1376	586	427	570
Ethanol	2065	798	742	973
Avg solvent conc in exit gas (ppm)				
Acetone	586	288	570	876
Ethanol	798	376	973	1690
Inlet gas solvent absorbed (%)				
Total solvent[a]	80.5		-116.5	
Acetone	57.4	50.9	-33.5	-53.7
Ethanol	61.4	52.9	-31.31	-73.7
Absorbent solvent concentration (wt %)[b]				
Total solvent	0.21	0.17	0.22	0.19
Acetone	0.04	0.05	0.05	0.06
Ethanol	0.17	0.12	0.17	0.13
Test conditions:				
Absorbent solution temperature	ambient	ambient	ambient	ambient
Inlet gas temperature	49°C (120°F)	27°C (80°F)	49°C	27°C
Avg air flow of exit gas	262 L/min (9.2 cfm)	262 L/min	262 L/min	262 L/min
Avg absorbent flows (mL/min)	500	110	500	110
Test time (h)	3.5		3.5	

---

[a] % absorbed by dual-column system.
[b] At end of test.

Table 23. General membrane terminology

Term	Definition
Feed	Gas stream to be treated by membrane unit
Residue	Gas stream that has been treated by membrane unit
Permeate	Gas stream from membrane unit containing highly concentrated solvent vapors (the stream separated from the feed stream)
Separation factor, α	$\frac{\text{Concentration of solvent in permeate}}{\text{Concentration of solvent in feed}}$
Selectivity factor, β	$\underline{\qquad\qquad\beta\qquad\qquad}$, where $1-(Vi''/Vi')$ $1-(Vj''/Vj')$
	Vi" is partial pressure of solvent in
permeate	
	Vi' is partial pressure of solvent in
feed	
	Vj" is partial pressure of air Vj' is partial pressure of solvent
	Note: Want an $\alpha \geq 100$ to 200
Membrane flex, J, in cm (STP)/cm_2S*	$\frac{-Ddc}{dx}$, where
	D is the diffusion coefficient of the solvent(s)
	dc/dx is the concentration gradient of the dissolved solvent in the membrane

---

* STP - standard temperature and pressure.

Table 24. Laboratory-scale absorbent studies with 95% H_2SO_4 as an absorbent

Trial	Average temp. °C(°F)	Time (h)	Averaged inlet gas concentration (ppm)		Breakthrough exit gas concentration (ppm)		Solvent absorbed (%)
			Acetone	Ethanol	Acetone	Ethanol	
1	27(81)	17.0	751	1,221	ND*	ND	100
2	34(93)	4.0	57,058	31,380	13,061	174	85
3	37(99)	6.5	32,593	17,636	2,440	ND	95
4	6(43)	6.4	49,731	27,429	2,129	ND	97

---

*ND - not detected.

Table 25. Advantages/disadvantages of H_2SO_4 as an absorbent

Advantages	Disadvantages
*Absorbs ethanol, acetone, ether - 20 wt % levels	*Absorbs water
*Readily available from NAC/SAC or SAR	*Corrosion problems
*Regenerate or reuse acid in SAR	*If recover solvents for reuse, may need cooling equipment
*May recover most of solvents in ether manufacturing plant	*Transportation of acid throughout plant
*Fuel value of solvents can reduce fuel requirements for the oleum	*Need safety measures to assure acid does not contact propellants
*Requires one absorber column	
*H_2SO_4 is not volatile	
*Concentrated H_2SO_4 destroys NG under controlled conditions	
*Costs seem favorable for acid usage	
*NG is soluble in concentrated H_2SO_4 (26%)	

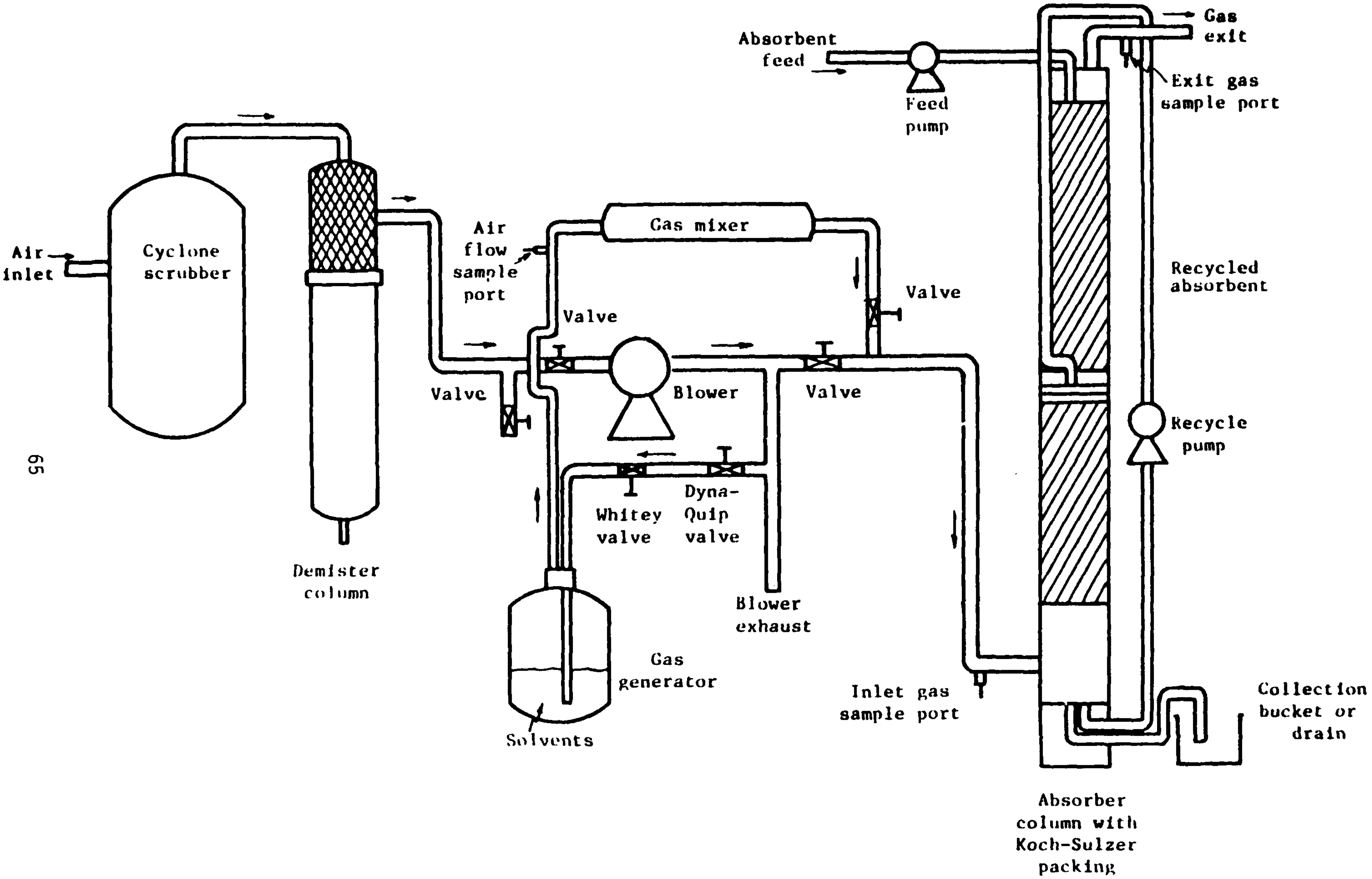
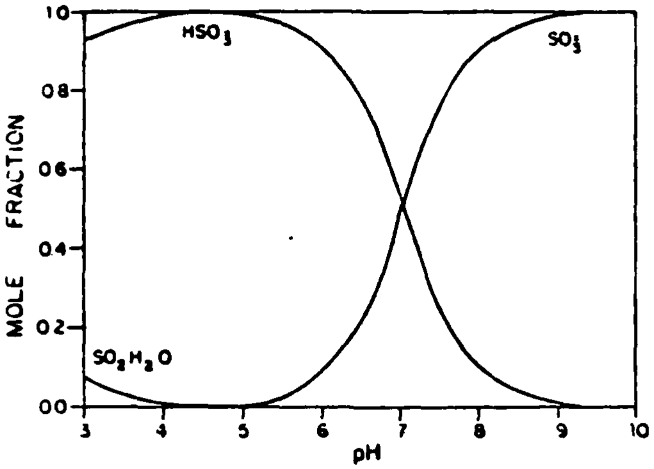


Figure 1. Schematic of bench-scale absorter unit



Conditions: 0.02 M Na_2SO_3, 40°C (104°F)

Figure 2. Effect of pH on sulfur (S IV) species

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*D. B. Nurmi, et al, "Sulfite Oxidation in Organic Acid Solutions," <u>Flue Gas Desulfurization</u>, American Chemical Society, 1982, pp 173-189

Figure 2. Effect of pH on sulfur (S IV) species

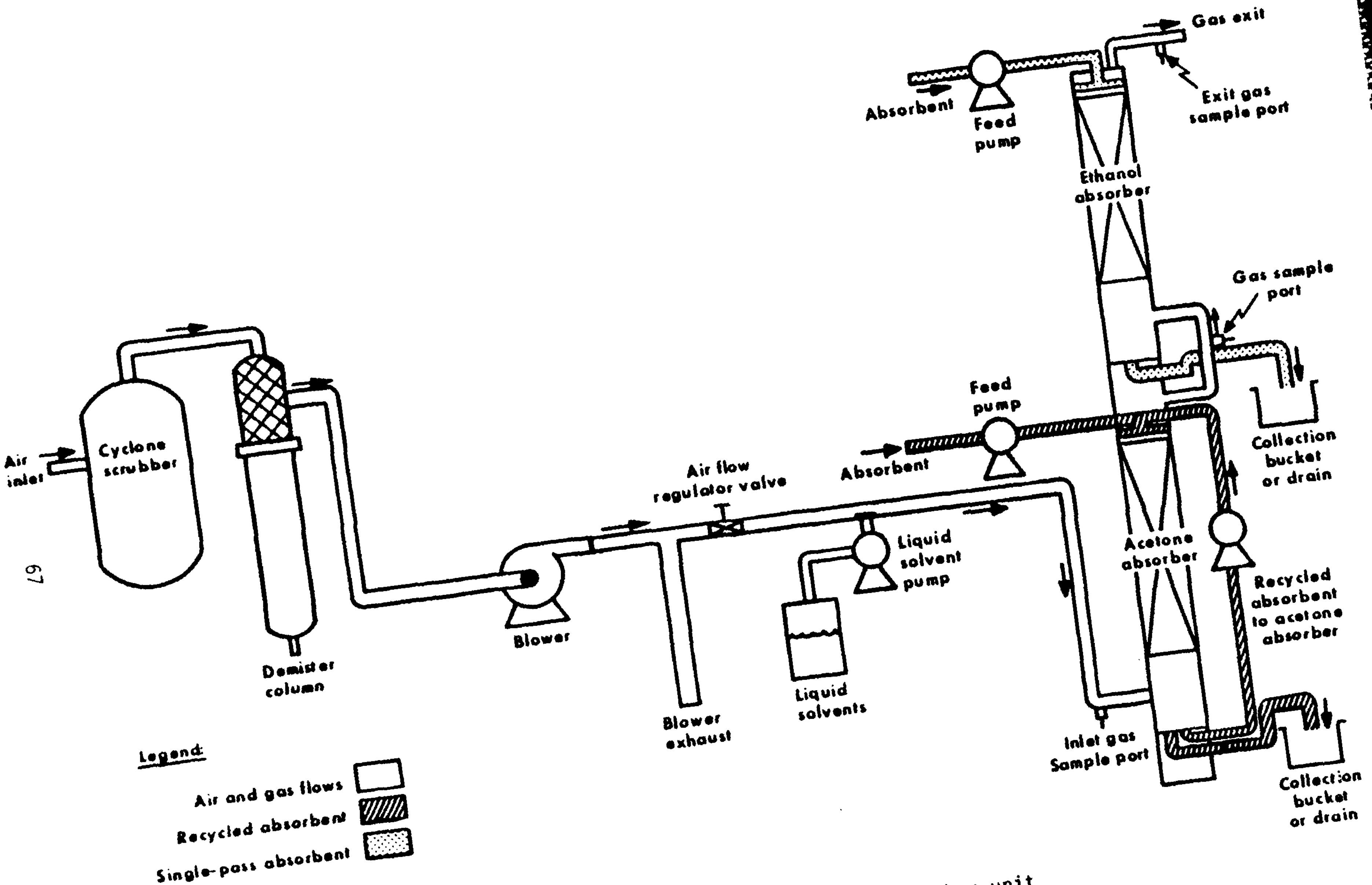


Figure 3. Schematic of dual-column bench-scale absorber unit

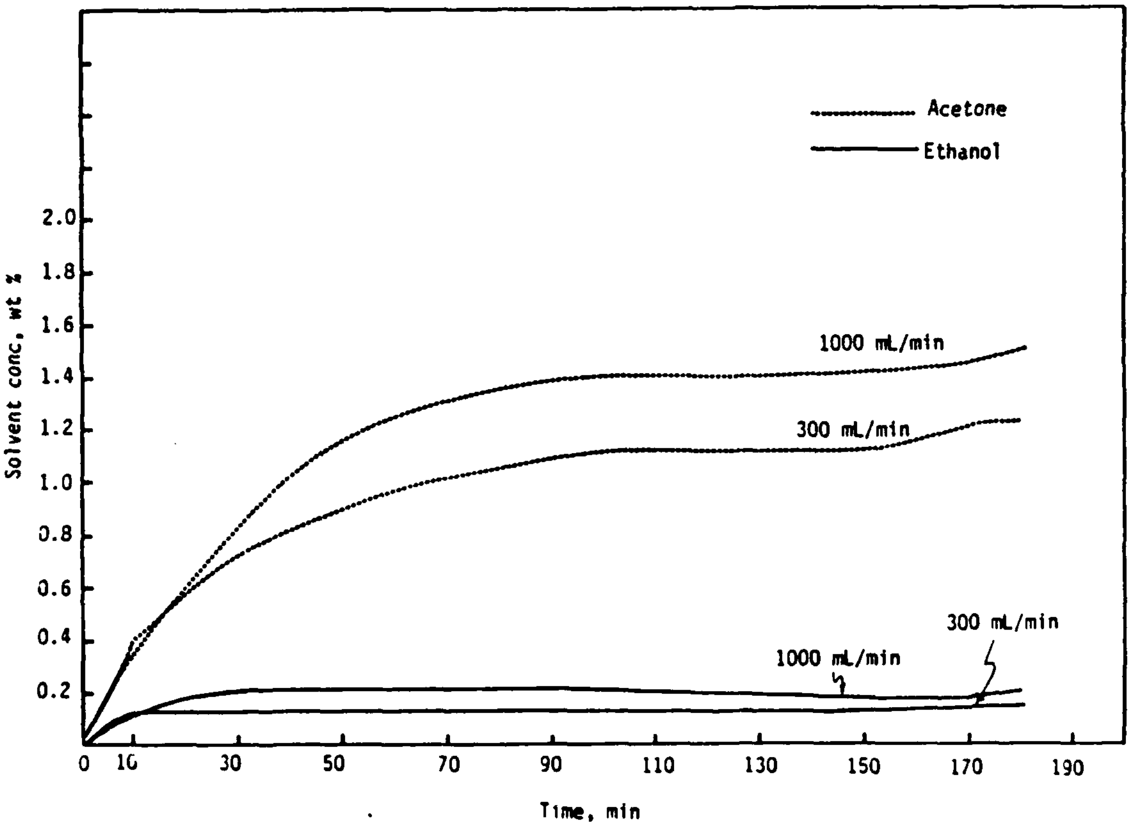


Figure 4. Recycle efficiency tests using 5 wt % Na_2SO_3/0.05 wt % EDTA at pH 5

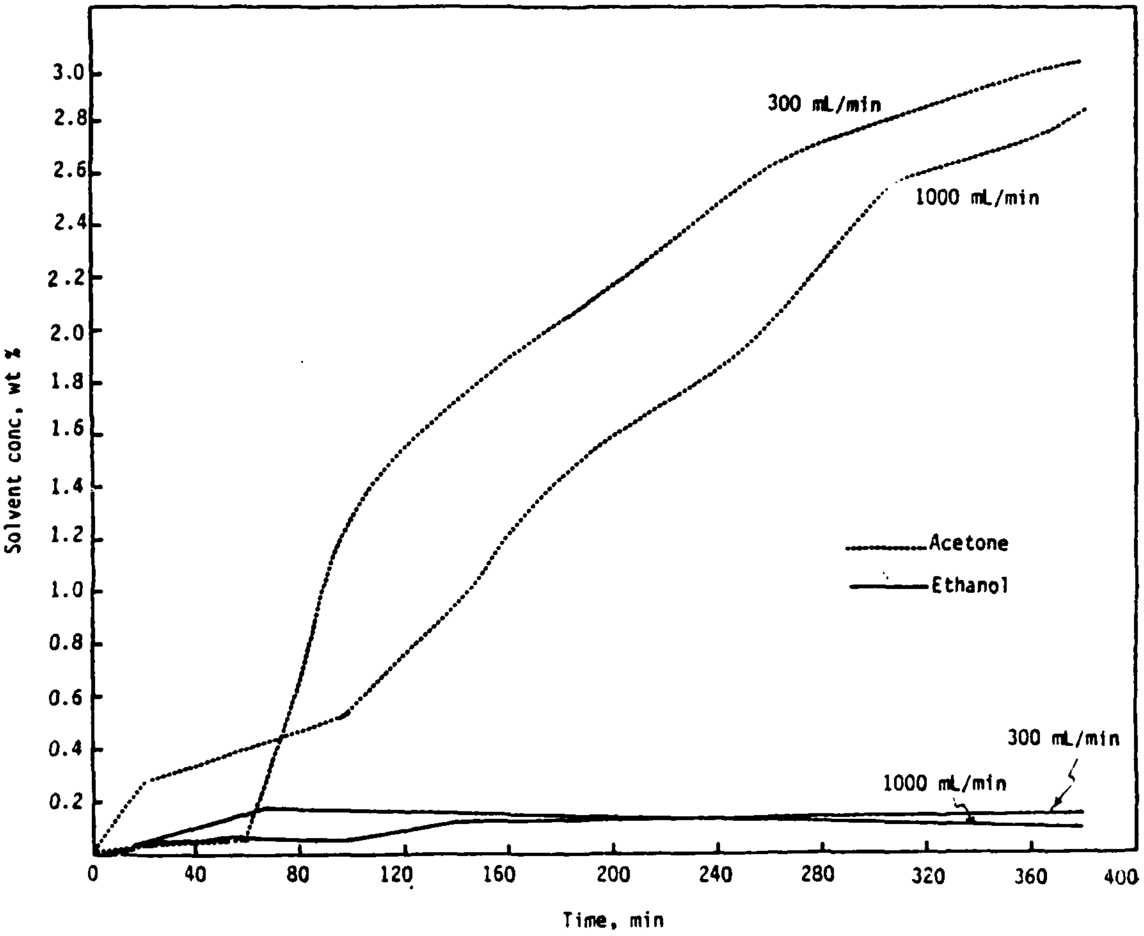


Figure 5. Recycle efficiency tests using 15 wt % Na_2SO_3/0.05 wt % EDTA at pH 5

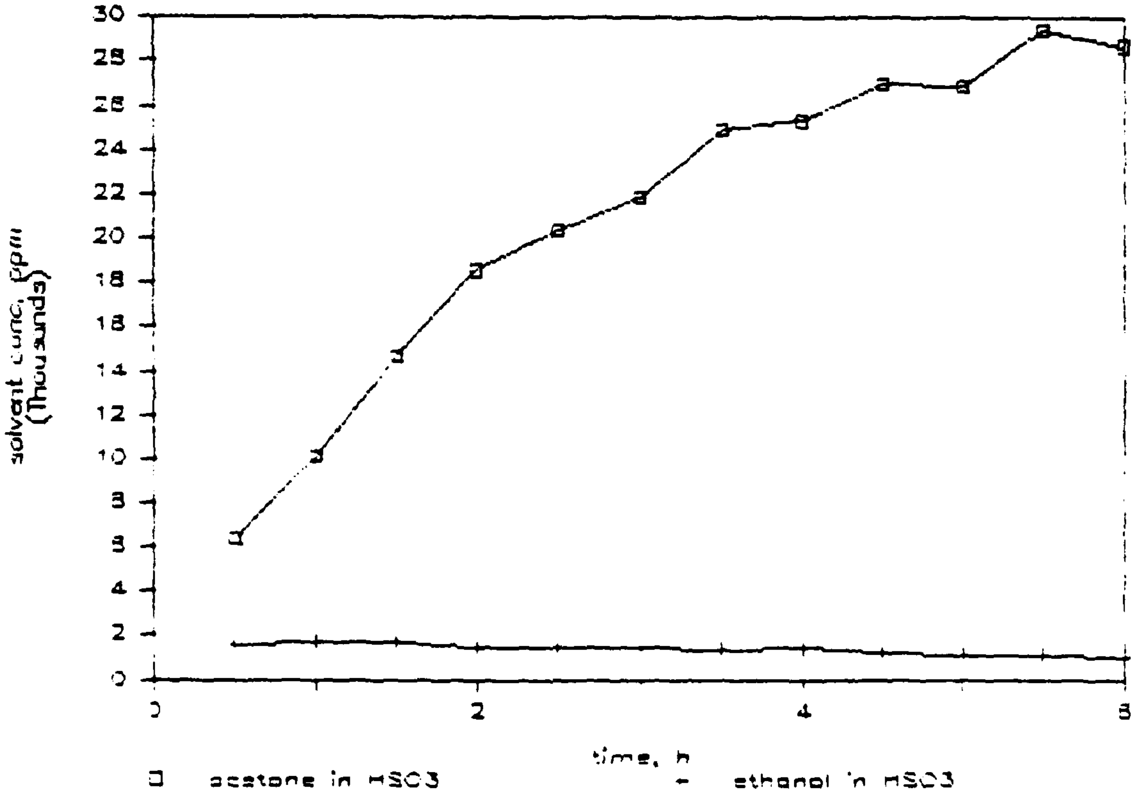


Figure 6. Solvent concentrations in recycle column HSO_3 absorbent solution, test 1 of fractional factorial (1/2 replicate) experiment

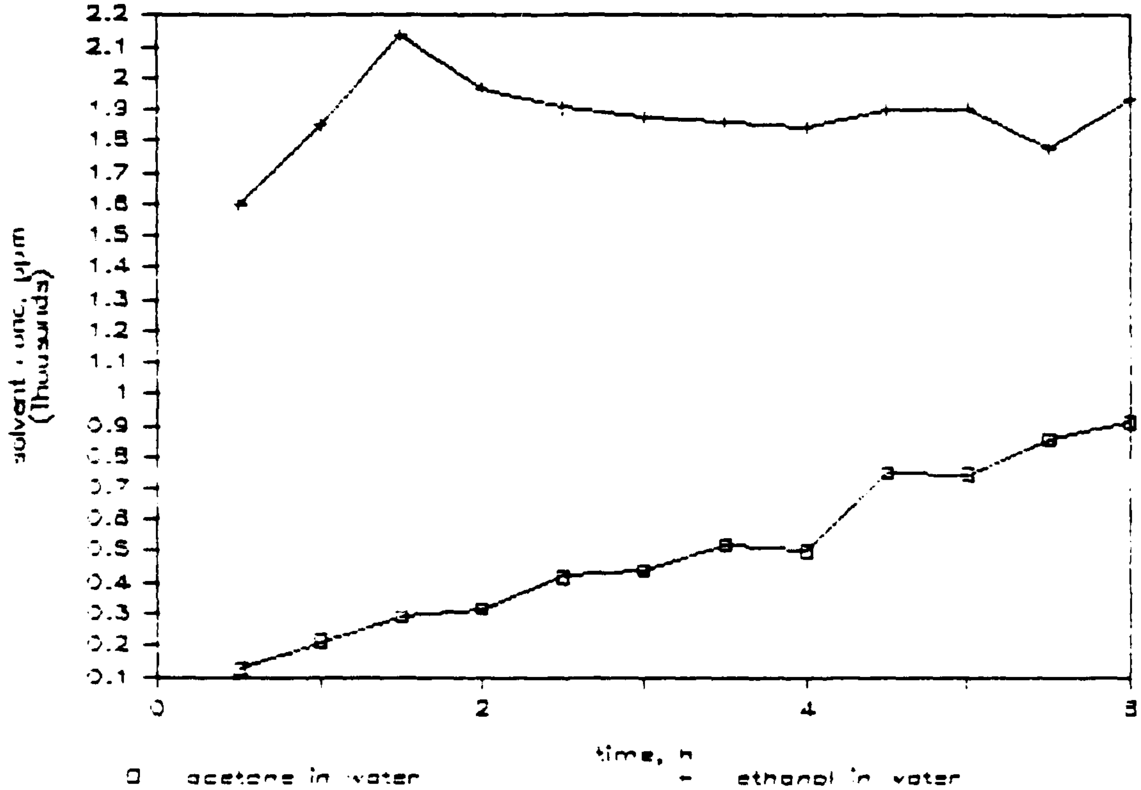


Figure 7. Solvent concentrations in single-pass column absorbent (plant process water), test 1 of fractional factorial (1/2 replicate) experiment

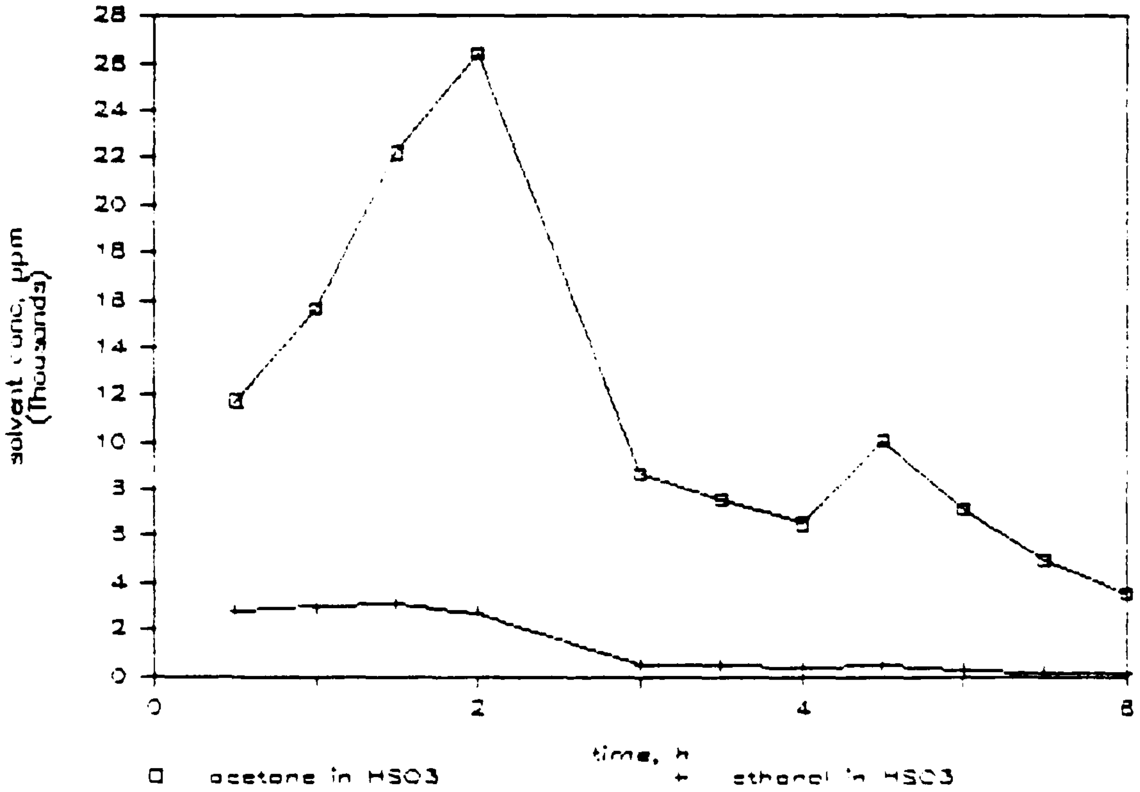


Figure 8. Solvent concentrations in recycle column HSO_3^- absorbent solution, test 2 of fractional factorial (1/2 replicate) experiment

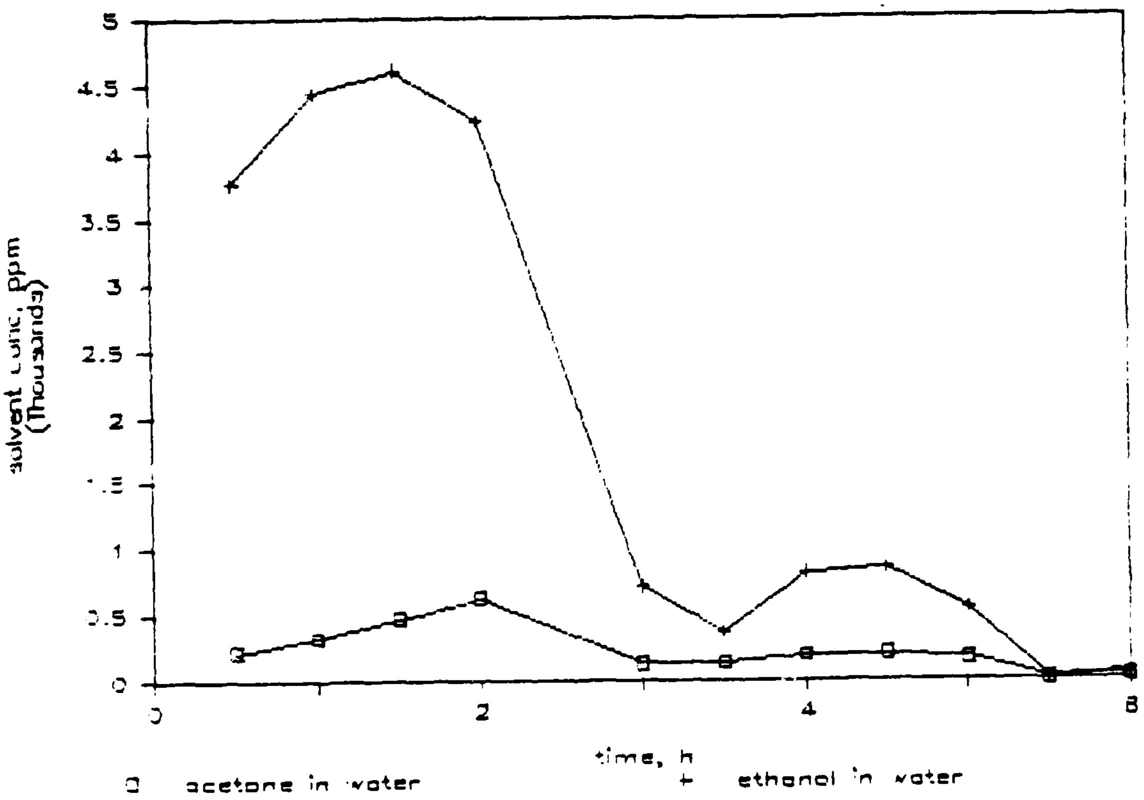


Figure 9. Solvent concentrations in single-pass column absorbent (plant process water), test 2 of fractional factorial (1/2 replicate) experiment

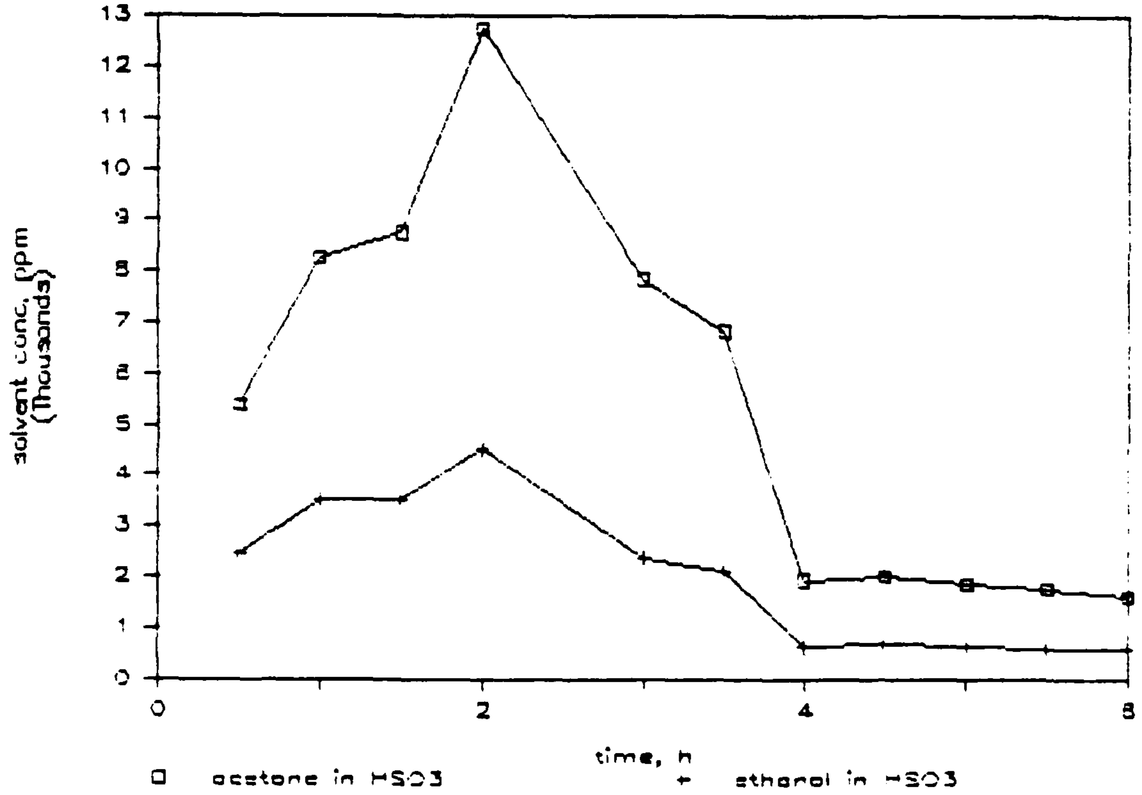


Figure 10. Solvent concentrations in recycle column HSO_3^- absorbent solution, bcde interaction of fractional factorial (1/2 replicate) experiment

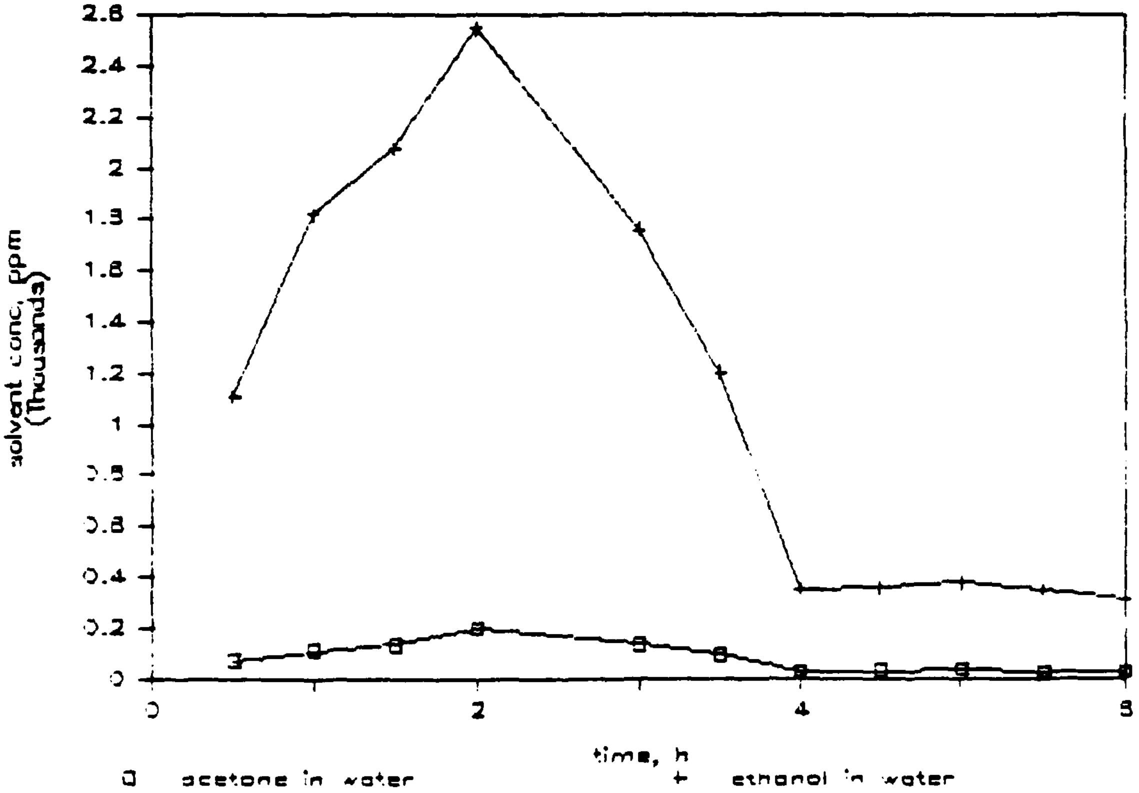


Figure 11. Solvent concentrations in single-pass column absorbent (plant process water), bcde interaction of fractional factorial (1/2 replicate) experiment

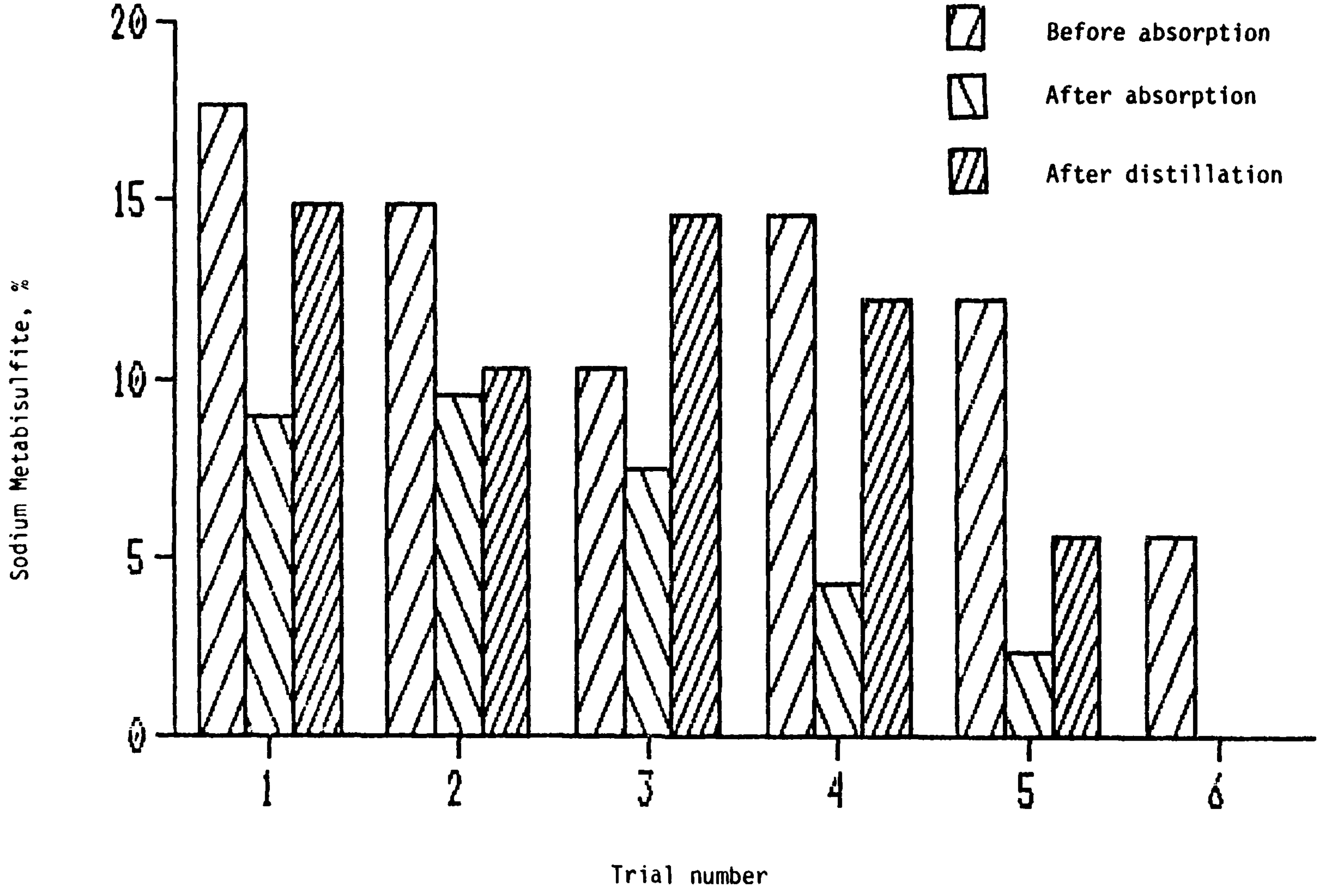


Figure 12. Sodium metabisulfite trends

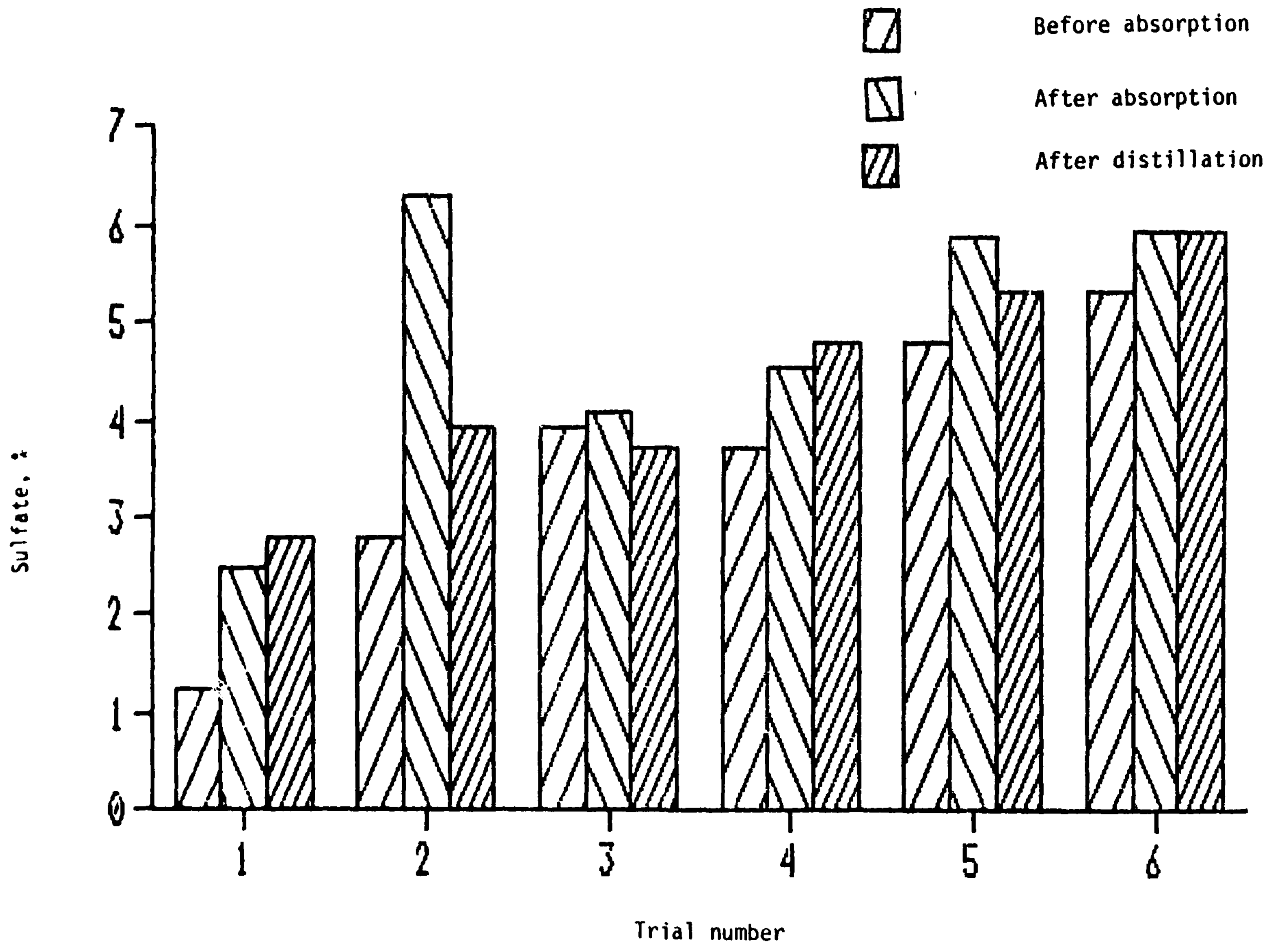


Figure 13. Sulfate trends

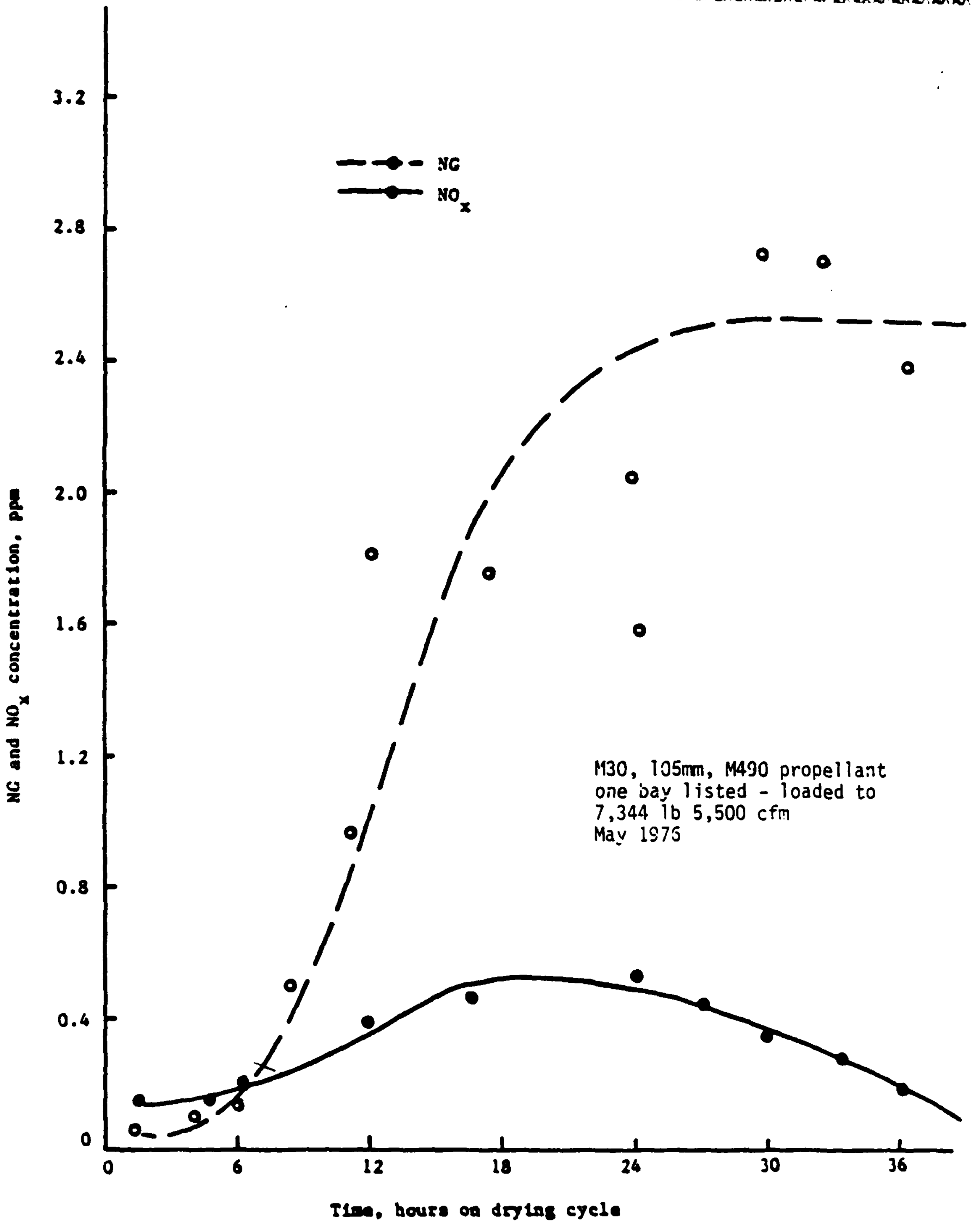
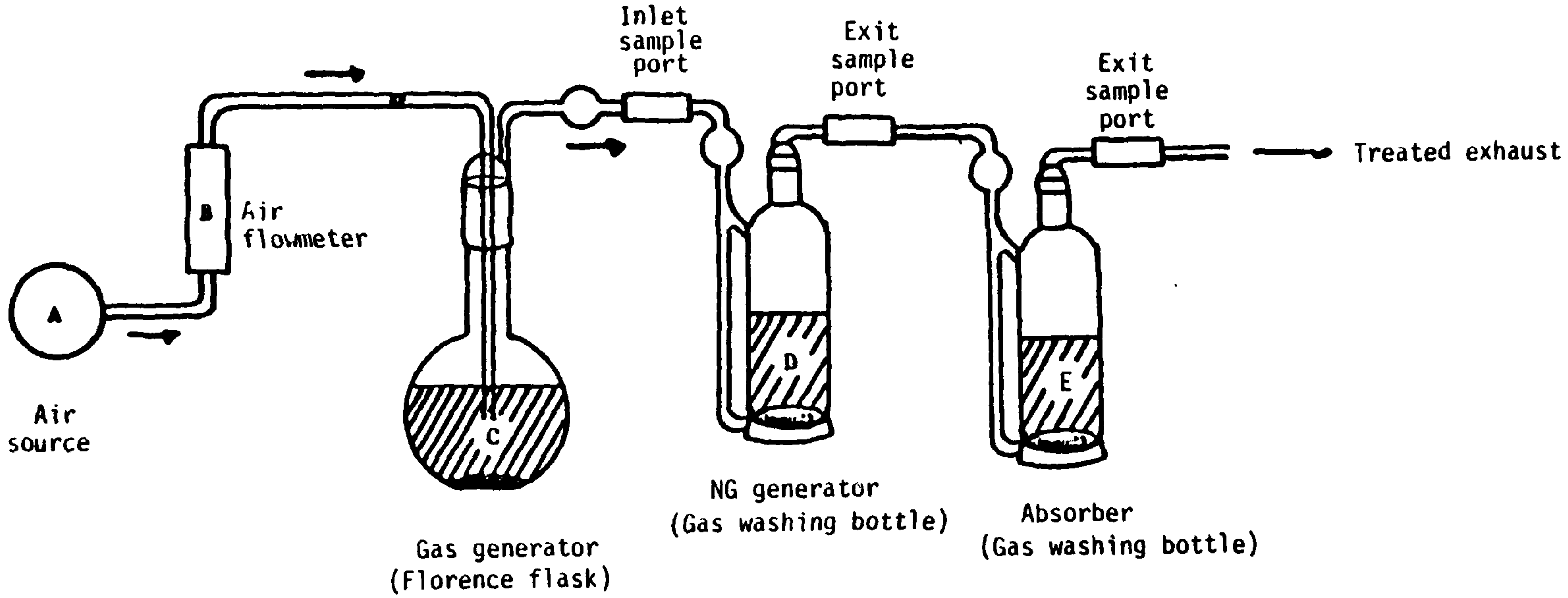


Figure 14. FAD exhaust curve



Legend:

A - laboratory air
B - air flowmeter, 32m/min (105 ft/min)
C - gas generator containing 1000 mL of 1.5 wt % ethanol and 0.25 wt % acetone in water
D - NG generator containing 150 g of warm N5 propellant
E - absorber containing 100 g of 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA

Figure 15. Laboratory-scale unit used in NG study

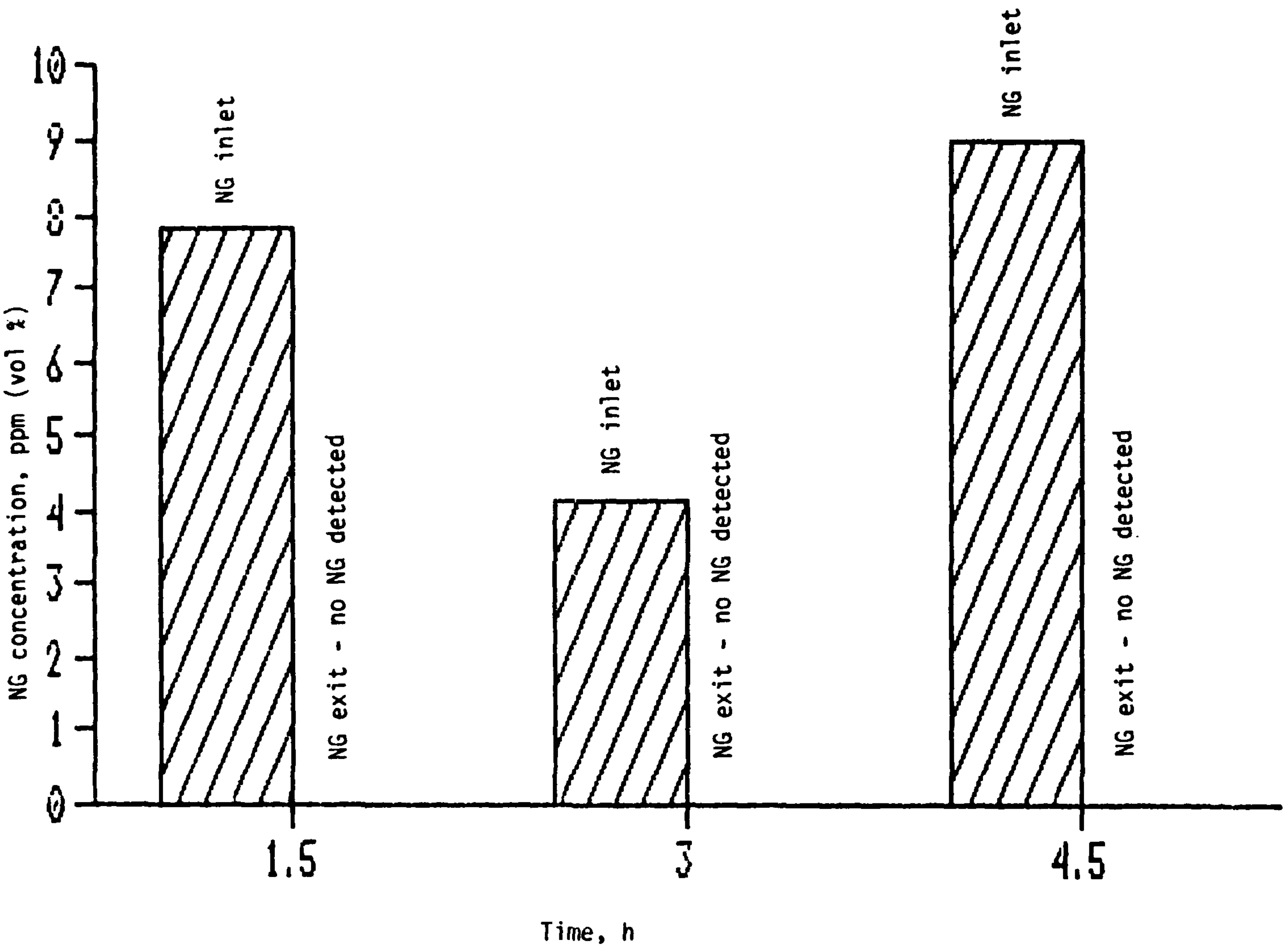


Figure 16. Gas chromatographic results of NG concentrations in inlet and exit absorber gas streams using heated N5 propellant to generate NG vapors

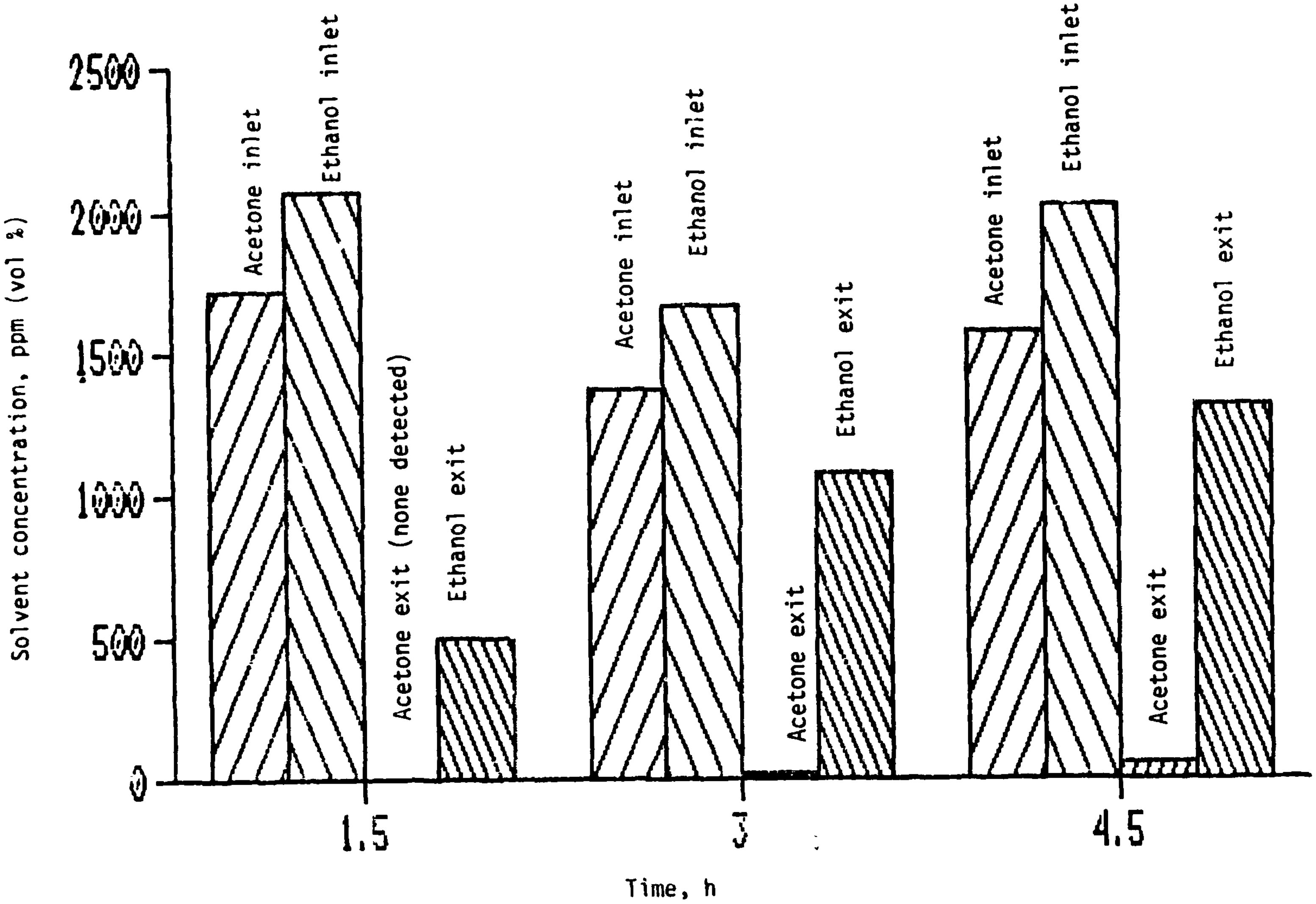
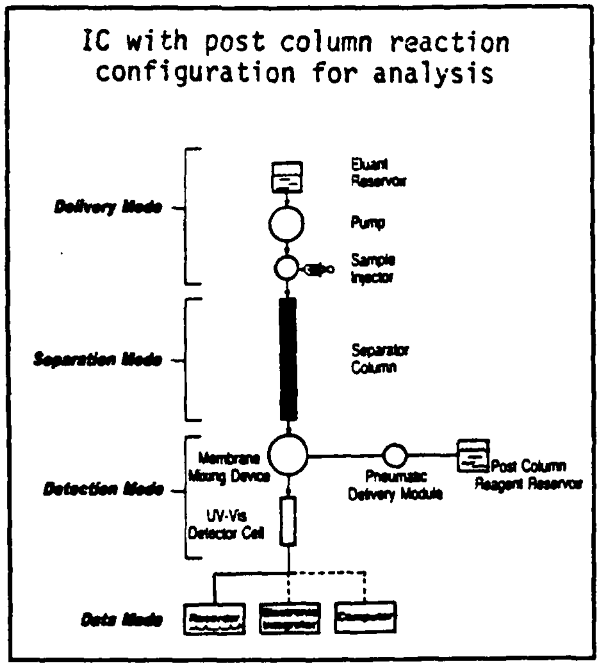
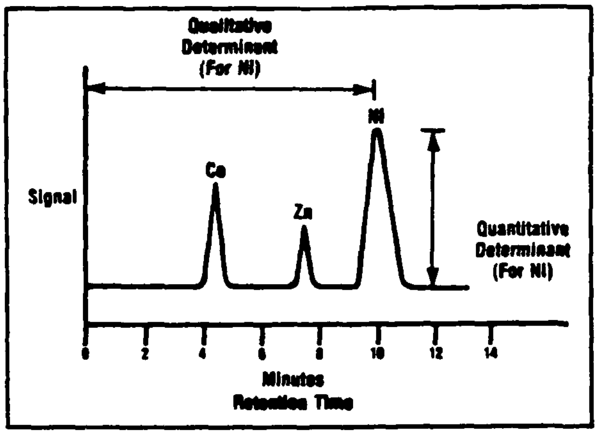


Figure 17. Gas chromatographic results of acetone and ethanol concentrations in inlet and exit absorber gas streams





Regardless of the element or compound of interest, all Dionex Chromatographs operate according to the same basic principles.

By selecting the appropriate column for separating the ions of interest in a sample, chemists can now separate and analyze the oxidation state of many metals, determine Group I and II metals, metal complexes, and a complete range of inorganic and organic ions in a sample with excellent speed and sensitivity.

A liquid sample is introduced at the top of the ion exchange analytical column (the separator column). An eluant is pumped through the system. This causes the ionic species to move through the column at rates determined by their affinity for the column resin. The differential migration of the ions allows them to separate into discrete bands.

As these bands move through the column, they are delivered, one at a time, into the detection system. The bands can then be detected by the appropriate detection mode. In the case of anion complex detection, a conductivity cell is employed.

The detector is set to measure the complexed ionic band at a pre-selected conductivity. The results appear in the form of a chromatogram, essentially a plot of time the band was retained on the column versus the signal it produces in the detector. Each ion in the sample can be identified and quantified by comparing the chromatogram against that of a standard solution.

"The Alternative to AA and ICP" Dionex pamphlet LPM 32631 7/85, Dionex, Sunnyvale, CA

Figure 18. Principles of ion chromatography

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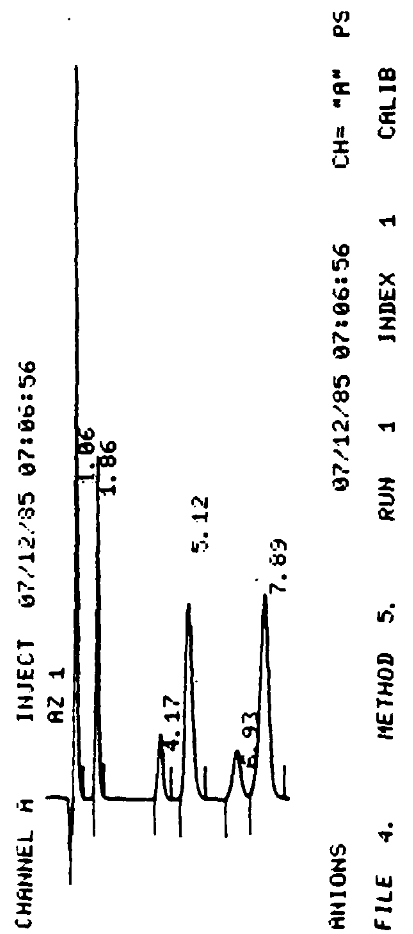
APPLICATION REPORT

DIONEX

Standard Anions

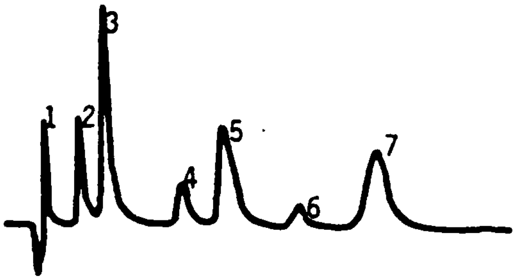


Eluent:	0.75mM $NaHCO_3$
	2.2mM Na_2CO_3
Separation	HPIC-AS4a
Mode:	HPIC-AG4a
Detection	
Mode:	IonChrom/Cond.
Range:	30uS Full Scale
Flow:	2ml/min.
Sample Loop:	50ul
Chart Speed:	0.5cm/min.
Misc:	

---

1. 3ppm F^-
2. 3ppm Cl^-
3. 4ppm Br^-
4. 5ppmSO_3^{2-}
5. 2ppm NO_3^-
6. 10ppm SO_4^{2-}
7. ____
8. ____
9. ____
10. ____

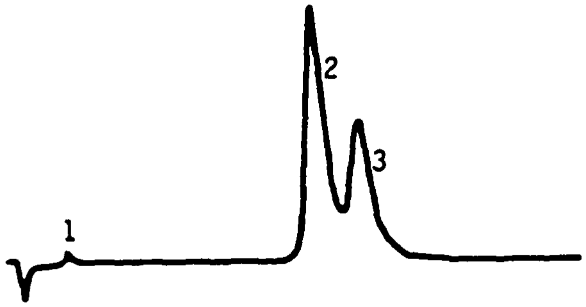
Figure 19. Anion standard



Eluent: 0.75 mM $NaHCO_3$
2.2 mM Na_2CO_3
Separation mode: HPIC-AS4a
HPIC-AG4a
Detection mode: Ion Chrom/Cond.
Range: 30 µS full scale
Flow: 2 mL/min
Sample Loop: 50 µL
Chart speed: 1.0 cm/min

1. 2 ppm F^-
2. 3 ppm Cl^-
3. 10 ppm NO_2^-
4. 10 ppm PO_4^{3-}
5. 5 ppm Br^-
6. 10 ppm NO_3^-
7. 10 ppm SO_4^{2-}

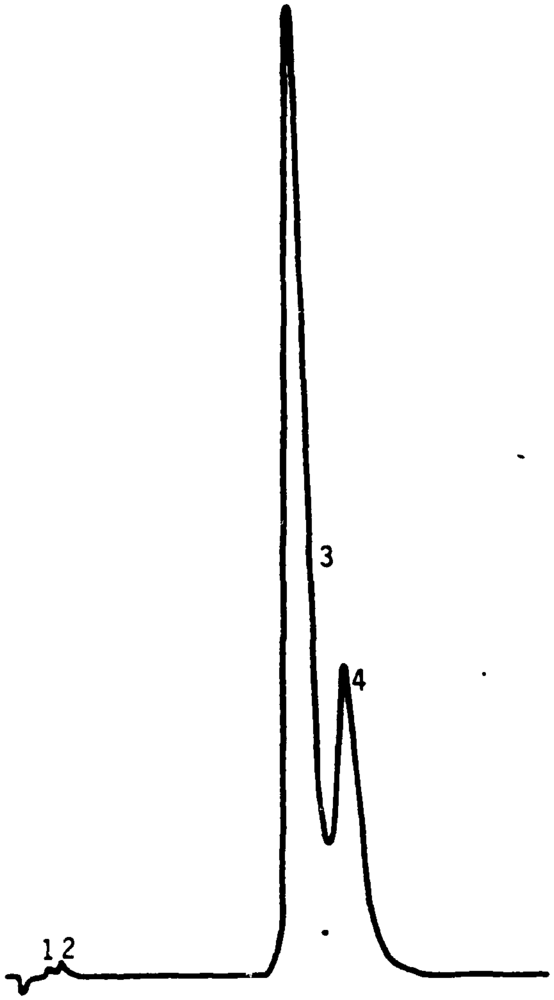
Figure 20. Ion chromatograph anion standard



Eluent:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
Separation mode:	HPIC-AS4a HPIC-AG4a
Detection mode:	Ion Chrom/Cond.
Range:	30 µS full scale
Flow:	2 mL/min
Sample loop:	50 µL
Chart speed:	1.0 cm/min
Misc:	1:500 dilution

1. 71 ppm Cl^-
2. 6,809 ppm SO_3^{2-}
3. 7,750 ppm SO_4^{2-}

Figure 21. IC analyses of 6.5 g Na_2SO_3 in 93.5 g deionized H_2O



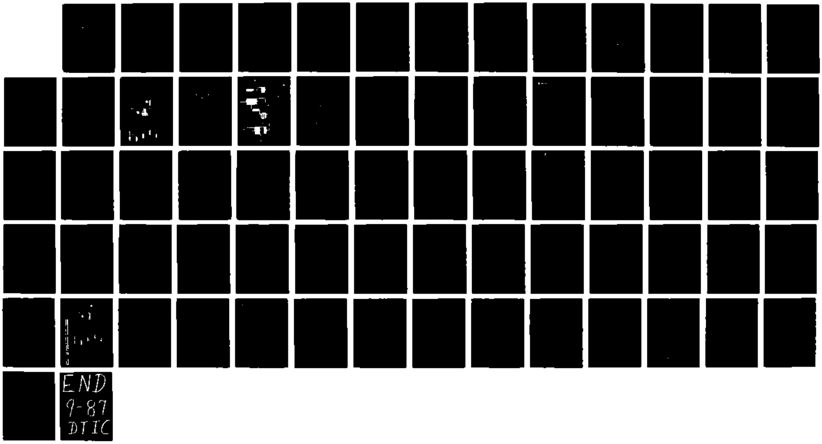
Eluent:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
Separation mode:	HPIC-AS4a HPIC-AG4a
Detection mode:	Ion Chrom/Cond.
Range:	30 µS full scale
Flow:	2 mL/min
Sample loop:	50 µL
Chart speed:	1.0 cm/min
Misc:	1:500 dilution

1. Unknown
2. 71 ppm Cl^-
3. 34,9[illegible] ppm [illegible]
4. 21,250 ppm SO_4^{2-}

Figure 22. IC analyses of 15 [illegible] Na [illegible] deionized H_2O

AD-A183 735 VOLATILE ORGANIC CARBON EMISSIONS PHASE 2(U) HERCULES INC RADFORD VA C A JAKE FEB 87 AMXTH-TE-CR-87116 DAAA09-86-Z-0003 2/2

UNCLASSIFIED F/G 24/1 NL



END
9-87
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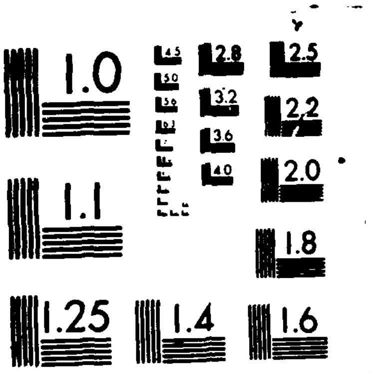
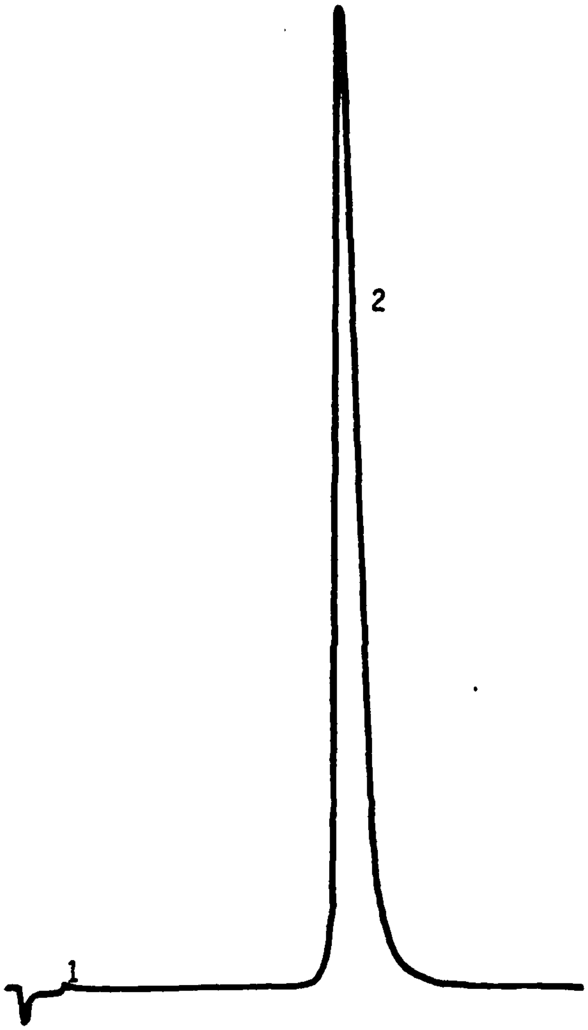


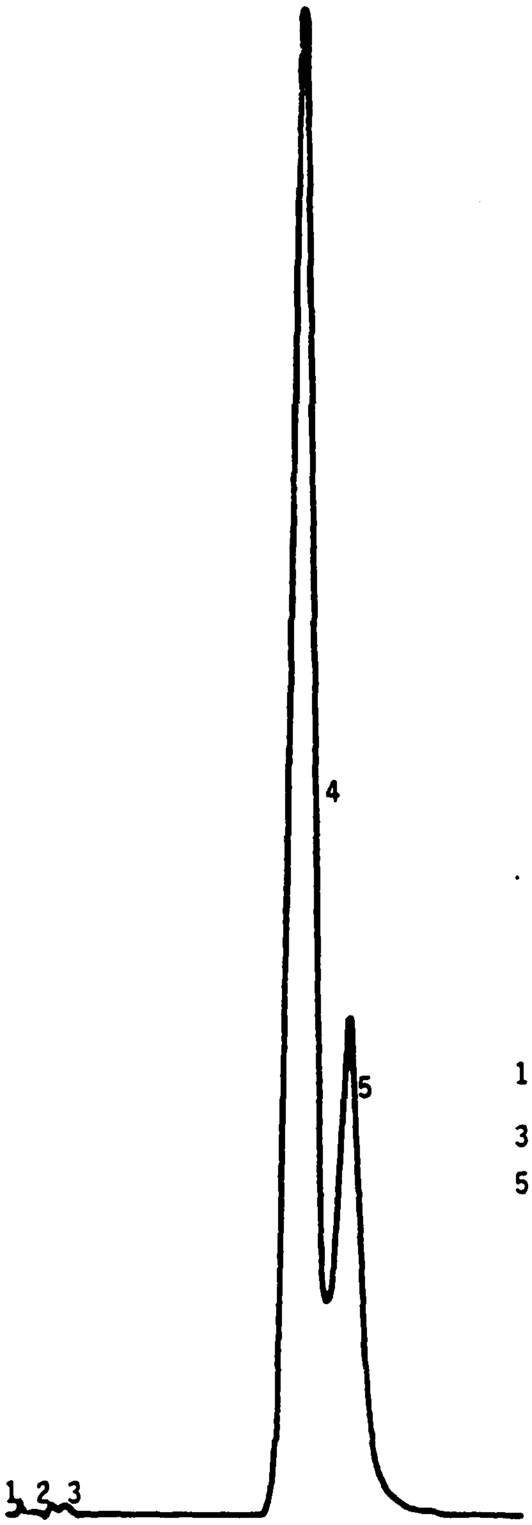
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



Eluent:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
Separation mode:	HPIC-AS4a HPIC-AG4a
Detection mode:	Ion chrom/Cond.
Range:	30 μS full scale
Flow:	2 mL/min
Sample loop:	50 μL
Chart speed:	1.0 cm/min
Misc:	*1:500 dilution*

1. 71 ppm Cl^-
2. 67,000 ppm SO_4^{2-}

Figure 23. IC analyses of 15 g $Na_2S_2O_5$ + 6.5 g Na_2SO_3 in 78.5 g deionized H_2O



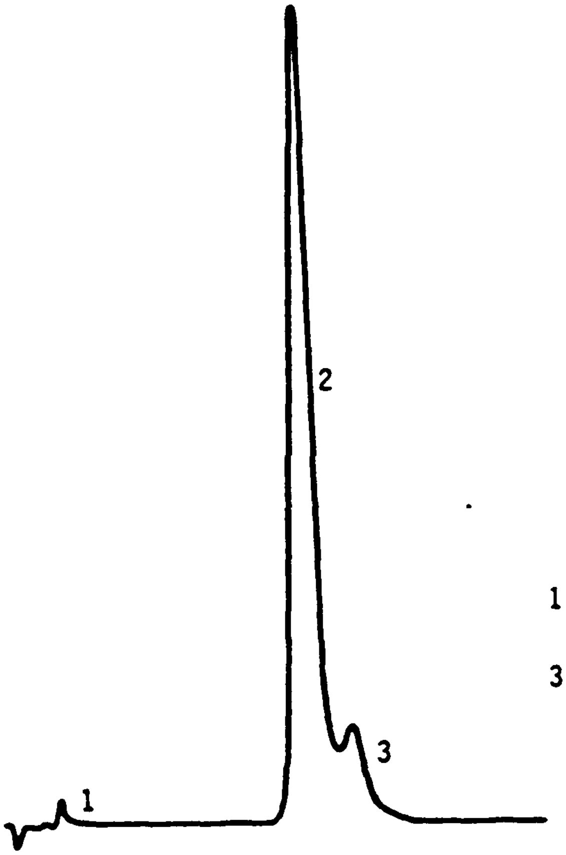
Eluent:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
Separation mode:	HPIC-AS4a HPIC-AG4a
Detection mode:	Ion Chrom/Cond.
Range:	30 µS full scale
Flow:	2 mL/min
Sample loop:	50 µL
Chart speed:	1.0 cm/min
Misc:	1:500 dilution

1. Unknown 2. 308 ppm F^-

3. Unknown 4. 59,541 ppm SO_3^{2-}

5. 34,000 ppm SO_4^{2-}

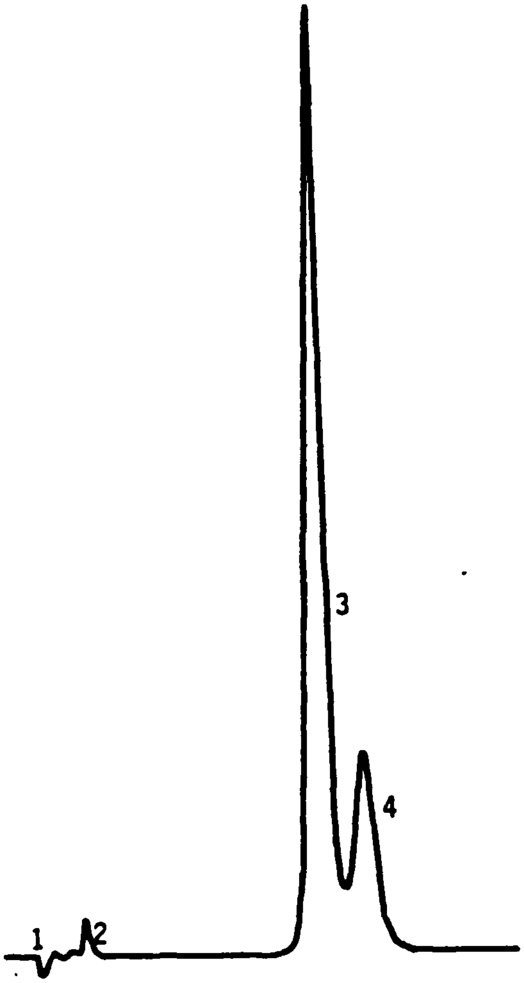
Figure 24. IC analyses of 15 g $Na_2S_2O_5$ + 6.5 g Na_2SO_3 + 0.05 g EDTA in 78.5 g deionized H_2O



<u>Eluent</u>:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
<u>Separation mode</u>:	HPIC-AS4a HPIC-AG4a
<u>Detection mode</u>:	Ion Chrom/Cond.
<u>Range</u>:	30 µS full scale
<u>Flow</u>:	2 mL/min
<u>Sample loop</u>:	50 µL
<u>Chart speed</u>:	1.0 cm/min
<u>Misc</u>:	1:1000 dilution

1. 462 ppm Cl^-
2. 59,274 ppm SO_3^{2-}
3. 18,000 ppm SO_4^{2-}

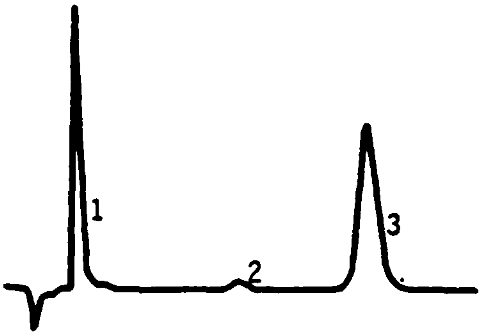
Figure 25. IC analyses of 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/0.05 wt % EDTA in plant process water before testing



Eluent:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
Separation mode:	HPIC-AS4a HPIC-AG4a
Detection mode:	Ion Chrom/Cond.
Range:	30 μS full scale
Flow:	2 mL/min
Sample loop:	50 μL
Chart speed:	1.0 cm/min
Misc:	1:1000 dilution

1. 154 ppm F^-
2. 1,429 ppm Cl^-
3. 50,864 ppm SO_3^{2-}
4. 24,500 ppm SO_4^{2-}

Figure 26. IC analyses of 15 wt % $Na_2S_2O_5$/6.5 wt % Na_2SO_3/ 0.05 wt % EDTA in plant process water after testing

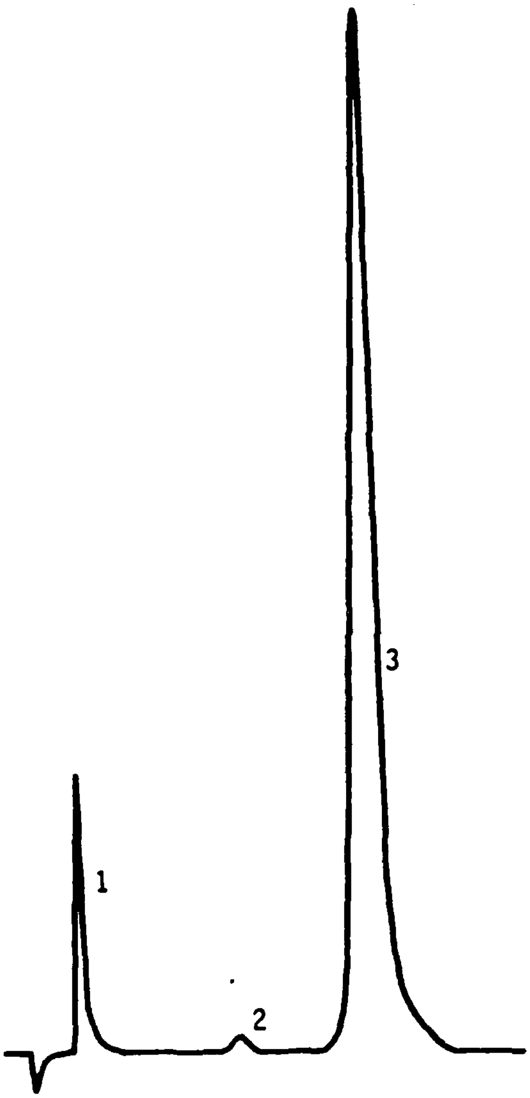


Eluent:	0.75 mM $NaHCO_3$ 2.2 mM Na_2CO_3
Separation mode:	HPIC-AS4a HPIC-AG4a
Detection mode:	Ion Chrom/Cond.
Range:	30 μS full scale
Flow:	2 mL/min
Sample loop:	50 μL
Chart speed:	1.0 cm/min

1. 5 ppm Cl^-
2. 0.3 ppm Br^-
3. 17 ppm SO_4^{2-}

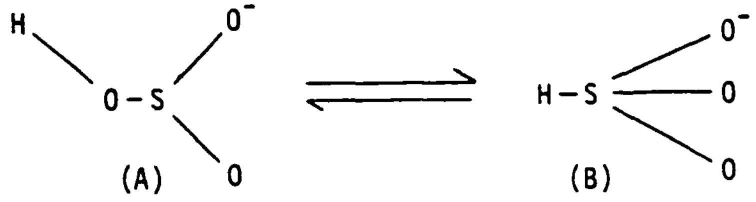
Figure 27. IC analyses of plant process water before testing

Eluent: 0.75 mM $NaHCO_3$
2.2 mM Na_2CO_3
Separation mode: HPIC-AS4a
HPIC-AG4a
Detection mode: Ion Chrom/Cond.
Range: 30 μS full scale
Flow: 2 mL/min
Sample loop: 50 μL
Chart speed: 1.0 cm/min

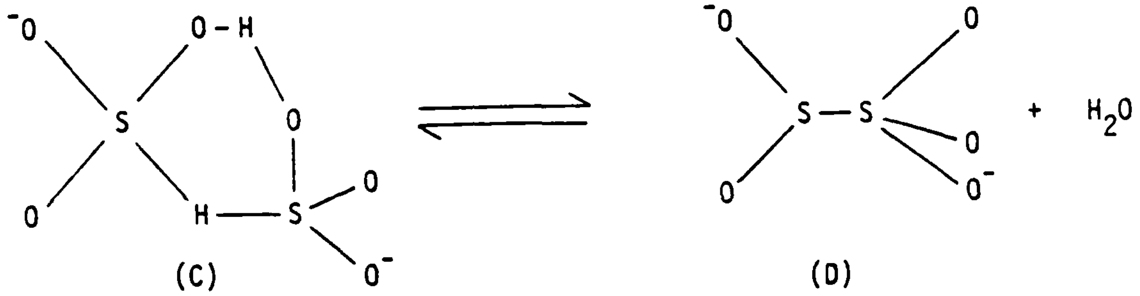


1. 5 ppm Cl^- 2. 0.8 ppm Br^- 3. 140 ppm SO_4^{2-}

Figure 28. IC analyses of plant process water composite after testing



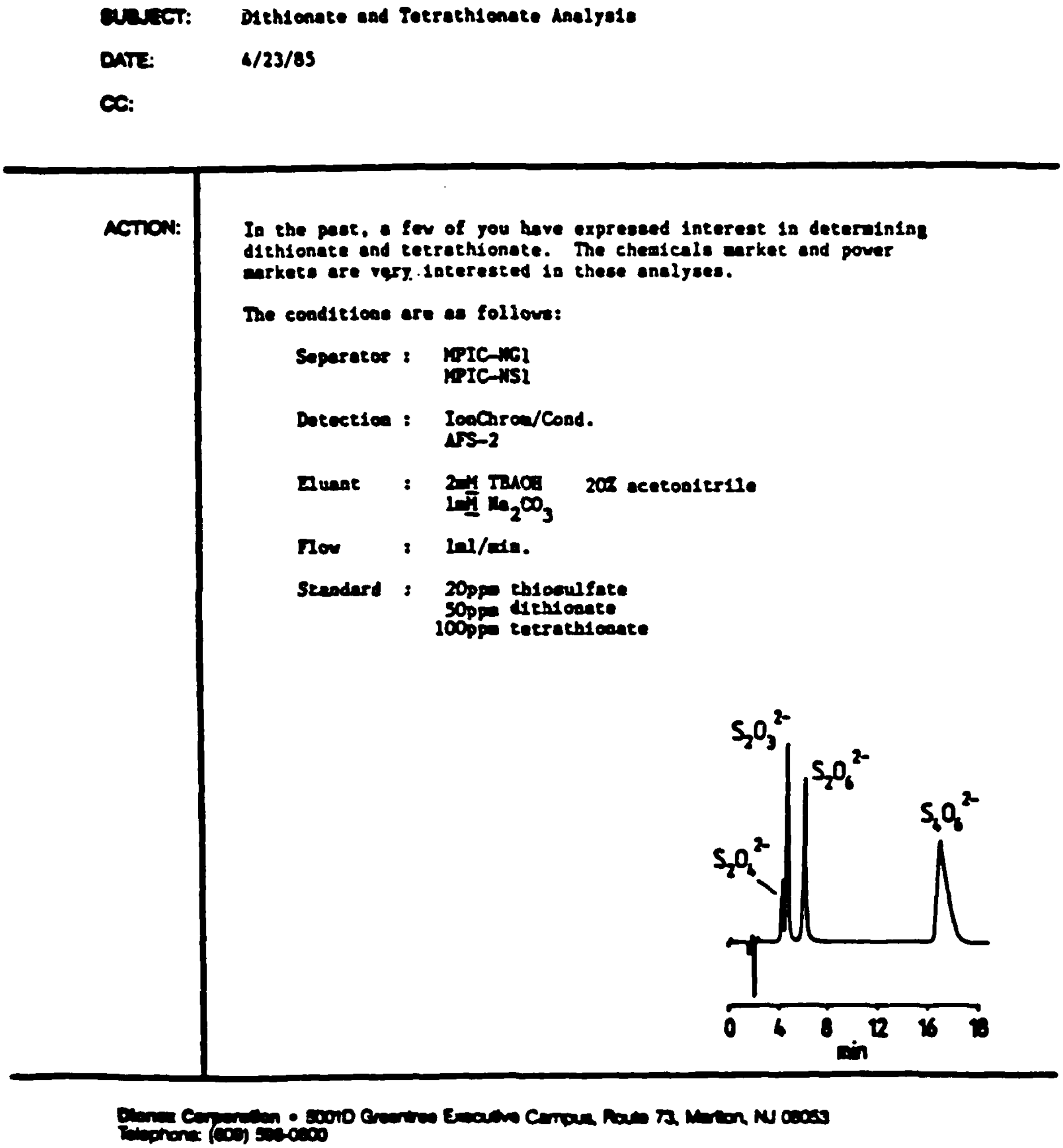
Tautomers (A) and (B) exist at low concentrations (3 x 10^{-3} M)



Tautomers (C) and (D) exist at high concentrations (7 x 10^{-2} M)

"Sodium Bisulfite Anhydrous", Virginia Chemicals Inc. technical data Bulletin 704 (76-502683V), Virginia Chemicals Inc., Portsmouth, Virginia 23703

Figure 29. Four species in $NaHSO_3$ solutions



SUBJECT: Dithionate and Tetrathionate Analysis

DATE: 4/23/85

CC:

ACTION:

In the past, a few of you have expressed interest in determining dithionate and tetrathionate. The chemicals market and power markets are very interested in these analyses.

The conditions are as follows:

Separator	:	MPIC-NG1 MPIC-NS1
Detection	:	IonChrom/Cond. AFS-2
Eluant	:	2mM TBAOH 20% acetonitrile 1mM Na_2CO_3
Flow	:	1ml/min.
Standard	:	20ppm thiosulfate 50ppm dithionate 100ppm tetrathionate

Dionex Corporation • 5001D Greentree Executive Campus, Route 73, Marlton, NJ 08053
Telephone: (609) 596-0800

Figure 30. Dithionate and tetrathionate IC analyses

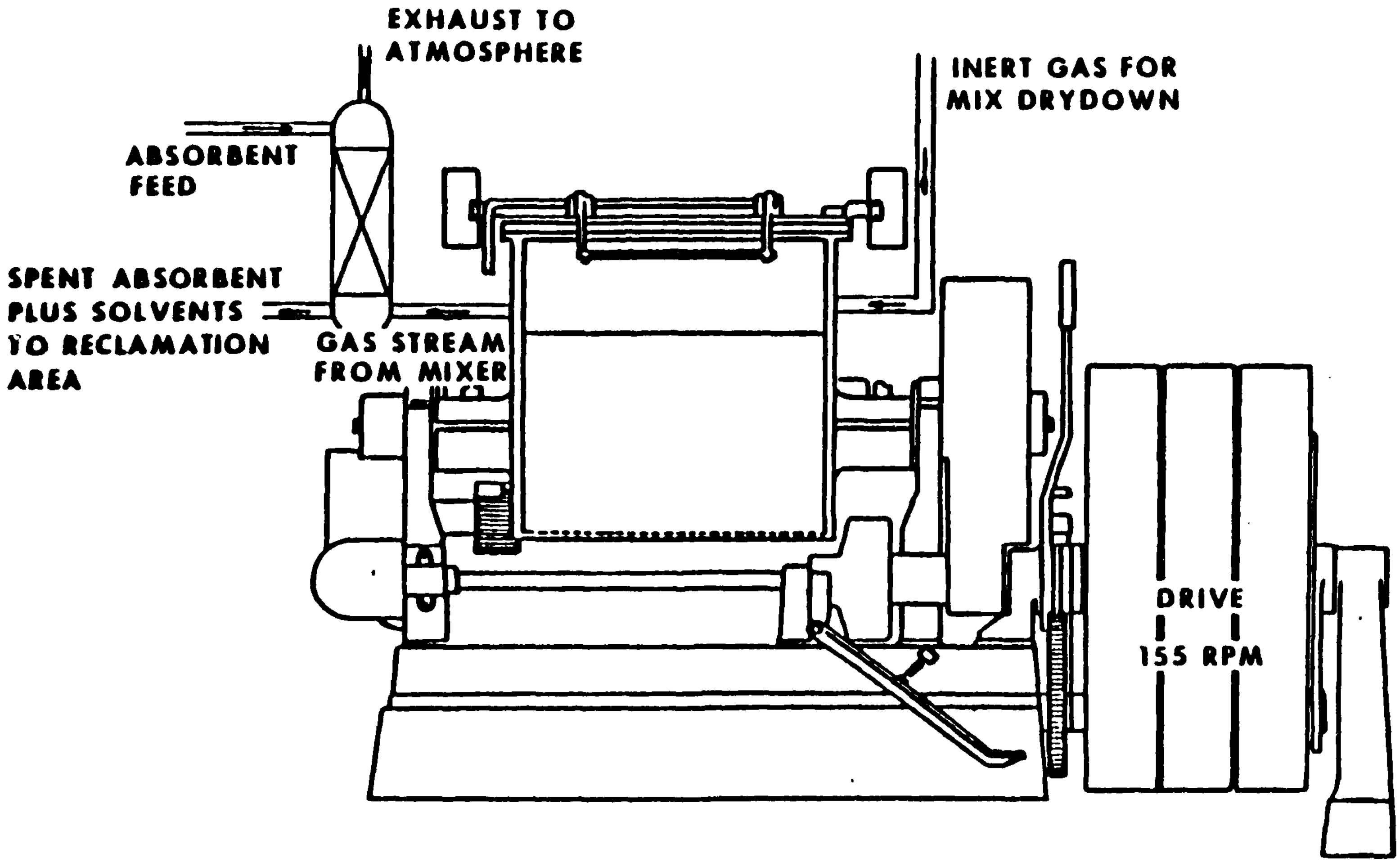
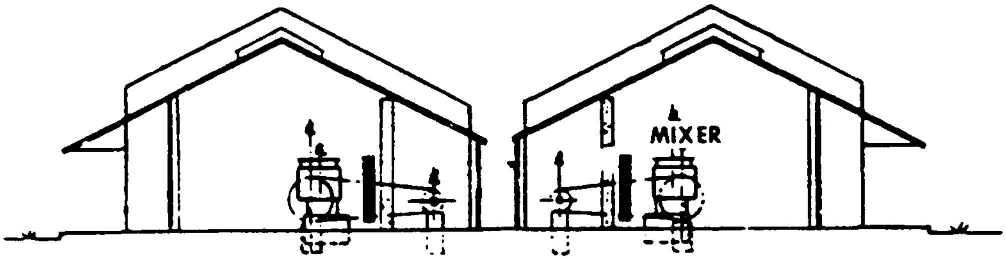
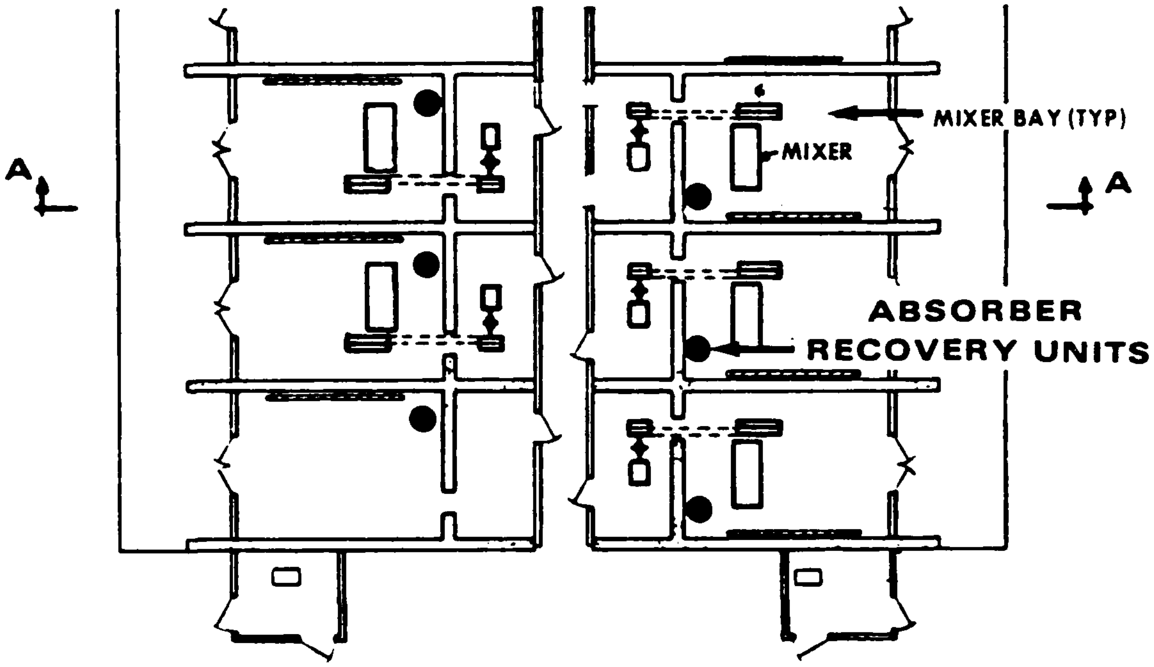


Figure 31. Absorber design for solvent recovery in mix bay



SECTION A - A



PARTIAL FLOOR PLAN

Figure 32. Placement of solvent recovery units in mix house

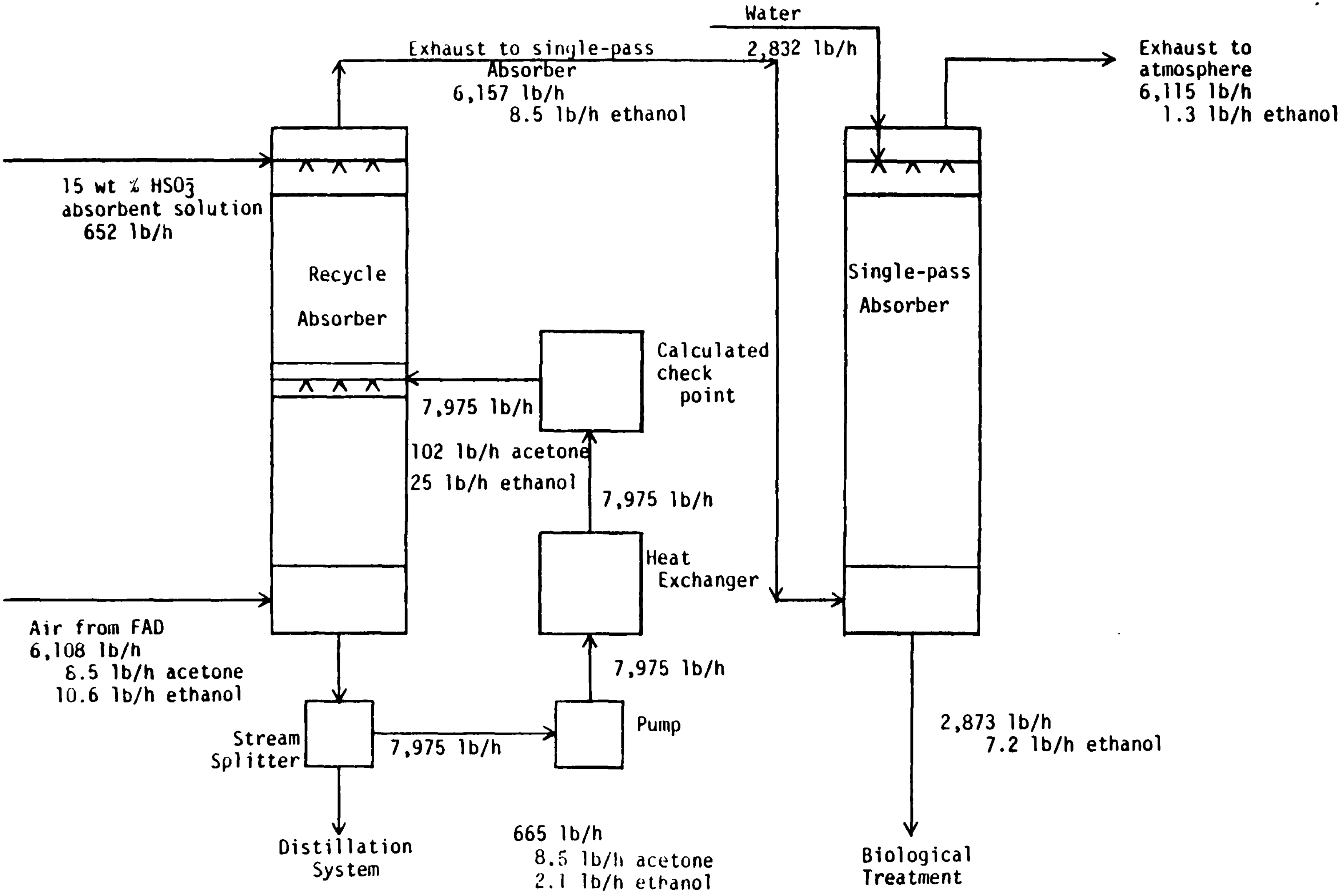
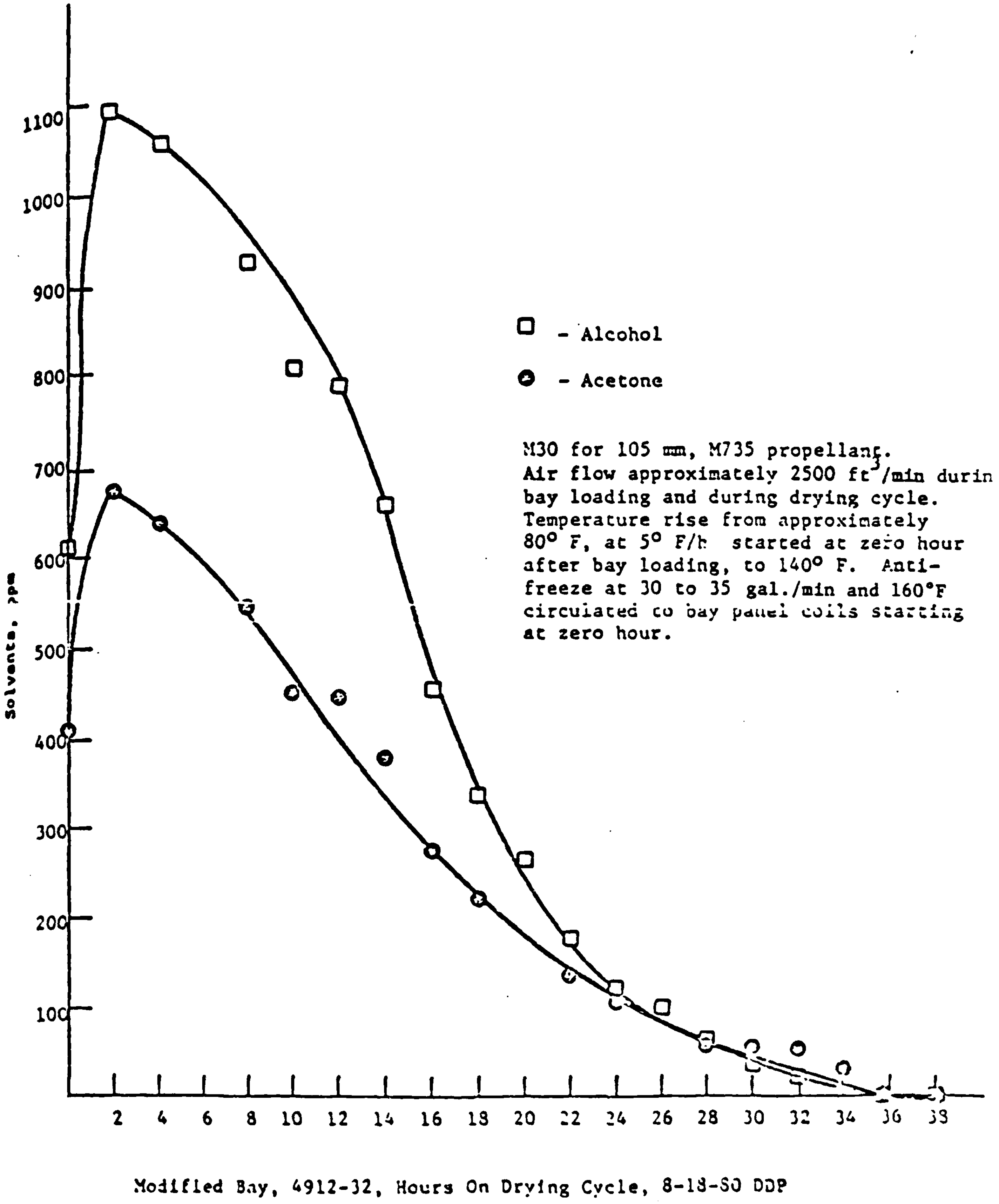
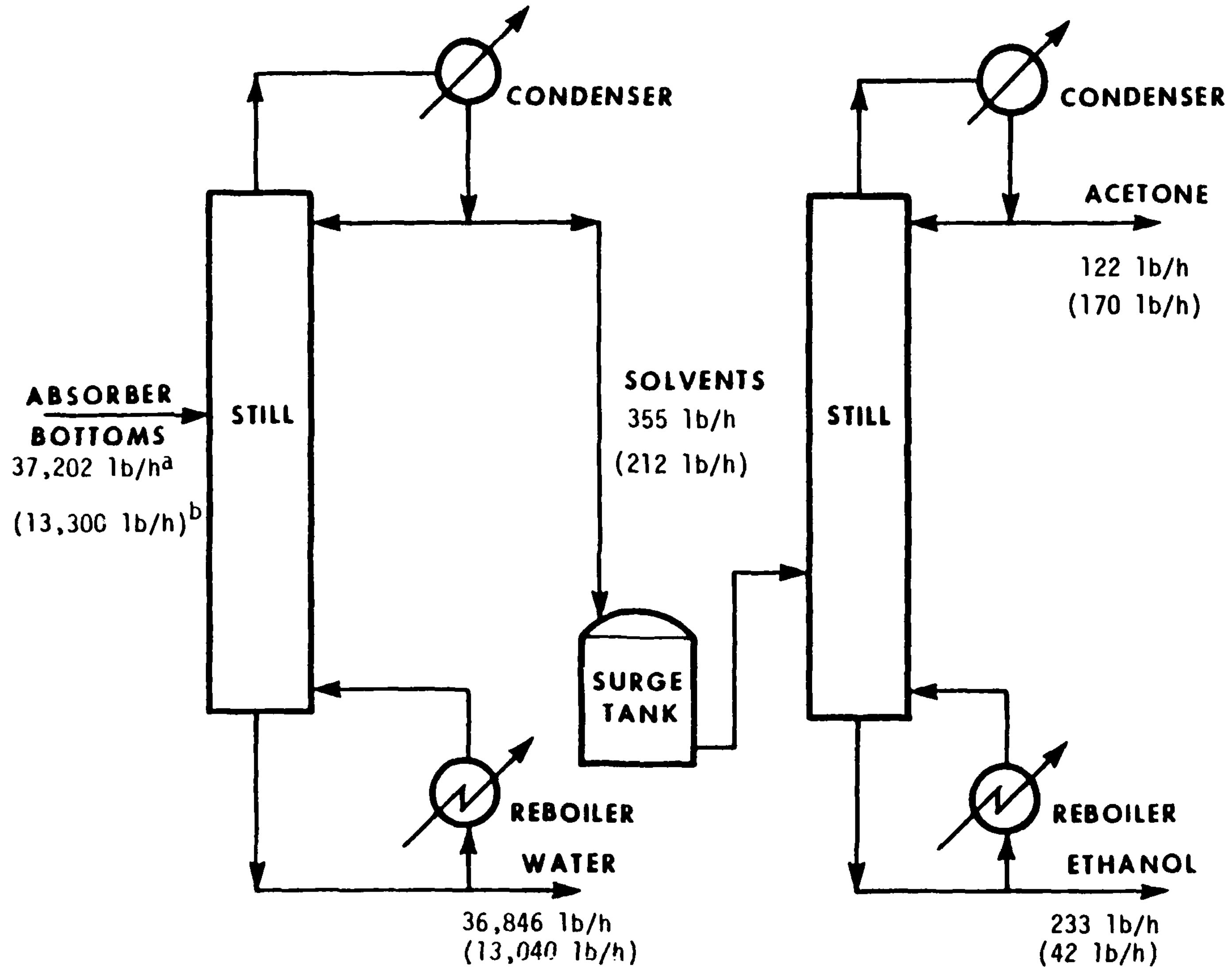


Figure 33. Flowsheet simulation



M30 for 105 mm, M735 propellant.
Air flow approximately 2500 ft^3/min durin
bay loading and during drying cycle.
Temperature rise from approximately
80° F, at 5° F/h started at zero hour
after bay loading, to 140° F. Anti-
freeze at 30 to 35 gal./min and 160°F
circulated to bay panel coils starting
at zero hour.

Figure 34. Solvent concentration vs time of FAD cycle



a - Flowtran model.

b - Model based on bench scale data.

Figure 35. Computer model of distillation system for solvent reclamation in drying operation

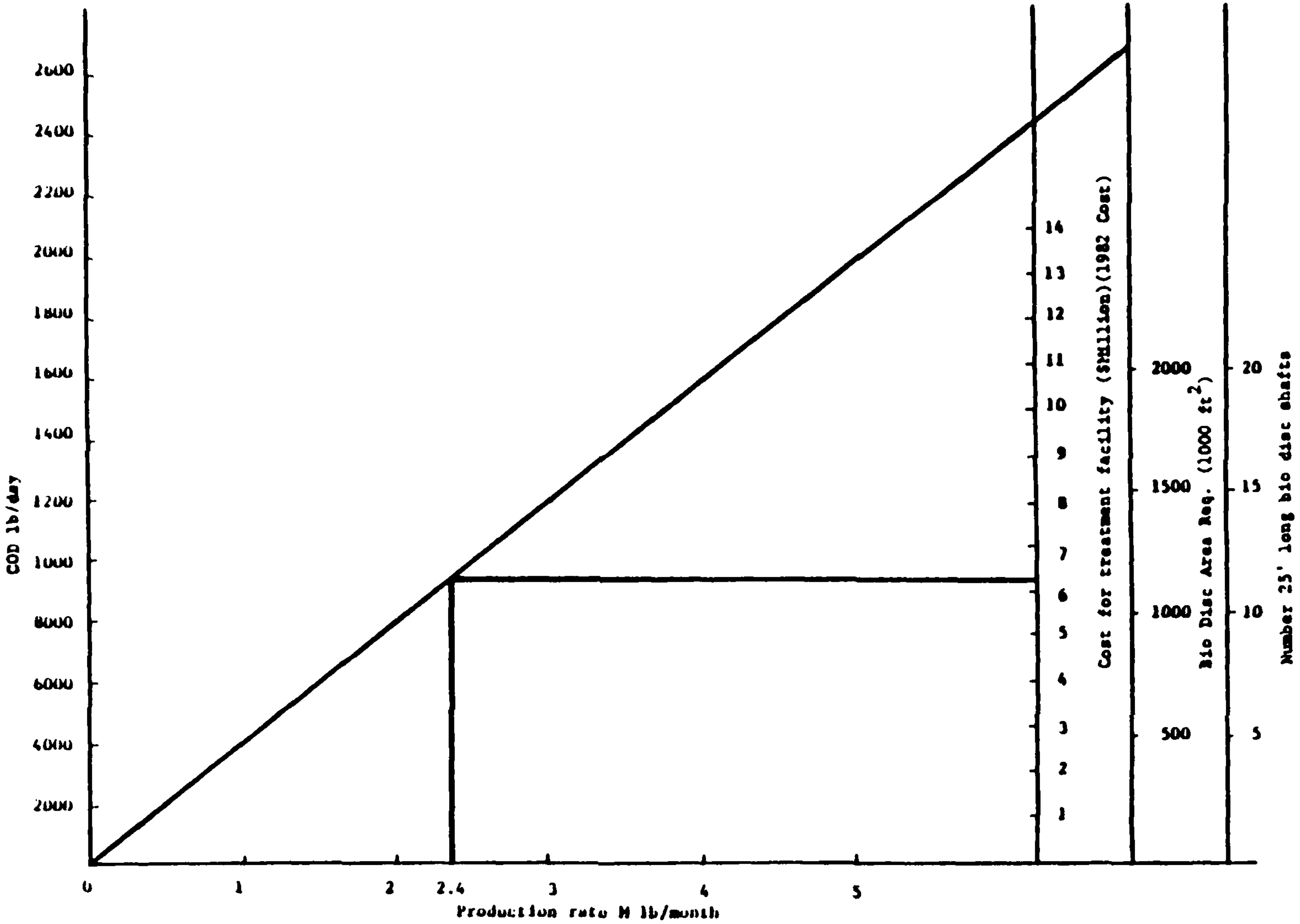
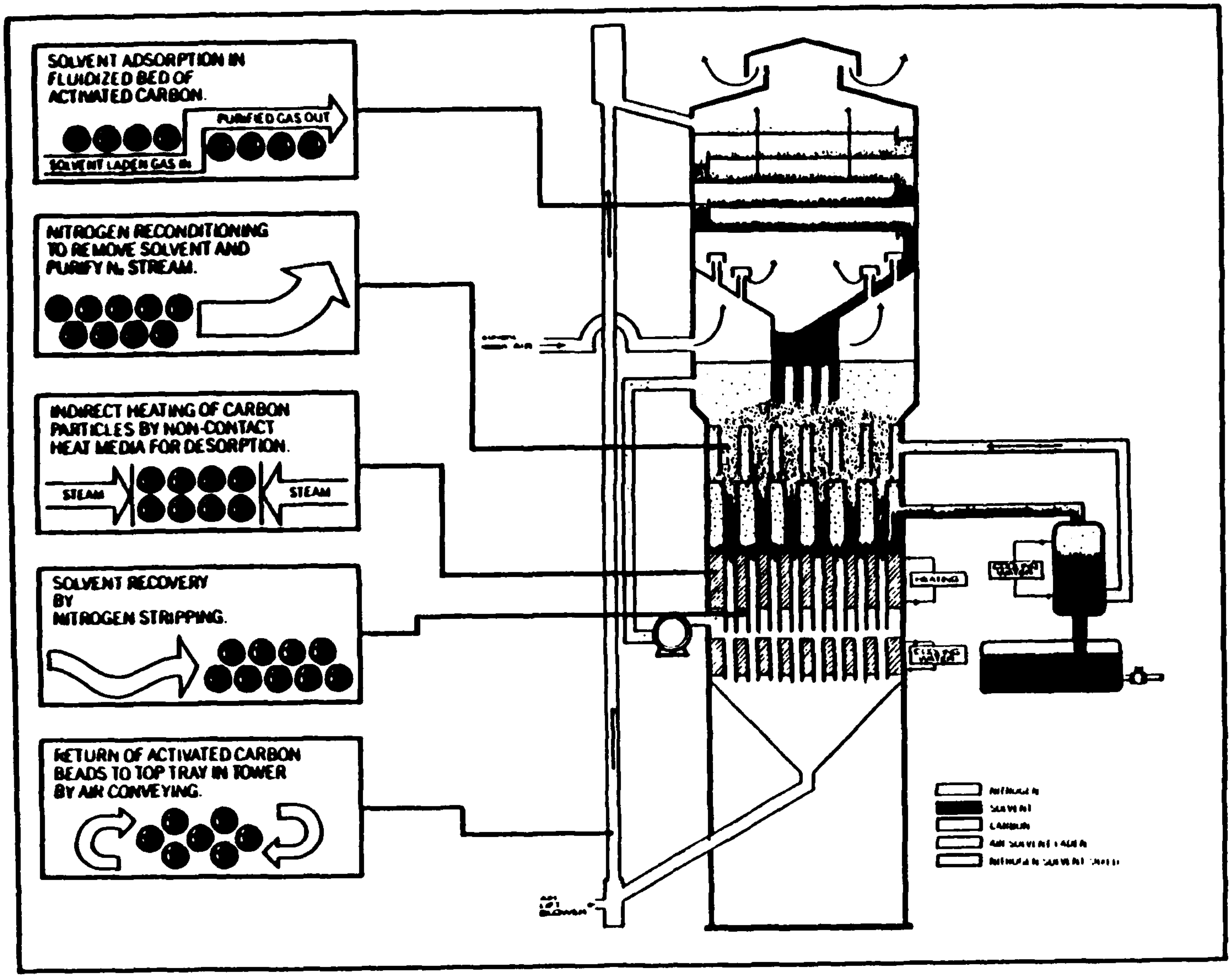


Figure 36. Biological treatment facility cost vs COD influent



HOW IT WORKS

The solvent-laden air is introduced into the bottom of the adsorber section and passes upward countercurrent to the fluidized carbon beads in a series of perforated trays. The carbon beads flow downward from tray to tray by overflowing a weir/downcomer arrangement.

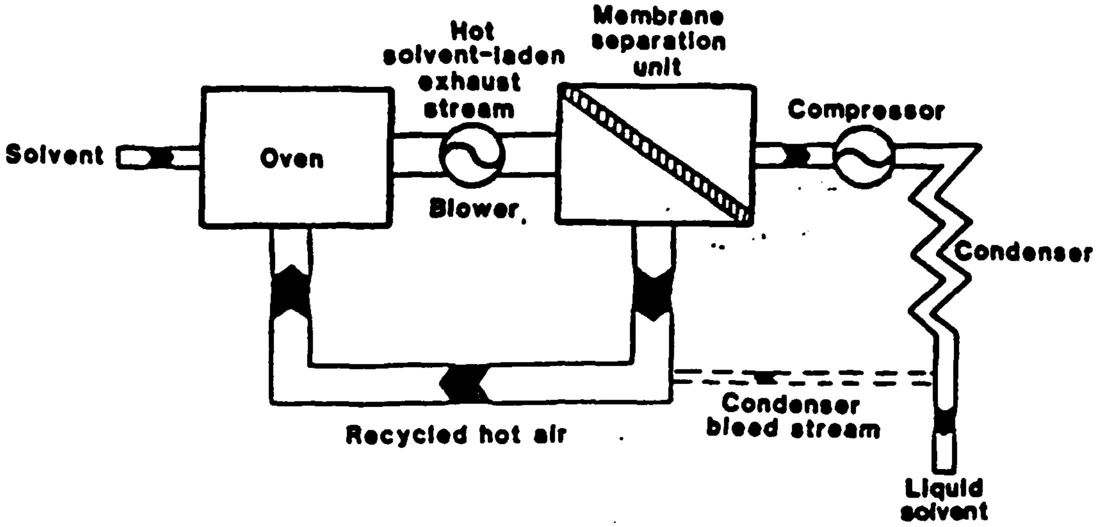
When it leaves the bottom tray of the adsorber section, the carbon is no longer fluidized. It flows as a dense bed through the desorption section of the column. Here the carbon with its adsorbed solvent, passes through the tube side of a shell-and-tube heat exchanger, where it is indirectly heated to the desorption temperature.

Solvent is desorbed from the activated carbon by the introduction of direct-contact nitrogen. This stripping gas carries the solvent to the condenser and separator

The nitrogen exiting from the condenser must be reconditioned because it is saturated with hydrocarbons. The nitrogen reconditioning takes place in the secondary adsorber and the gas is then recycled for reuse. Following desorption, the activated carbon is cooled to ambient temperatures in an indirect cooler The carbon is then air conveyed to the top tray of the adsorption section by a blower

This nitrogen stripping technique offers a unique advantage for recovering water-soluble hydrocarbons. Except for the moisture present in the solvent-laden air, the system does not introduce water which would otherwise contaminate the recovered solvent If the relative humidity of the incoming air is less than 60 percent, the solvents recovered will, in most cases, contain less than 5 percent water by weight.

Figure 37. PURASIV HR solvent recovery system

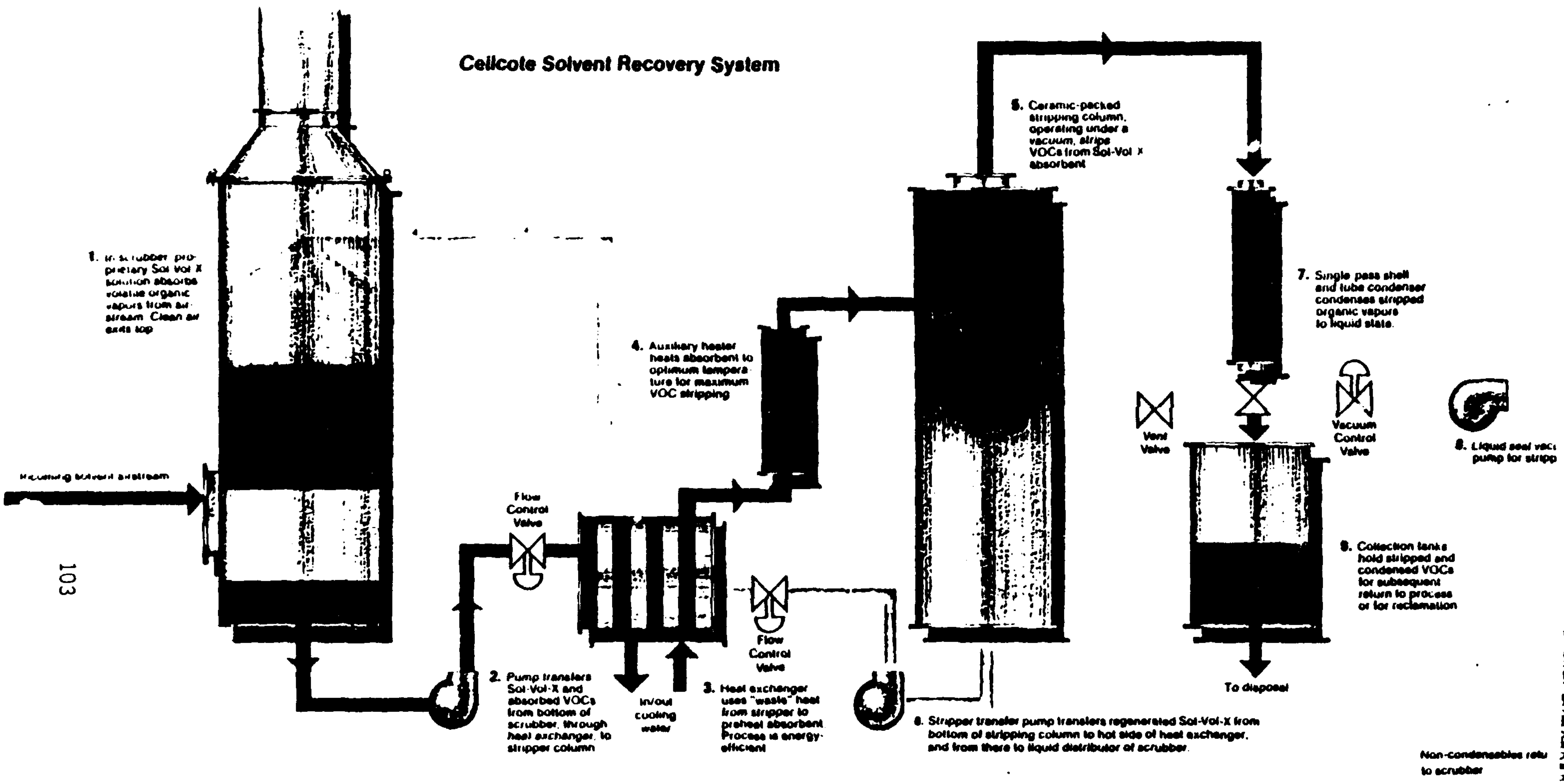


Process Description

Hot solvent-laden exhaust streams from solvent drying ovens are passed over the surface of a membrane much more permeable to organic vapors than to air. The organic vapors pass through the membrane and are condensed to recover the solvent. The air and remaining solvent are recycled to the oven.

Figure 38. MTR's proposed membrane system for solvent recovery

Ceilcote Solvent Recovery System



How the Ceilcote system works:

VOCs are absorbed in a scrubber, then stripped and recovered as shown above. The proprietary organic absorbing fluid Sol Vol X®, has low vapor pressure, a high flash point and a much higher boiling point. Stripping is efficient and non hazardous.

The Sol-Vol-X is recycled continuously. A cost-effective heat exchanger pre-heats the absorbent with energy recovered from the stripping operation. Where gases must be pre-cooled, we add an inexpensive water quench.

The system is closed-loop, continu-ous, microprocessor-controlled. It operates unattended. The control system provides safety interlocks and annunciator alarms to preclude injury to personnel and prevent damage to equipment.

Flexibility of the Ceilcote system permits separate absorbers to be located near individual sources of contaminants and connected to a central stripper by small diameter pipe. This arrangement eliminates the need for costly space-consuming duct-work and adds considerable flexibility to the solution of specific VOC emission control problems.

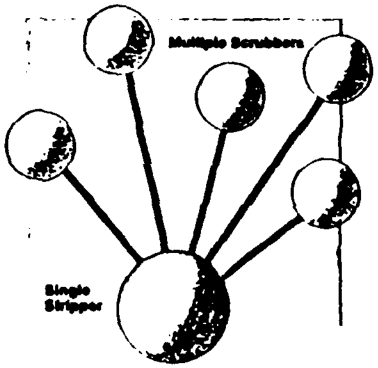


Figure 39. Ceilcote solvent recovery system

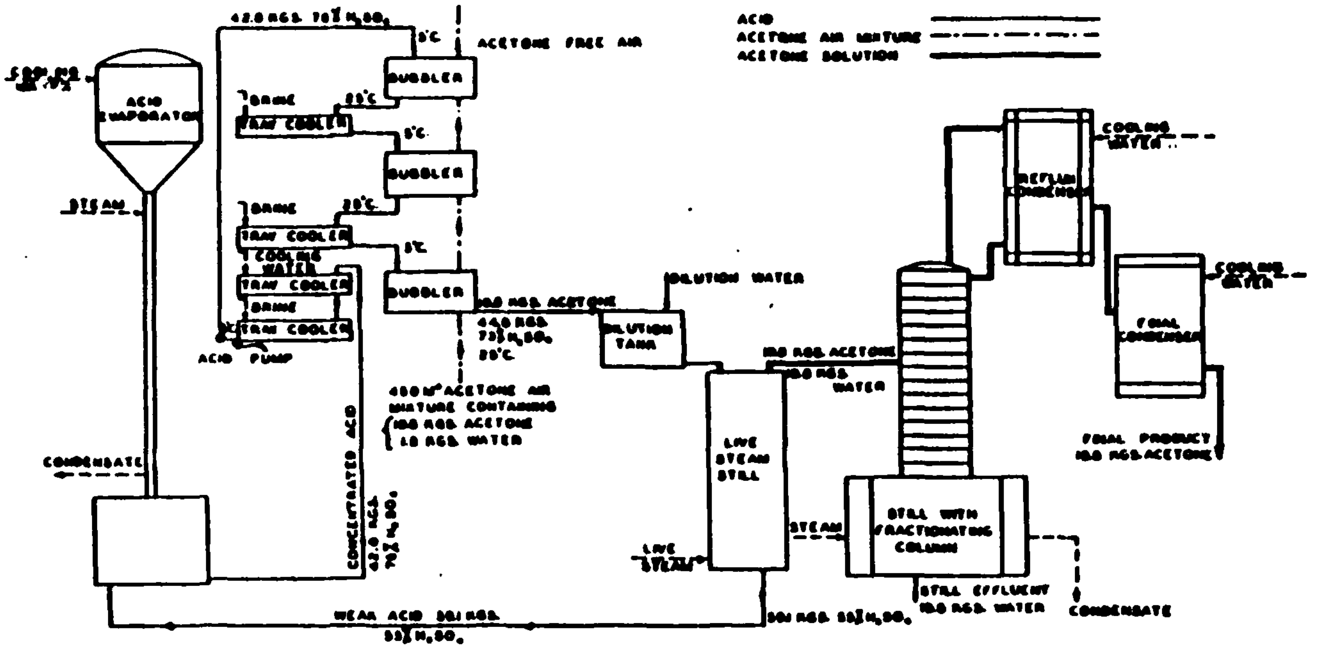


Figure 40. W. R. Ormandy's conceptual design for acetone recovery with sulfuric acid

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3. C. A. Jake and L. L. Smith, "Volatile Organic Carbon Emissions, Phase I," Technical Report RAD 220.10, Hercules Incorporated, Radford AAP, Radford, VA, January 1986.
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15. M. L. Dillard and C. A. Jake, "Nitrate Ester Removal by Absorption/Recycle, Vol II," Technical Report RAD 210.10, Hercules Incorporated, Radford, AAP, Radford, VA, October 1983.

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17. Southchem Incorporated, Forest, VA 24551, Radford AAP, Purchase Order No. RP-67488, April 16, 1985.

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22. Tadeusz Urbanski, Chemistry and Technology of Explosives, Vol. III, Pergammon Press, New York, NY, 1965, p. 603.

APPENDIX A

GENERAL SAFETY REQUIREMENTS

HERCULES
RADFORD ARMY AMMUNITION PLANT

Safety is part of your job.

Memorandum

March 2, 1987

HI-87-M-19
General Safety Guidelines for a Bisulfite Scrubbing
Column Plant Concept for Volatile Organic Carbon Emissions

Summary and Conclusions

This safety review provides general safety guidelines for a Bisulfite Scrubbing Column concept for volatile organic carbon emissions. These safety guidelines provided design criteria for scaling up this Bisulfite Scrubbing Column to the pilot plant level.

Table 1 lists these safety guidelines for several categories including equipment, materials, operations, procedures, and maintenance. These, along with safety guidelines issued in references 2 and 3 will provide enough design criteria for the pilot plant scale-up. Further Hazards evaluation including a Preliminary Hazards Analysis (PHA) and a risk analysis must be performed during the design, installation, and proveout phases of this project.

Material Response

The three combustibles capable of introducing potentially hazardous conditions are the volatile solvents, ethanol and acetone, and the liquid explosive ingredient, NG. Concentrations of ethanol and acetone vapors entering the system are less than 1%, which are below their lower explosive limits (LEL) of 3.3% and 2.6%, respectively. Therefore, the electrostatic initiation and sustained burning potentials of these two solvents are considered as minimal.

NG vapors in air within the scrubber equipment could range in concentrations from 2-14 ppm. Even though its concentration is low, NG is the most impact, friction, and thermally sensitive compound present in this scrubbing unit. Future quantitative safety analyses should therefore be based upon initiation data for NG (see Table 2).

MJS:bpw

Attachments

REFERENCES

[1] T. W. Ewing and W. A. Cabbage, "A Compilation of Hazards Test Data for Propellants and Related Materials," PE-489, September 1975.

[2] D. A. Connolley, "Hazards Analysis for a Nitroguanidine Wastewater Treatment Pilot Plant (PE-230), HA-84-R-2.

[3] M. J. Sullivan, "Hazards Evaluation of an Ion Exchange System for Treatment of Nitramine Wastewater." September 4, 1986, HI-86-M-84.

Table 1

General Safety Guidelines for a Pilot Plant Concept of the Bisulfite Scrubbing Column for Volatile Organic Carbon Emissions

Item Reviewed	Safety Control	Benefit
I. Equipment		
A. Exhauster/Blower	1. Eliminate metal/metal contact in the exhauster design.	1. Minimize/eliminate impact or friction initiation of NG.
	2. Ensure the exhauster areas exposed to the vapors are free of crevices.	2. Prevent NG from accumulating in exhauster.
B. Air Flow Regulator Valve	1. Eliminate metal/metal contact in the valve design.	1. Minimize/eliminate frictional initiation of NG.
	2. Ensure the valve housing is free of crevices.	2. Prevent NG from accumulating in valve housing.
C. Gas Sampling Ports	1. Ensure the port contains no pinch points.	1. Prevent NG from accumulating.
D. Absorbent Recycle Pump	1. Design pump for NG service.	1. Eliminate potential NG initiation in pump.
E. Solvent Collection Drains	1. Eliminate crevices in tanks and ensure all welds in tank are Class A for NG service.	1. Prevent NG from accumulating in Solvent Collection Drains.
F. Electrical Equipment	1. Ensure all motors are rated for Class I, Groups C and D service.	1. Prevent acetone and alcohol ignition.

Table 1 (cont)

Item Reviewed	Safety Control	Benefit
II. Materials		
A. Column	A. Ensure column material does not absorb NG.	A. Prevent initiation of columns due to NG absorbtion in column.
B. Column Packing Material	B. Use Koch-Sulzer packing or other packing compatible with NG.	B. Ensure compatibility of column packing material with NG.
III. Operations		
A. Controls		
1. Inlet Gas Sampling Port	1. Interlock air flow regulator valve to close upon high sampling concentration of NG in inlet gas sampling port.	1. Prevent more than 14 ppm of NG from entering system.
2. Exit Gas Sampling Port	2. Interlock air flow regulator valve to close upon high concentration of NG in exit gas sampling port.	2. Prevent high NG concentration from exiting system.
3. Absorbent Flows	3. Add flow controllers to absorbent lines following feed pumps.	3. Ensure correct flow of absorbent.
4. Collection Drain	4. Place level controls in collection drains.	4. Prevent overflow of flammable solvents.
B. Surface Temperatures	B. Ensure surface temperatures of columns, exhauster, and pumps do not exceed 100°C.	B. Keep temperatures below the onset ignition temperature for NG.

Table 1 (cont)

Item Reviewed	Safety Control	Benefit
IV. Procedures	Draft specific procedures for operation and control of process; procedure requires human error analysis.	Avoid incidents caused by human error.
V. Maintenance	Flush system with water prior to performing any maintenance operations.	Flush out any NG which is trapped in the system and avoid frictional initiation.
VI. Safety	Perform hazards studies including a PHA and risk analysis during system design and prior to operating a pilot Bisulfite Scrubbing Unit.	Ensure safety of system prior to operation.

APPENDIX B

CARBONACEOUS ABSORBENTS

MEMORANDUM

January 11, 1982

HA-82-M-4

Thermal Decomposition Behavior of Nitrate Esters Absorbed on Carbonaceous Resins in Denitration Tests

SUMMARY AND CONCLUSIONS

Several samples of nitrate esters absorbed on Amberlite XAD-4 carbonaceous resin were denitrated remotely in exploratory Hazards tests. Temperatures increased to approximately 90°C in these tests. Boiling of the denitration solution was indicated when one sample spewed from the column. Increasing resin bed size increased the rate of temperature rise during denitration. Denitration solutions used were concentrated above those necessary in the process to investigate the rapid reaction in abnormal process situations. It is concluded that positive controls would be required on ethanol, caustic, and NG concentrations to ensure adequate safety in processing.

A sample of Ambersorb XE-348 resin containing nitrate esters was maintained at elevated temperatures for one week to investigate its stability. No exothermic reaction was observed. This indicates that, with further testing verification, the XE-348 resin might be used in propellant operations. This resin failed the rigorous Modified Talliani compatibility test.

FUTURE WORK

The initial testing performed indicates that destruction of nitrate esters absorbed on carbonaceous resins by denitration on the resin to be viable. However, a total systems safety risk analysis and a thorough evaluation of resin sensitivity and denitration reaction characteristics is required to establish safe operating conditions before a pilot operation is established. Positive system controls to eliminate excess ethanol and caustic in the denitration solution, and free NG in the resin bed, are a needed safety feature. Sensitivity initiation levels as well as investigation of burning/explosion characteristics of the wet and dry resin is necessary to provide information to assess safe handling methods and personnel safety protection in the operation.

INTRODUCTION

Wastewater from the NG area contains nitrate esters which are undesirable environmental contaminants. One scheme for removing them from the wastewater is being investigated by PE-598. Nitrate esters dissolved in the wastewater are removed when the water is circulated through a carbonaceous resin bed. Denitration of the nitrate ester is performed on the resin bed by circulating an ethanol/water/caustic solution through the bed. The ethanol extracts the nitrate esters from the resin, and the caustic (NaOH) acts to break them down. Investigation is being performed to see if the resin can be reused.

Exploratory sensitivity testing was performed to investigate the thermal decomposition behavior of nitrate esters absorbed on these resins. The effect of heat of denitration on samples was investigated in limited testing, and long-term stability of the nitrate ester absorbed on the resin was investigated in one test.

EXPERIMENTAL

Several samples of Amberlite XAD-4 and Ambersorb XE-348 resin were denitrated in the apparatus depicted in figure 1. Thermocouples in the resin bed provided a time/temperature profile of the denitration reaction as it progressed. The apparatus was located remotely in the hazards test pit. Flow rate through the column was approximately eight bed volumes per minute.

One test was performed using ambersorb XE-348 resin to investigate its thermal stability when mixed with NG. A one-inch diameter by eight-inch deep resin bed was maintained at a temperature of 100°F for 48 hours, 150°F for 48 hours, and 200°E for 24 hours. Thermocouples in the resin monitored the temperature.

All samples were prepared by flowing NG-contaminated wastewater through the resin. NG concentration was determined by analyzing input and exit NG concentration. Table 1 summarizes the results obtained from four denitration tests. In the trial using a two-inch diameter bed (all other tests were one-inch diameter), the top two to three inches of the resin spewed out. No damage to the containing glass column occurred. Figures 2, 3, and 4 graph the time/temperature relationship during denitration.

The test in which XE-348 resin was maintained at increased temperatures for a week showed no visible signs of reaction. The thermocouples did not indicate any increase above the maintained temperatures.

DISCUSSION

XAD-4 Denitrations

Three samples of nitrate esters absorbed on XAD-4 resin were denitrated. The ethanol and caustic concentrations used were above those planned for a production operation, in order to investigate the behavior of the resin at elevated process temperatures. In all three denitrations, the column temperature approached 90°C, the approximate boiling temperature of the denitration solution. In the trial in which the resin spewed from the column, the condition of the column could be explained by the denitration solution boiling and spewing out of the column. These observations suggest that the denitration reaction may be halted when the denitration solution begins to boil at the resin/solution interface. Removing NG into solution may be halted or slowed down. It does appear that boiling may act as a relief in the process, and process equipment should be designed to allow boilover without pressurization.

NG loading on the resins and denitration solution strength was altered slightly in the three tests, but no significant difference was noted in the three trials.

Rate of the temperature rise in the larger (two-inch diameter) column was double that of the maximum rate of rise in the smaller (one-inch diameter) column. This suggests that remote testing is required for the proposed four-inch diameter pilot column, in order to establish safe operating parameters and reactions in the column in abnormal operating conditions. Increasing temperature rate of increase in a larger column may result in a runaway exothermic NG reaction.

XE-348 Denitrations

The single sample of XE-348 resin on which NG was absorbed was denitrated with no observed temperature rise. Samples taken of the resin after the denitration process was performed showed that all NG was not removed from the resin. The laboratory analysis could not conclusively ascertain whether any denitration had been performed. Therefore the lack of a temperature rise in this resin when tested is most likely due to there being no actual denitration reaction occurring. Changes in the process to correct this should be tested remotely.

Compatibility of Resins

Ambersorb XE-348 resin did not pass the standard Modified Talliana compatibility test with HEN-12 propellant or NG casting solvent. This rigorous screening test is operated above the expected operating temperatures for this resin. A single test of a resin bed loaded with 46 weight percent NG, and maintained at temperatures between 100 and 200°F was performed to evaluate this resin's reaction in situations approaching the operating environment. No reaction was observed, as noted in the results section, indicating relative stability in the operating range of interest. The resin was water-wet initially in the test. In the process, it is a reasonable safety precaution to maintain the resin water-wet at all times. Further testing is required to define the safety of long-term maintenance of NG on this resin.

Reactivity of Water-Wet XE-348 Resin

A controller malfunction subjected water-wet XE-348 resin to temperatures exceeding 300°C. The resin reacted sufficiently to blow out of the top or burn in the one-inch diameter glass column in which it was held. No damage occurred to the glass column. This indicates that NG may be sufficiently bound to the resin to burn more as in a propellant formulation than explode as in free NG. Further testing is mandated if this is to be verified.

Differential Thermal Analyses

Table 2 lists differential thermal analysis (DTA) results for various samples of XE-348 and XAD-4 resins. Most of these samples were used as a verification of NG presence in samples tested. A potential area of concern was the onset of an exothermic reaction at 110°C with the single XAD-4 resin sample tested. This is below the 160°C minimum onset temperature of NG decomposition. A XAD-4 blank was not run, and the sample of XAD-4 blank was loaded with ~60% NG, which is above the 30% maximum loading previously observed. This condition could result in an unusually sensitive combination of resin and NG. This should be investigated in future testing.

In all of the tests performed, as shown in table 2, decomposition occurred below the 150°C onset of decompostion for nitrate esters. This suggests that either NG or other contaminants in the wastewater are interacting with the resin. Contaminants may also be interacting with NG. Further investigation should be performed to identify hazards associated with this behavior.

ALM/mwm

Attachment

Table 1

Summary of Trial Denitrations

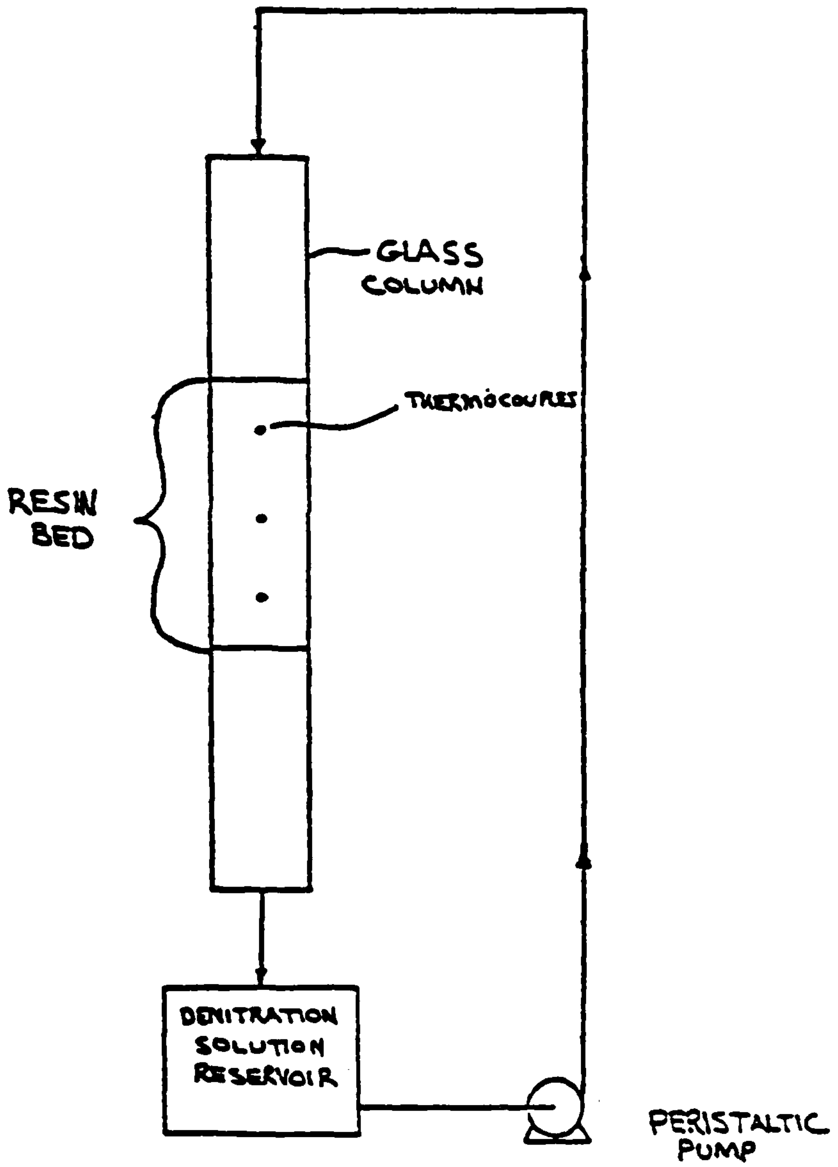
Resin	NG Loading (%)[1]	Sample Size	Denitration Solution WT% (NaOH/Etoh/H_2O)	Maximum Temperature(°C)	Maximum Temperature(°C/s)	Nitrates Remaining
XAD-4	25.2	1" Dia. x 8" Ht.	5/30/65	85	1.2	Yes[2]
XAD-4	21.8	1" Dia. x 8" Ht.	5/40/55	87	0.5	Yes[2]
XAD-4	56.7	2" Dia. x 18" Ht.	10/30/60	89	2.4	No
XE-348	43.5	1" Dia. x 8" Ht.	10/30/60	No Increase	-	Yes

1/ Determined by LC analysis of influent and affluent streams

2/ Minor residual, not quantified

FIGURE 1

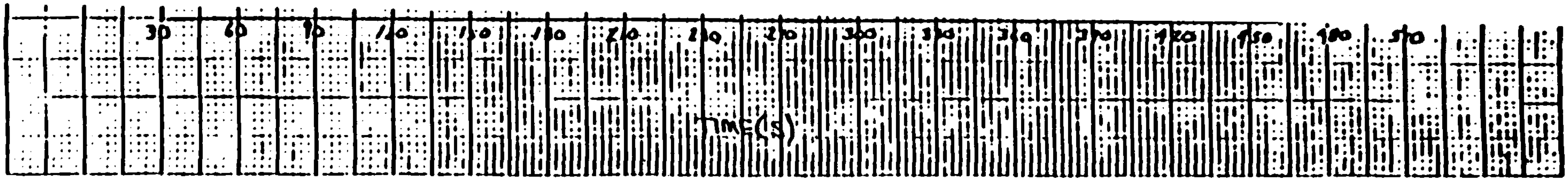
DENITRATION TEST APPARATUS SCHEMATIC



Summary of Differential Thermal Analysis Results

Resin	NG Loading	Onset of Exothermic Reaction	Sample History
XAD-4	57%	110°C	Sample used before denitration in 2" column
XE-348	*	130°C	Sample after long-term compatibility test
XE-348	*	138°C	Sample after long-term compatibility test
XE-348	*	146°C	Sample after long-term compatibility test
XE-348	43%	120°C	Sample prepared for denitration of resin in table 1
XE-348	17%	104°C	Sample prepared by PE-598 personnel during preliminary research
XE-348	0%	None Noted	Blank
NG	100%	150°C	Reference sample

* - Undetermined



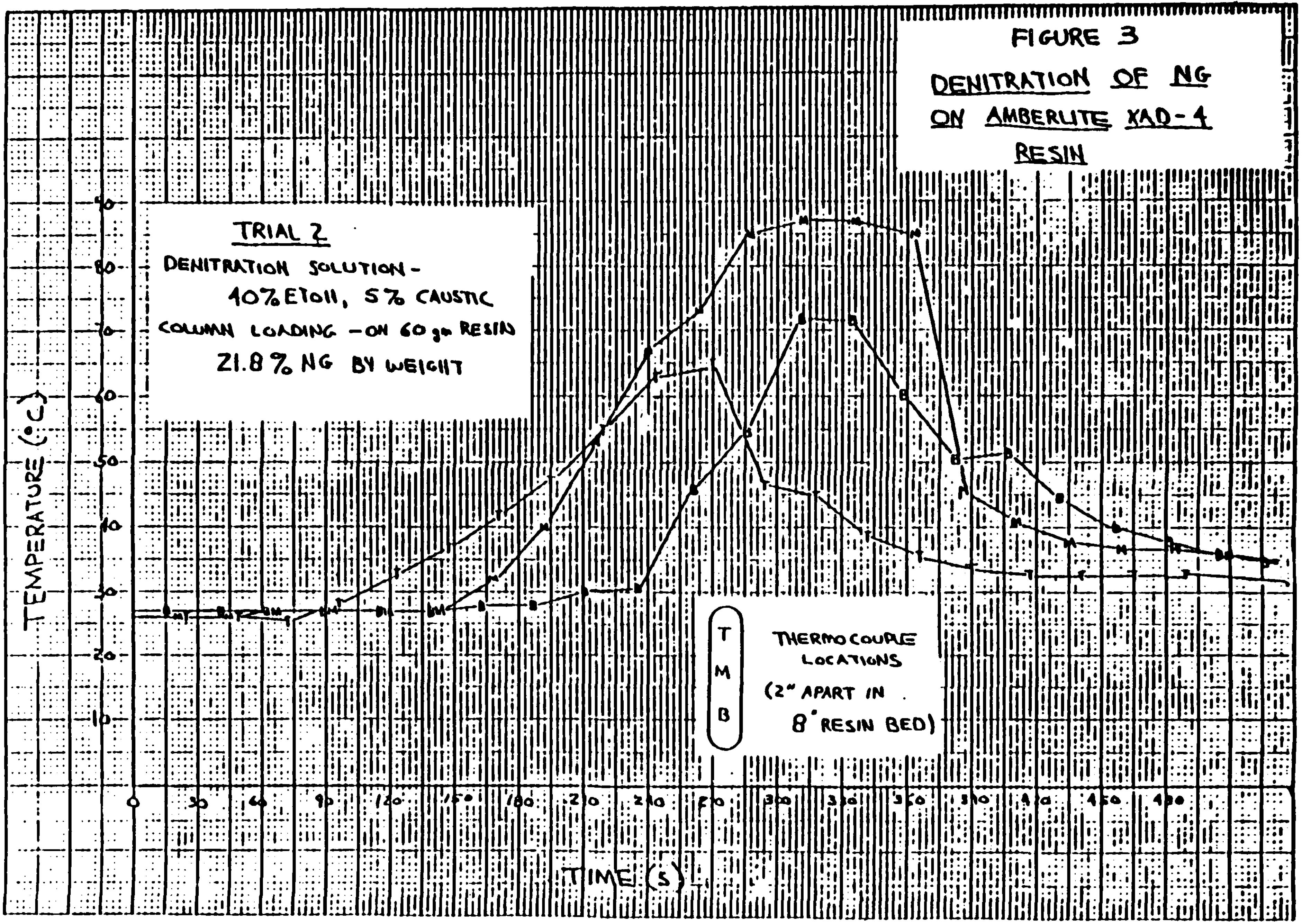


FIGURE 3

DENITRATION OF NG ON AMBERLITE XAD-4 RESIN

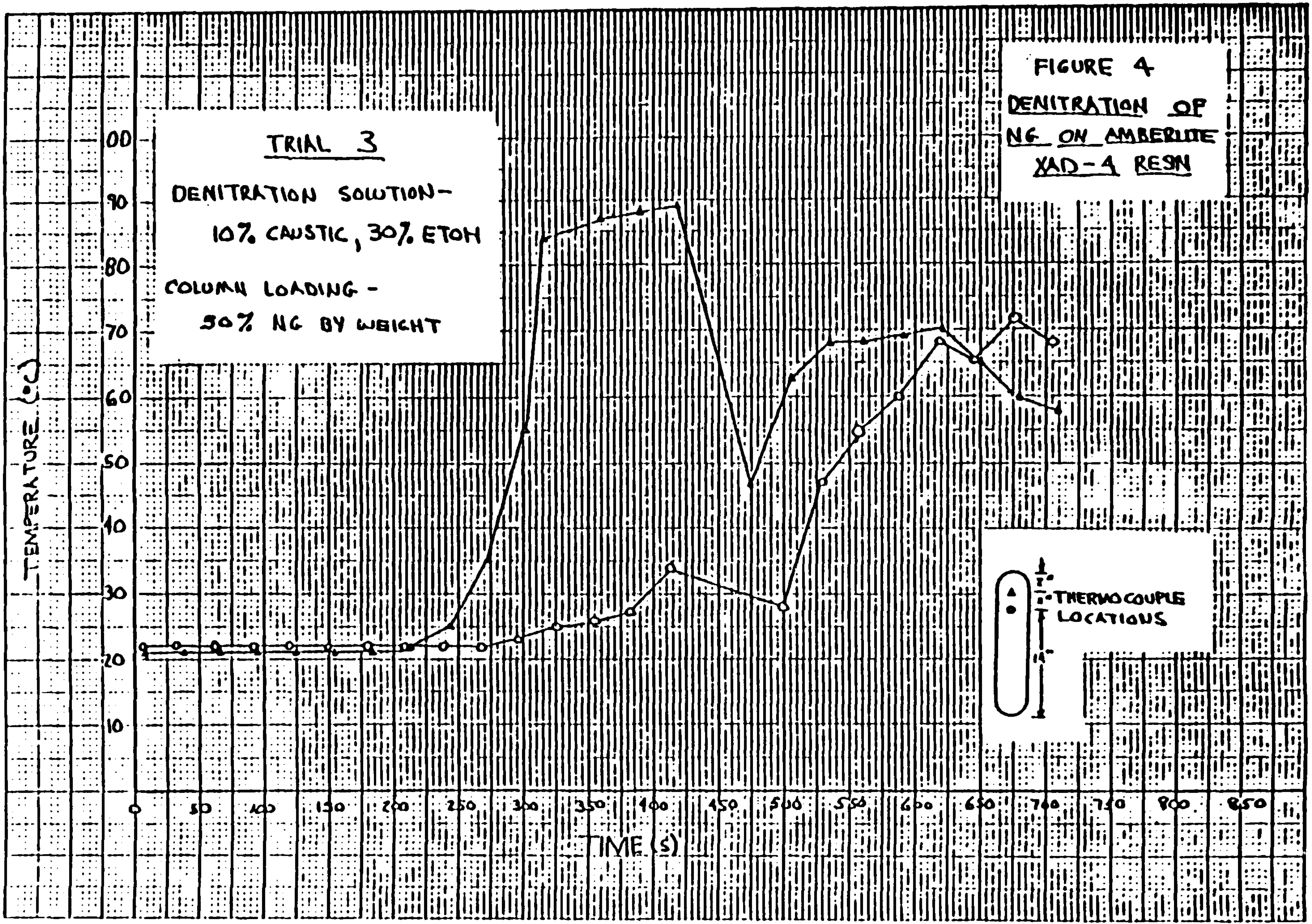


FIGURE 4
DENITRATION OF NG ON AMBERLITE XAD-4 RESIN

APPENDIX C

MIXER ABSORBER CALCULATIONS
(SOFTWARE ARTS, INC., TK! SOLVER (R) PROGRAM)

```
S Rule
- ----
  "Calculations of inert gas (IG) flow for propellant dry down
  "    Basis:1 in. process line reduced to 4 -.25 in. polyflow tubing (.156 ID)
  "          Temperature reading 40F
  "          Pressure reading 72 psig
  "Assumption:IG is 100% nitrogen (N2)   (Note:IG composition is 80-85% N2)
```

```
S Rule
- ----
* Mi=128.5*K*Y2*(d^2)*((p2*hw)/(z*T*S))^.5  "Volume flow of Inert gas, ref. 1
* Y2=(A*B*C*E)^.5   "Gas expansion factor, ref.2
* A=r^(2/k)
* B=k/(k-1)
* C=(1-r^((k-1)/k))/(1-r)
* E=(1-beta^4)/(1-(beta^4*r^(2/k)))
* hw=((p1-p2)*33.9*12)/14.7
* beta=d/D
* M=4*Mi
* r=p2/p1
* sL=(M*1000)/35.3145
```

```
St Input      Name     Output      Unit        Comment
-- -----      ----     ------      ----        -------
              M        35.196260   SCF/min     Standard cubic feet/min; flowrate
   .985       K                                Coefficient of discharge
              Y2       .36437181               Gas expansion factor based on p2
   .15625     d                    in.         Internal diameter of orifice
   14.7       p2                   psia        Absolute pressure at downstream tap
              hw       1992.4898   in. H2O     Differential head (in. water (60F))
   .99        z                                Gas compressibility factor, ref. 3
   499.67     T                    R           Absolute temperature at upstream tap
   .96955017  S                                Specific gravity relative to air
              A        .07924967               Part of gas expansion factor
              B        3.5                     Part of gas expansion factor
              C        .47891941               Part of gas expansion factor
              E        .99945116               Part of gas expansion factor
              r        .16955017               p2/p1
   1.4        k                                Specific heat ratio,Cp/Cv
              beta     .15625                  d/D
   86.7       p1                   psia        Absolute pressure at upstream tap
   1          D                    in.         Internal diameter of upstream pipe
              Mi       8.7990649   SCF/min     Flow rate from individual nozzles
              sL       996.65179   sL/min      Standard liters/min; flowrate
```

```
S Rule
- ----
  "Convert bench-scale gas flow to standard temperature and pressure (STP)
  " to calculate gas load, G (ft3/ft2) @ STP
  "   Basis:9.2 CF/min  at 38C and 28.5 in. Hg


S Rule
- ----
* P*V=n*R*T        "Actual bench-scale conditions
* P=(28.5)*(1)/(29.921)     "Convert pressure to atmospheres
* T=1.8*38+32+459.67     "Convert degree C to degree R
* Ps*Vs=n*R*Ts     "Bench-scale conditions @ STP
* A=pi()*(2/12)^2
* G=Vs/A    "Gas load @ STP

St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------
             P       .95250827 atm       Actual pressure
   9.2       V                 CF/min    Actual cubic feet/min
             n       .02142755 lb-mole   Actual lb-moles
   .7302     R                           Gas constant
             T       560.07    R         Actual temperature
   1         Ps                atm       Standard pressure
   492       Ts                R         Standard temperature
             Vs      7.6980260 SCF/min   Standard volume
             A       .08726646 ft2       Area of bench-scale unit
             G       88.212880 ft3/ft2   Gas load
```

```
S Rule
- ----
  "Diameter of column for mixer absorber
  "    Basis:1 min
  "    Assumption:No pressure drop in Koch-Sulzer packing, ref.4


S Rule
- ----
* Aig=M/G       "Column area for inert gas flow @ STP
* Aig=pi()*r^2
* r=d/2
* din=d*12

St Input      Name     Output     Unit      Comment
-- -----      ----     ------     ----      -------
   35.19626   M                   SCF       Standard cubic feet of inert gas
   88.21288   G                   ft3/ft2   Gas load @ STP
              Aig      .39899230  ft2       Column area for inert gas flow @ STP
              r        .35637507  ft        Radius of inert gas column
              d        .71275015  ft        Diameter of inert gas column
              din      8.5530018  in.       Diameter of inert gas column
```

```
S Rule
- ----
  "Height of column for mixer absorber, ref.5
  "    Basis:1 min
  "       Assumption:No pressure drop in Koch-Sulzer packing, ref.4
  "       Data:4 HETP to scrub 85% acetone out of 7.7 SCF/min gas (Bench-scale)
  "              1 HETP=6.75 in. Koch-Sulzer packing, ref.5


S Rule
- ----
* H=((4*HETP)/Vs)*M


St Input      Name     Output     Unit      Comment
-- -----      ----     ------     ----      -------
              H        10.287259  ft        Height of inert gas column
   .5625      HETP                ft        Height equivalent theoretical plate
   7.698026   Vs                  SCF       Standard cubic feet of gas
   35.19626   M                   SCF       Standard cubic feet of inert gas
```

```
S Rule
- ----
  "Calculate liquid load,L as gpm/ft2 or lb/m/ft2
  "    Basis:300mL/min absorbent recycle rate (Bench-scale)


S Rule
- ----
* A=pi()*r^2
* gpm=mL/(1000*3.785)
* lbm=(mL*spg)/453.593
* Lgpm=gpm/A
* Llbm=lbm/A


St Input      Name     Output     Unit      Comment
-- -----      ----     ------     ----      -------
              A        .08726646  ft2       Area of bench-scale unit
   .16666667  r                   ft        Radius of bench-scale unit
              gpm      .07926024  gpm       Gallons/min of absorbent recycle rate
   300        mL                  mL        mL of absorbent recycled/min
              lbm      .79366304  lb        lb of absorbent recycled/min
   1.2        spg                 spg       Specific gravity of absorbent
              Lgpm     .90825542  gpm/ft2   Liquid load
              Llbm     9.0947085  lb/m/ft2  Liquid load
```

```
S Rule
- ----
  "Calculate flowrate of absorbent recycled in inert gas column
  "    Basis:Liquid load,L calculations for bench-scale absorber



S Rule
- ----
* Aig=pi()*r^2
* gpm=mL/(1000*3.785)
* lbm=(mL*spg)/453.593
* Lgpm=gpm/Aig
* Llbm=lbm/Aig


St Input     Name     Output     Unit      Comment
-- -----     ----     ------     ----      -------
   .3989923  Aig                 ft2       Area of inert gas column
             r        .35637507  ft        Radius of inert gas column
             gpm      .36238691  gpm       Gallons/min of absorbent recycle rate
             mL       1371.6345  mL        mL of absorbent recycled/min
             lbm      3.6287185  lb        lb of absorbent recycled/min
   1.2       spg                 spg       Specific gravity of absorbent
   .9082554  Lgpm                gpm/ft2   Liquid load in inert gas column
   9.094708  Llbm                lb/m/ft2  Liquid load in inert gas column
```

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2. Robert H. Perry and Cecil H. Chilton, Chemical Engineers' Handbook, McGraw-Hill Book Company, Inc., New York, NY, 5th Edition, 1973, pp. 5-11.
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4. "Koch-Sulzer Plastic Packing," Bulletin KSP, Koch Engineering Company Inc., New York, NY 10017.
5. C. A. Jake, "Enhanced Scrubbing of Organic Vapors," Technical Report RAD 200.100, Hercules Incorporated, Radford AAP, Radford, VA, February 1984, p. 15.

APPENDIX D

ECONOMIC ANALYSIS OF HSO_3^- ABSORBENT SYSTEMS

SHEET NO. 1 of 6

COST ESTIMATE SHEET

[illegible] in text

JOB TITLE [illegible] and Operation of 36 Mixer Absorbers, [illegible] Year ASSIGNMENT NO [illegible]

ITEM NO.	DESCRIPTION	QUANTITY	UNIT	LABOR		MATERIAL		TOTAL COST
				UNIT PRICE	COST	UNIT PRICE	COST	
	Facilities Costs							
1	Solvent A[illegible]	3	[illegible] ft.			[illegible]	[illegible]	[illegible]
2	[illegible] Packing[b]	4.5	ft^3			5[illegible]	3,750	[illegible]
3	Pump ([illegible])[c]	[illegible]				[illegible]	[illegible]	[illegible]
4	[illegible]	2	[illegible]			[illegible]	[illegible]	[illegible]
	[illegible] Costs							19,478
5	[illegible]							72,8[illegible]
	Total Installed Costs[a]							92,326
	Total Installed Costs for							x 36
	36 Mixer Absorbers							3,32[illegible]
	TOTAL							3,323,73[illegible]
6	[illegible]							
	Sales Tax - 4.[illegible]% [illegible]							[illegible]
	Insurance on labor - 15%							4[illegible]
	Subtotal							3,827,345
	Overhead and Profit - [illegible]%							1,014,[illegible]
	Subtotal							4,841,591
	Contingencies - 10%							484,159
	Subtotal							5,325,750
	S.I.O.H. - 5.5%							266,28[illegible]
	Total Costs for 36 Mixer							5,59[illegible]
	Absorbers							

[a] Ref. 16 in text [b] = [illegible] estimate [c] Ref. 19 in text

Made by: ________ Date ________ Checked by: ________ Date ________

SHEET NO. 2 of 6

COST ESTIMATE SHEET

JOB TITLE Installation and Operation of 36 Mixer Absorbers/3 Mixer Buildings/Year **ASSIGNMENT NO** CY E6 ROM Estimate

ITEM NO.	DESCRIPTION	QUANTITY	UNIT	LABOR		MATERIAL		TOTAL COST
				UNIT PRICE	COST	UNIT PRICE	COST	
	Operating Costs							
1	Labor (3 manshifts/d)[a]	3	man-shift	52.[illegible]	[illegible]			[illegible]
2	Chemicals (250 days/y)							
	-1200 gal./y							
	Sodium Metabisulfite[c]	1802.40	lb			0.34	612.82	61[illegible]
	Sodium Sulfite[a]	781.04	lb			0.18	140.59	140.5[illegible]
	EDTA[f]	6.01	lb			1.[illegible]		5.65
	Water[a]	9426.55	lb			0.01/1000 gal.		0.[illegible]
3	Maintenance (2 manshifts/2 weeks)	2	man-shift	179.12	358.24			358.24
4	Electrical (250 days)	924	Kw·h			33.76/1000	14.[illegible]6	[illegible]
	Total Labor ([illegible] man-shifts/yr)	720	man-shift	82.16	59,155			59,15[illegible]
	Total Chemicals	1200	gal.			0.64	768	768
	Total Maintenance	52	man-shift	179.12	9314.24			9,31[illegible]
	Total Electrical	924	Kw·h			33.76/1000	31.20	31
	Total Operating Costs (250 days)							69,265
5	Solvent Savings at 1.6 wt%							
	total in absorber bottoms							
	[illegible]	580	lb			/1000 lb	205.00	120
	Total Operating Costs —							69,265
	Total Solvent Savings =							- 120
	TOTAL Deficit							(69,145

[a] RAAP costs [c] Ref. 17 in text [f] Ref. 18 in text

Made by: ______ Date ______ Checked by: ______ Date ______

SHEET NO. 3 of 6

COST ESTIMATE SHEET

Basis and assumptions are in text

JOB TITLE Installation and Operation of 80 FAD Solvent Absorption Systems /80 FAD Buildings/ ASSIGNMENT NO. C456 ROM Estimate

ITEM NO.	DESCRIPTION	QUANTITY	UNIT	LABOR UNIT PRICE	LABOR COST	MATERIAL UNIT PRICE	MATERIAL COST	TOTAL COST
	Facilities Costs							
	– Recycle Absorber Column							
1	Solvent Absorber Column[a]	1				9,125	9,125	9,125
2	Koch Packing[a]	18	ft^3			840	15,120	15,120
	Capital Costs[a]							24,245
3	Installation Costs[a]				73,925			73,925
	Total Installed Costs[a]							98,170
	Total Installed Costs for							x 80
	80 FAD Recycle Absorbers							7,853,600
	– Single-Pass Absorber Column							
4	Solvent Absorber Column[a]	1				7,860	7860	7,860
5	Koch Packing[a]	16	ft			840	13,440	13,440
	Capital Costs[a]							21,300
6	Installation Costs[a]				63,030			63,030
	Total Installed Costs[a]							84,330
	Total Installed Costs for							x 80
	80 FAD Single-Pass Absorbers							6,746,400
	TOTAL							14,600,000
7	Corps of Engineers Costs							
	Sales Tax – 4.5% on Material							163,962
	Insurance of Labor – 18%							1972,152
	Subtotal							16,736,114
	Overhead and Profit – 26.5%							4435,070
	Subtotal							21,171,184
	Contingencies – 10%							2,117,118
	Subtotal							23,288,302
	S.I.O.H. – 5%							1,164,415
	Total Costs for 80 FAD							
	Solvent Absorption Systems							24,452,717

[a] Flowtran® estimate

Made by: ____________ Date ____________ Checked by: ____________ Date ____________

SHEET NO. 4 of 6

COST ESTIMATE SHEET

JOB TITLE Installation and Operation of 80 FAD Solvent Absorption Systems/20 FAD Buildings/Year **ASSIGNMENT NO.** C786 ROM Estimate

ITEM NO.	DESCRIPTION	QUANTITY	UNIT	LABOR UNIT PRICE	LABOR COST	MATERIAL UNIT PRICE	MATERIAL COST	TOTAL COST
	Operating Costs							
1	Electrical[b]							1,206,230
2	Operating and Maintenance[b]				965,315			965,315
3	Chemicals (250 days/y)							
	– 1,693,250 gal./y							
	Sodium Metabisulfite[c]	2,541,000	lb			0.34	863,940	863,940
	Sodium Sulfite[d]	1,101,100	lb			0.18	148,198	198,198
	EDTA[e]	8470	lb			1.44	12197	12,197
	Water[d]	13,259,430	lb			0.21/1000 gal.	335	335
	TOTAL							3,186,25

[b] Ref. 5 in text [c] Ref. 17 in text [d] RAA costs [e] Ref. 18 in text

Made by: Date Checked by: Date

SHEET NO. 5 of 6

COST ESTIMATE SHEET

Basis and assumptions are in text

JOB TITLE Installation and Operation of Distillation System

ASSIGNMENT NO. C4.86 ROM Estimate

ITEM NO.	DESCRIPTION	QUANTITY	UNIT	LABOR UNIT PRICE	LABOR COST	MATERIAL UNIT PRICE	MATERIAL COST	TOTAL COST
	Facilities Costs							
1	Distillation Feed Storage Tank[a]	1					661,100	661,1
2	1st Distillation Column[b]	1					37,430	37,4
3	Tray Cost[b]	36	tray			332	11,952	11,952
4	Column Installation[b]				148,100			148,100
5	1st Column Condenser[b]	1					13,222	13,222
6	Condenser Installation[b]				52,890			52,89
7	1st Column Reboiler[b]	1					26,070	26,07
8	Reboiler Installation[b]				104,295			104,295
9	2nd Distillation Column[b]	1					35,150	35,15
10	Tray Cost[b]	49	tray			280	13,720	13,720
11	Column installation[b]				146,550			146,55
12	2nd Column Condenser[b]	1					5,500	5,500
13	Condenser installation[b]				22,020			22,020
14	2nd Column Reboiler[b]	1					2,690	2,69
15	Reboiler installation[b]				10,770			10,770
16	Piping[c]						1,411,870	1,411,87
	Subtotal				484,645		2,218,704	2,703,3
17	Corps of Engineers Costs							
	Sales Tax - 4.5% on Material							99,84
	Insurance on Labor - 18%							87,23
	Subtotal							2,890,4
	Overhead and Profit - 26.5%							765,9
	Subtotal							3,656,3
	Contingencies - 10%							365,6
	Subtotal							4,022,0
	S.I.C.H. - 5%							201,1
	Total Cost for Distillation System							4,223,12

[a] Fig. 6 in text

[b] Flowtran® estimate

[c] Ref. 5 in text

Made by: ______ Date ______ Checked by: ______ Date ______

SHEET NO. 6 of 6

COST ESTIMATE SHEET

JOB TITLE Installation and Operation of Distillation System

ASSIGNMENT NO. C456 ROM Estimate

ITEM NO.	DESCRIPTION	QUANTITY	UNIT	LABOR		MATERIAL		TOTAL COST
				UNIT PRICE	COST	UNIT PRICE	COST	
	Operating Costs/Year							
1	Utility Costs[b,c]							
	1st Condenser Coolant Cost	2500	h			$/h	3.28	8,200
	1st Reboiler Steam Cost	2500	h			$/h	57.13	142,825
	Subtotal							151,025
	2ND Condenser Coolant Cost	2500	h			$/h	0.69	1,725
	2ND Reboiler Steam Cost	2500	h			$/h	2.40	6,000
	Total Utility Cost for							
	Distilling Bottoms from 20							
	FAD Absorbers							158,750
								x 4
	Total Utility Cost for							
	Distilling Bottoms from							
	80 FAD Absorbers							635,000
2	Operating and Maintenance[e]				457,240			457,240
	Total Operating Costs							1,092,240
3	Solvent Savings at 1.6wt%							
	total in absorber bottoms							
	Solvents	813,120	lb			1000 lb	205.00	166,690
	Total Operating Costs –							1,092,240
	Total Solvent Savings =							– 166,690
	Total Deficit							(925,550

e Ref. 5 in text

Made by: _______ Date _______ Checked by: _______ Date _______

APPENDIX E

PRELIMINARY HAZARDS ANALYSIS OF PURASIV HR SOLVENT RECOVERY SYSTEM

MEMORANDUM

September 30, 1985

HI-85-M-69
Hazards Evaluation of Systems to Reduce
Volatile Organic Carbon Emissions

Summary and Conclusions

A Preliminary Hazards Analysis (PHA) determined that the proposed concept for using the PURASIV® HR fluidized carbon bed solvent recovery system is not safe for recovery of solvent vapor/air mixtures laden with NG. The activated carbon adsorbant is not compatible with NG. Selection of the PURASIV® HR recovery system would require replacing the activated carbon with a compatible material and fabrication and maintenance of the operation to Army and Corporate standards for equipment in contact with NG.

Industry has used the PURASIV® HR recovery system for 10+ years to remove acetone and alcohol from solvent laden air. A literature search reveals no accidents involving the recovery system; therefore, the PURASIV® HR recovery system would appear to be safe for removing acetone and alcohol vapors from solvent laden air, providing it is free of liquid explosives.

The final design for the solvent recovery system selected for this project (PE-694) will be quantitatively risk assessed to ensure compliance with Army safety criteria in MPBMA OSM 385-1.

Recommendations

Safety design considerations for the PURASIV® HR operation are given in table 1.

® Registered trademark of Union Carbide Corporation, USA.

Future Work

No additional work is planned on the PURASIV® HR system unless it is modified to handle NG vapors or selected for vapor streams free of liquid explosives. Hazards Analysis studies are integrated into this project to support and ensure equipment designs and procedures (operation and maintenance) that will provide adequate safety for personnel and facilities and ensure compliance with MPBMA OSM 385-1.

Introduction

The original technology for solvent recovery by carbon adsorption was developed in the 1930's and used a fixed bed batch system. The PURASIV® HR continuous fluidized bed system developed by the Union Carbide Company was introduced in the mid-1970's and is shown and described in figure 1.

The PURASIV® HR solvent recovery system is being investigated by Process Engineering for reducing acetone, alcohol, and NG vapors being emitted to the atmosphere during multi-base green propellant manufacture. The PURASIV® HR system is being investigated as one concept to comply with Virginia clean air regulations and to reduce propellant manufacturing costs.

Discussion

The PHA evaluation (table 1) of the PURASIV® HR solvent recovery concept revealed noncompatible activated carbon beads and NG vapors in the incoming solvent laden air as unacceptable. Activated carbon is not compatible with NG in the standard taliani test. Pressure readings exceeded the limitations of the test.

NG condensate is also not acceptable in the proposed PURASIV® HR operation. Equipment construction and all welds in the system must be capable of preventing NG from collecting in crevices. The operation must be easily cleaned and contain no ledges, corners, etc., where NG can be trapped. Safety design considerations must also include interlocks and controls for flows and temperatures in the desorber and cooler systems, NG neutralizing capability in the solvent recovery tank, NG analyzer and alarm in the solvent line going to the still, system cleanup, and a water wetting system for the operation if some event occurs and the operation stops.

Industry has used the PURASIV® HR solvent (acetone and alcohol) recovery system for 10+ years. A literature search does not mention any accidents in the operation. Therefore, many of the potential hazards including flammable vapor/air mixtures, electrical, heating, back flows, temperature, pumps, etc., associated with this system must have been addressed. A detailed assessment of system components will be made if the PURASIV® HR operation is adopted for solvent flow stream without liquid explosive or if modified for handling NG condensate.

If the above safety design considerations could be implemented and the activated carbon beads replaced with a compatible material, the PURASIV® HR operation could be assessed for compliance to Army safety criteria.

The PURASIV HR System–Simple, Continuous, Efficient

The original technology for solvent recovery by carbon adsorption was pioneered by Union Carbide in the 1930's. This fixed bed batch system remained the industry standard until the development and introduction of the continuous PURASIV® HR fluidized bed system in the mid-1970's.

HOW IT WORKS

The solvent laden air is introduced into the bottom of the adsorber section and passes upward countercurrent to the fluidized carbon beads in a series of perforated trays. The carbon beads flow downward from tray to tray by overflowing a weir/downcomer arrangement.

When it leaves the bottom tray of the adsorber section, the carbon is no longer fluidized. It flows as a dense bed through the desorption section of the column. Here the carbon, with its adsorbed solvent, passes through the tube side of a shell and tube heat exchanger, where it is indirectly heated to the desorption temperature.

Solvent is desorbed from the activated carbon by the introduction of direct-contact nitrogen. This stripping gas carries the solvent to the condenser and separator.

The nitrogen exiting from the condenser must be reconditioned because it is saturated with hydrocarbons. The nitrogen reconditioning takes place in the secondary adsorber and the gas is then recycled for reuse. Following desorption, the activated carbon is cooled to ambient temperatures in an indirect cooler. The carbon is then air conveyed to the top tray of the adsorption section by a blower.

This nitrogen stripping technique offers a unique advantage for removing water-soluble hydrocarbons. Except for the moisture present in the solvent laden air, the system does not introduce water which would otherwise contaminate the recovered solvent. If the relative humidity of the incoming air is less than 60 percent, the solvents recovered will, in most cases, contain less than 5 percent water by weight.

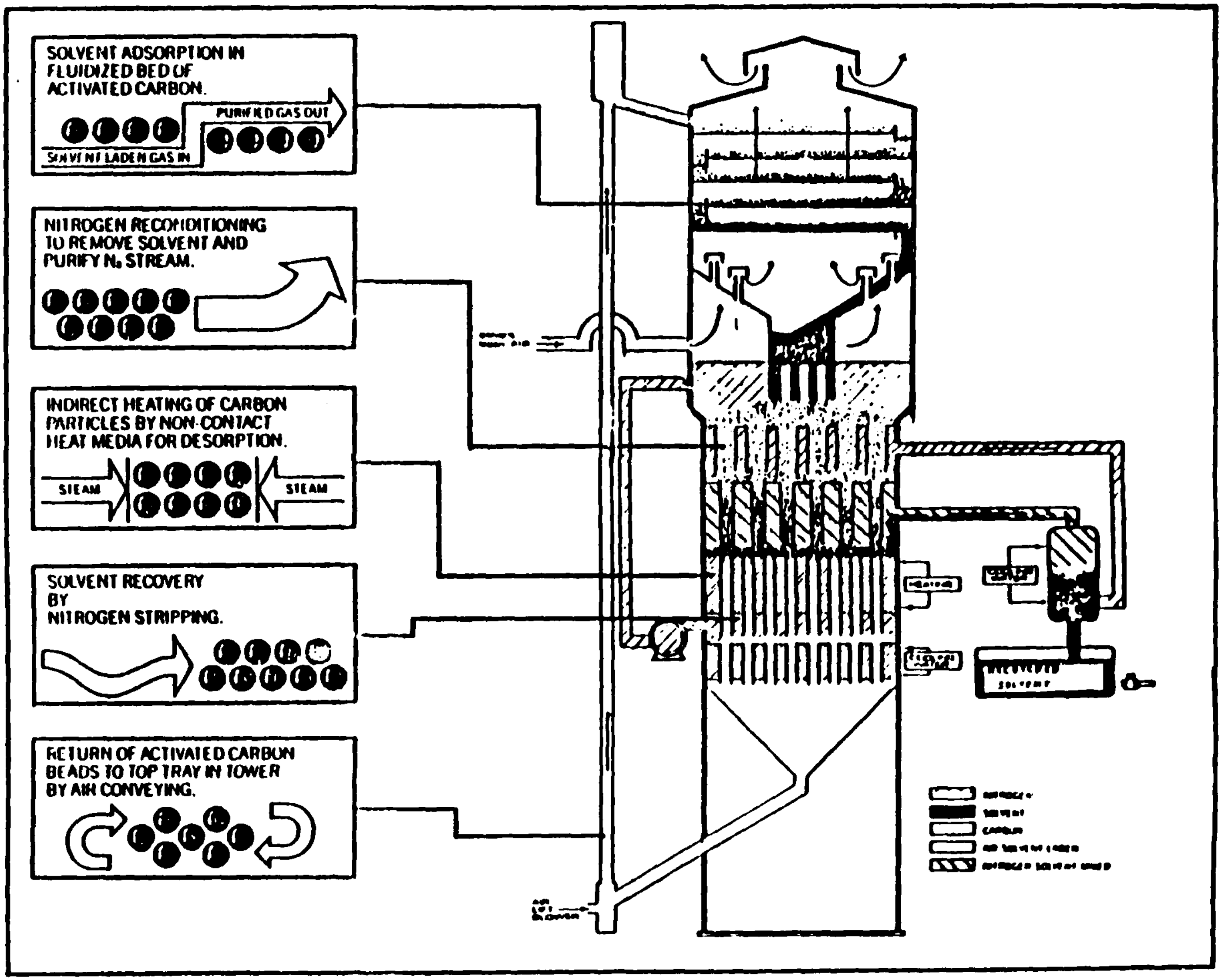

Figure 1. PURASIV® Solvent Removal System

Table 1. Preliminary Hazards Analysis of Union Carbide PURASIV® HR Solvent Recovery System

Item Reviewed	Potential Hazard	Recommendations for Improving Safety	Authority
1. Items Related to NG Service			
a. Adsorbant bed of activated carbon	NG and activated carbon are not compatible	Use a compatible material in the adsorbant bed	-
b. Equipment welds	NG condensate collects in pits and crevices and and ignited when maintenance performed	Tooling shall be designed to prevent entrapment of NG	Standard APS-2
c. Nitrogen desorbing system	Thermal decomposition of NG in the nitrogen makeup/reconditioning system	Provide heat system controls to maintain a temperature < 130°C	Standard safety practice
d. System temperature controls	NG condensate freezes and ignited when thawing occurs	Control system temperature to prevent NG from freezing	Standard safety practice
e. Equipment cleaning operation	Operation cannot be thoroughly cleaned of NG condensate and initiation occurs while performing maintenance	Install ports to facilitate cleaning operation	Standard safety practice
2. Items Related to Non-NG Service			
a. Nitrogen desorbing system	Acetone and alcohol vapors thermally ignited in the pump or air lift blower	Prevent vapors from accumulating in the flammable range	Standard safety practice
b. Electrical service, motors, and drives	Solvent vapors initiated by malfunctioning equipment	Use only electrical equipment rated Class I, Groups C and D and Class II, Group F	AMCR 385-100

APPENDIX F

CEILCOTE PROPOSAL

GS CEILCOTE
[illegible]

PROPOSAL NO. SME-8652 BUDGET

December 1, 1986

Hercules, Inc.
Radford, Virginia 24141-0299

We are pleased to submit our proposal to furnish a Ceilcote VOC control system in response to your meeting with Art Ehrler and our representative, Meredith Winn, of Daco Technical Sales.

DESIGN BASIS

Exhaust air flow: 5,000 CFM

Air flow temperature: 140° F. max

Solvent usage: Unknown

Individual Hydrocarbon	Concentration	Expected Average Removal Efficiency*
Acetone	675 ppm max.	90%+
Ethanol	1,100 ppm max.	90%+

* For all concentrations greater than 100 ppm.

140 SHELDON ROAD BEREA, OHIO 44017 PHONE 216-243-0700

SYSTEM DESCRIPTION

Removal of the hydrocarbon vapors is carried out in a scrubber using Sol-Vol-X, a proprietary high boiling point organic liquid. Recovery of the solvents is achieved in a stripper column equipped with a fractionation section and a condenser. After stripping, regenerated Sol-Vol-X from the stripper column bottom is recycled for re-use in the scrubber. The complete system functions as follows: (See Bulletin No. 12-18 which shows a schematic arrangement of the equipment.)

The scrubber ① absorbs organic vapors from the airstream using Sol-Vol-X as a scrubbing solution. Clean air exits the scrubber at the top.

A scrubber transfer pump ② transfers Sol-Vol-X containing absorbed VOC's from the bottom of the scrubber through the heat exchanger to the stripper column.

A plate and frame heat exchanger ③ heats cold Sol-Vol-X transferred from the scrubber sump with hot stripped Sol-Vol-X being recycled from the sump of the stripper column. This heat recovery process is critical to the energy efficiency of the system.

Heated Sol-Vol-X from the heat exchanger is then heated further in an auxiliary heater ④ to maximize VOC stripping and thus overall system efficiency.

A stripping column ⑤, using ceramic packing, strips VOC's from the heated Sol-Vol-X. The stripper column is operated under vacuum which is supplied by a liquid ring seal vacuum pump ⑧ .

A stripper transfer pump ⑥ then transfers Sol-Vol-X stripped of organic compounds from bottom of stripping column to hot side of heat exchanger and from there to liquid distributor of scrubber.

A single pass shell and tube condenser ⑦ condenses stripped organic vapors to liquid state.

The stripped and condensed VOC's are then collected in two cylindrical tanks ⑨ for subsequent return to process or reclamation.

Instrumentation and Control - A single control panel contains all of the necessary equipment needed to monitor and control the total automatic operation of the system including sequential startup and shutdown. Temperatures are monitored and controlled to the scrubber and stripper. Flows to and from these units are also controlled automatically. The panel also contains annunciator alarms on all temperatures, flows, liquid levels, and pressures necessary for the automatic startup, operation, and shutdown of the system. The control system also provides all necessary safety interlocks to prevent any damage to the equipment or personnel in the event of loss of electrical power, cooling water, or Sol-Vol-X.

SCOPE OF SUPPLY

The proposed Ceilcote VOC control system will consist of the following basic component parts integrated into a fully automatic system.

Scrubber - One standard Ceilcote VTS-35-6 tray scrubber complete with inlet transition and outlet exhaust stub stack. The tray scrubber incorporates adjustable inlet and outlet weirs on each tray for total liquid flow control adjustment and maximum scrubbing efficiency. The scrubber contains integral sump and entrainment separator sections.

Scrubber Transfer Pump - Horizontal gear type pump equipped with TEFC motor for transferring Sol-Vol-X containing absorbed organic vapors from the bottom of the scrubber through the heat exchanger to the stripper column.

Heat Exchanger - Plate and frame design for preheating the Sol-Vol-X from the scrubber sump with the hot recycling Sol-Vol-X from the stripper column. Designed for maximum energy recovery.

Stripping Column - Standard Ceilcote SPT packed bed design using ceramic packing. Unit includes integral Sol-Vol-X storage sump and reflux condenser for maximum separating efficiency.

Stripper Transfer Pump - Horizontal gear type pump equipped with TEFC motor for transferring Sol-Vol-X stripped of organic compounds from the bottom of stripping column to the hot side of heat exchanger and from there to the liquid distributor of scrubber.

Stripping Column Vacuum Pump - Liquid ring seal type vacuum pump for maintaining vacuum on stripper column. Unit equipped with mechanical seals and TEFC motor.

Condenser - Single pass shell and tube design using cooling water transferred from owner source to condense stripped organic vapors to liquid state.

Recovered Solvent Tanks - Two (2) cylindrical tanks with storage capacity equal to a minimum of one day of recovered material. Automatic discharge and venting can be provided if required.

Instrumentation and Control - The control panel will contain a programmable controller to monitor and control the total automatic operation of the system including sequential startup and shutdown. Temperatures and flows to and from the scrubber and stripper will be monitored and controlled. The panel will also contain annunciator alarms (with first out indication) on all temperatures, flows, liquid levels, and pressures necessary for the automatic startup, operation, and shutdown of the system. The control system will provide the necessary safety interlocks to prevent any damage to the equipment or personnel in the event of loss of electrical power, cooling water, Sol-Vol-X, etc., that might occur during operation.

A non-refrigerated air dryer capable of supplying approximately 15 CFM of -30o D.P. instrument air is provided.

MATERIALS OF CONSTRUCTION

All components including process vessels and piping in contact with Sol-Vol-X will be fabricated from carbon steel, stainless steel, or brass as appropriate.

HEAT SOURCE

The heat input requirements for the system based on a 20°F heat exchanger approach temperature are listed below. Closer approach temperatures can be selected to lower power consumption. However, additional capital expenditures would be required. The proposed system is designed to use electricity as the source of heat. Alternate sources such as steam or natural gas can be used. We would be pleased to modify our proposal accordingly if you wish.

COOLING WATER

Cooling tower water can be used in the heat exchanger, if necessary. Normally, plant service water is used. The amount of cooling water required is shown below.

UTILITY REQUIREMENTS

Normal operating requirements are as follows and apply **only during full scale** system operation. During system shutdown, no energy is consumed. The system can be brought to full operation in as little as 30 minutes after a 24 hour shutdown. "Cold start" of the system requires no more than 90 minutes.

System CFM	5,000 CFM
Electrical power for pumps	20 H.P.
Heat source	450,000 Btu/hour
Cooling water	15 GPM

EQUIPMENT SIZE AND WEIGHT

System CFM	5,000
System Length	10'
System Width	21'
System Height	22'
System Operating Weight	32,500

DRAWING AND DELIVERY SCHEDULE

The shipping date for the above system is 20 weeks after purchaser's approval of Ceilcote drawings. Approval drawings would be submitted 6 - 8 weeks after receipt of written purchase order. A site visit will be made immediately after order placement to insure that no unforeseen site conditions delay the approval cycle.

STARTUP ASSISTANCE

Ceilcote will provide one qualified factory engineer to assist the customer in equipment startup and debugging at a charge of $ 500.00 per day plus living and travel expenses at cost.

SAFETY ISSUES

The buildup of nonstripped VOC's in carbon beds represents a serious fire hazard when the system is placed back into operation. No residual buildup occurs with the Ceilcote system thus eliminating this hazard. Sol-Vol-X has a flash point of over 300°F. Liquids with a flash point of over 200°F are classified as Class 3 flammable liquids. Class 3 liquids are relatively safe. They are slow burning and fires are easily extinguished. Where the Sol-Vol-X is heated, it is under vacuum. Therefore, no air is present for combustion.

PREVENTATIVE MAINTENANCE

Preventative maintenance is limited to bearing lubrication and periodic visual inspections.

YEARLY DOWNTIME

Twice a year, for a 1-2 day period, the system should be shut down, inspected, and serviced.

PRICING (BUDGET)

To furnish the proposed system, we are pleased to quote as follows:

Equipment Cost*	$195,000

* May vary with heat source supplied, ±10%

The above pricing is F.O.B. point of manufacture, freight collect, and does not include any state or local taxes should they be applicable.

The above prices are valid for 90 days from date of this proposal.

The attached "Standard Contract Terms and Conditions of Sale" and "Terms of Payment" are made a part of this proposal and shall apply in the event of an order.

We trust this information is complete and will enable you to evaluate our system.

Should you have further questions or we may be of other service to you, please contact us.

Sincerely,

THE CEILCOTE COMPANY

TERMS OF PAYMENT

1. 10% of contract price on submission of shop drawings for customer's approval. This to cover costs we have invested in engineering, initial work on tooling, jigs, fixtures, and inventorying of raw materials.
2. Monthly billings based on certification of percentage of completion of 80% of pro rata share of contract price.
3. 10%, 30 days after delivery.
4. These Terms of Payment are in lieu of Paragraph 4 of our Standard Terms and Conditions sheet which is also attached.

This page is made an integral part of our proposal and shall apply in the event of an order.

FOR ORDERS OF $50,000 AND OVER

A UNIT OF GENERAL SIGNAL

DIVISION OF GENERAL SIGNAL INDUSTRIES INC.

STANDARD CONTRACT TERMS AND CONDITIONS

GENERAL TERMS OF SALE

1. **Construction and Legal Effect** Seller's sale to Buyer is limited to and expressly made conditional on Buyer's assent to the typed, handwritten and printed terms and conditions of sale on the face and reverse side hereof, all of which form a part of this order and supersede and reject all prior writings, *representations and negotiations* with respect hereto and any conflicting terms and conditions of Buyer. Unless Buyer now expressly conditions Buyer's purchase documents, in a typed or handwritten portion of Buyer's purchase terms, upon assent to additional or different terms and conditions of Buyer, or unless Buyer otherwise communicates such an expressly conditioned objection to Seller within fifteen (15) days from receipt of this document, the sending of a purchase order for the goods referred to herein, whether or not signed by Buyer, any printed statement to the contrary notwithstanding, or Buyer's acceptance of goods or payment operates as *ACCEPTANCE BY BUYER of Seller's terms and conditions of sale*.

Any writing so expressly conditioned by Buyer shall be construed as an acceptance of all terms and conditions on which the parties agree on which appear only in Seller's sales documents, a rejection of the terms and conditions of Seller which are different from those of Buyer, and a counteroffer subject to written acceptance by Seller in respect *of those and any additional* Buyer terms and conditions.

Seller will furnish only the quantities and items specifically listed on the face hereof. Seller assumes no responsibility for furnishing other equipment or material shown in any plans and or specifications for a project to which the goods *ordered herein* pertain.

Any action for breach of contract must be commenced within one (1) year after the cause of action has accrued.

2. **Prices** Unless otherwise noted on the face hereof, prices are net F.O.B. Seller's point of manufacture. Service time of a factory-trained serviceman is not included and may be charged extra. The amount of any *applicable present or future tax or other* government charge upon the production, sale, shipment or use of goods ordered or sold will be added to billing unless buyer provides Seller with an appropriate exemption certificate.

3. **Defective Goods** Providing Buyer notifies Seller *promptly*, in writing, if, within one (1) year from date of shipment, goods or parts manufactured by Seller fail to function properly under normal and proper use and service *because of defects in material or* workmanship demonstrated to Seller's satisfaction to have existed at the time of delivery, Seller, reserving the right to either inspect them in Buyer's hands or request their return to Seller, will, at Seller's option repair or replace at Seller's expense F.O.B. Seller's point of manufacture, or give Buyer *proper credit* for such goods or parts determined by Seller *to be defective, with all dismantling and reassembly and necessary packaging and* transportation costs to be assumed by Buyer. The foregoing shall not apply to goods that shall have been altered or repaired after shipment to Buyer by anyone except Seller's authorized employees and Seller will not be liable in any event *for alterations or repairs, except those* made with its written consent. Buyer shall be solely responsible for determining suitability for use and Seller shall in no event be liable in this respect. The goods or parts manufactured by others but furnished by Seller will be repaired or replaced only to the extent of the original manufacturer's guarantee.

Seller's obligations and liabilities hereunder shall not be enforceable until such goods or parts have been fully paid for. Buyer agrees that if the goods or parts sold hereunder are resold by Buyer, Buyer will include in the contract for resale provisions which limit recoveries against Seller in accordance with this section. *In the case of Seller's failure* to fulfill any performance representation, it is agreed that Seller may at Seller's option *remove and* reclaim the goods or parts covered by this Agreement at Seller's own expense and discharge all liability by repayment to the Buyer of all sums received on account of the purchase price.

THE FOREGOING OBLIGATIONS ARE IN LIEU OF ALL OTHER OBLIGATIONS AND LIABILITIES INCLUDING NEGLIGENCE AND ALL WARRANTIES OF FITNESS OR MERCHANTABILITY OR OTHERWISE EXPRESSED OR IMPLIED IN FACT OR BY LAW, AND STATE SELLER'S ENTIRE AND EXCLUSIVE LIABILITY AND BUYER'S EXCLUSIVE REMEDY FOR ANY CLAIM OF DAMAGES IN CONNECTION WITH THE SALE OR FURNISHING OF GOODS OR PARTS OR SERVICES, THEIR DESIGN, SUITABILITY FOR USE, INSTALLATION OR OPERATION. *Seller will in no event be liable for any direct, indirect, special, incidental or consequential damages or losses whatsoever, and Seller's liability under no circumstances will exceed the contract price for the goods or parts for which liability is claimed.*

No employee or agent of Seller is authorized to make any warranty other than that which is specifically set forth herein. The provisions in any specification or chart issued by Seller or attached hereto are descriptive only and are not warranties or representations. Seller will *certify to a rated capacity* in any particular goods upon request.

4. **Credit and Payment.** Payment for goods shall be thirty (30) days net. Pro-rata payments shall become due with partial shipments. A late charge of one-and-one half percent (1½%) per month, a rate of eighteen percent (18%) per annum, or the maximum permitted by law, whichever is less, will be imposed on all past due invoices. Seller reserves the *right at any time* to suspend credit or to change credit terms provided herein, when in its sole opinion Buyer's financial condition so warrants. Failure to pay invoices at maturity date at Seller's election makes all subsequent invoices immediately due and payable irrespective of terms, and Seller may withhold *all subsequent deliveries until* the full account is settled, and Seller may terminate this Agreement. Acceptance by Seller of less than full payment shall not be a waiver of any of Seller's rights. Buyer reapesents by sending each purchase order to Seller that Buyer is not insolvent as that term is defined in applicable state or federal statutes. In the event Buyer becomes insolvent before delivery of any goods *purchased hereunder, Buyer* will notify Seller in writing. A failure to notify Seller of insolvency at the time of delivery shall be construed as a reaffirmation of Buyer's solvency at that time. Irrespective of whether the goods purchased hereunder are delivered directly to Buyer, or to a customer of Buyer's, and irrespective of the size of the shipment, Seller shall have the right to stop delivery of the goods by a bailee if Buyer becomes insolvent, repudiates, or fails to make a payment due before delivery, or if for any other reason Seller has a right to withhold or reclaim goods under the applicable state and federal statutes. Where Buyer is responsible for any delay in shipment, the date of completion *of goods may be treated by Seller as the date of shipment* for purposes of payment. Completed goods shall be held at Buyer's cost and risk and Seller shall have the right to bill Buyer for reasonable storage and insurance expenses. Regardless of price quoted, all orders will be invoiced in the *minimum amount* of $50.00 (Fifty Dollars) net.

5. ***Delivery.*** *Delivery, shipment and* installation dates are estimated dates only, and unless otherwise specified, *are figured from the date of receipt* of complete technical data and approved drawings as such may be necessary. In estimating such dates no allowance has been made, nor shall Seller be liable directly or indirectly for delays of carriers or delays from labor difficulties, shortages, strikes or stoppages of any sort, fires, accidents, failure or delay in obtaining materials or manufacturing facilities, acts of government affecting Seller directly or indirectly, bad weather or any causes beyond Seller's control or causes designated, Acts of God or force majeure by any statute or court of law, and the estimated delivery date shall be extended accordingly. Seller will not be liable for any damages, losses or penalties whatsoever, whether direct, indirect, special, incidental or consequential, resulting from Seller's failure to perform or delay in performing unless otherwise agreed in writing by an authorized officer.

6. **Shipping.** Unless Buyer specifies otherwise in writing, (a) goods will be boxed or crated as Seller may deem proper for protection against normal handling and extra charges will be made for *preservation, waterproofing, export boxing and similar* added protection of goods. (b) routing and manner of shipment will be at Seller's discretion, and may be insured at Buyer's expense, value to be stated at order price. On all shipments F.O.B. Seller's point of manufacture, delivery of goods to the initial carrier will constitute delivery to Buyer and thereafter be at Buyer's risk. A claim for loss or damage in transit must be entered with the carrier and prosecuted by Buyer. *Acceptance of goods from a common* carrier constitutes a waiver of any claims against Seller for delay or damage or loss.

7. **Assignment.** *Seller reserves* the right to subcontract all or any part of the work to be performed under this order, without obtaining the approval of Buyer. No notice to Buyer of any subcontracting by Seller is required. In the event of any subcontracting by Seller, Seller will remain *primarily responsible to Buyer for its obligations and responsibilities* under this order.

8. *Cancellation, Returned or Rejected Goods* Buyer may cancel orders only by written notice and only upon condition that Buyer make full payment to Seller for all goods which, upon receipt of such notice by Seller, are within thirty (30) calendar days of completion. Partial payment for all goods not within thirty (30) *calendar days of completion* shall be made by Buyer on the basis of actual costs of labor, *materials and supplies* applied to the production of such goods, plus overhead expenses, and plus fifteen percent (15%) of such costs and expenses. Goods may be returned only when specifically authorized and Buyer will be charged for placing returned goods in saleable condition, any sales *expenses then incurred by Seller, plus a restocking* charge and any outgoing and incoming transportation costs which Seller pays. If Buyer rejects any goods supplied pursuant to Buyer's purchase order, Buyer must notify Seller of such rejection within thirty (30) days of delivery. Any failure to make such notification constitutes *acceptance of the goods*.

9. **Termination.** Seller may by written notice to Buyer terminate the whole or any part *of this contract in any one of the following circumstances*: (1) If Buyer fails to remit payment within the time specified herein or any authorized extension thereof; or (2) If Buyer fails to perform any of the other provisions of this contract as to endanger performance of this contract in accordance with its terms; and Seller *shall not by reason of such termination* be liable to Buyer for any compensation, reimbursement, or damages including in particular, but not limited to any direct, indirect, special, incidental or consequential damages or losses whatsoever, on account of expenditures, investments or commitments.

10. **Patents, Trademarks and Proprietary Data** Buyer shall be solely liable for all claims related to patent infringement except for claims resulting *solely from the domestic* use or resale of Seller's goods in the manner prescribed and not resulting in any way *from the modification of the goods* or their combination with other goods; and then only if Buyer promptly advises Seller of any such claim and permits Seller to defend against or settle such claim, and if the goods were not designed to satisfy the Buyer's specifications, Seller's *liability hereunder being limited to the amount of judgment or settlement*, but not more than the selling price of the goods. If an injunction is issued against the further use of allegedly infringing goods, Seller shall have the option of procuring for Buyer the right to use the goods, or replacing them with non-infringing goods or of removing them and refunding the purchase price. Buyer is not licensed to use the goods with other goods that *are not manufactured* by Seller to form a combination that is covered by Seller's patents. Seller shall not use Buyer's trademarks or trade names except on Seller's goods, in the form prescribed. Any invention made by Seller in the performance of a contract with Buyer *shall be the exclusive property of Seller. Buyer agrees to maintain in confidence* any technical data, including data processing software, that is provided by Seller and labeled to be proprietary or confidential. Seller does not warrant any goods which are altered by Buyer without Seller's written approval, including data processing software. The foregoing expresses Seller's entire and exclusive warranty and liability as to patents, and Seller *will not be liable for any damages or losses whatsoever suffered by reason of any* infringements claimed, except as *provided herein*. Buyer will hold Seller harmless and indemnified against any and all claims, demands, liabilities, damages, costs and expenses resulting from or *connected with any claim of patent infringement arising out of the* manufacture by Seller of goods in accordance with a design or specifications which Buyer furnishes to Seller.

11. **Special Jigs, Fixtures and Patterns** Any jigs, fixtures, patterns and like items which may be included in an order will remain Seller's property without credit to Buyer. Seller will assume the maintenance and *replacement expenses of such items*, but shall have the right to discard and scrap them after they have been inactive for one (1) year without credit to Buyer.

12. **Records, Audits and Proprietary Data.** Unless otherwise specifically agreed to in writing signed by an authorized officer, neither Buyer nor any representative of Buyer, nor any other person, shall have any right *to examine or audit Seller's cost accounts*, books or records of any kind or on any matter, or be entitled to, or have control over, any manufacturing, engineering or production prints, drawings or technical data which Seller, in Seller's sole discretion, may consider in whole or in part proprietary to Seller.

13. **Compliance With Laws and Regulations:** Seller's performance of this order will comply (unless exempt) with all applicable laws, rules, *regulations, and orders of the United* States and of any state and political subdivision thereof, including, without limiting the generality of the foregoing, laws and regulations pertaining to labor, wages, hour and other conditions of employment and applicable price ceilings, and the goods delivered hereunder will be produced in compliance with (1) the requirements of the Fair Labor Standards Act, *as amended; (2) Executive Orders* Nos. 11246 & 11375, as amended, and all rules and regulations issued thereunder, regarding "Non-Discrimination Equal Opportunity Clause", including sending Buyer an executed certificate of non-segregated facilities, complying with the "Equal Employment Opportunity Clause" *which is made of part hereof*, completing and filing all required reports including from EEO-1 and implementing an Affirmative Action Program; and (3) Executive Order No. 11458, as amended, regarding the utilization of minority business enterprises.

Unless specifically agreed in writing, Seller does not warrant or represent that any of its goods by themselves *or in a system which other* goods will conform to or comply with the provisions of the Occupational Safety and Health Act of 1970 and the standards and regulations issued thereunder, or any other Federal, State or Local Law or regulation of the same or similar nature.

14. **Assignment.** The rights and obligations of Buyer hereunder may not be assigned *without the prior written consent of Seller*.

15. **Non-Waiver.** Seller's failure at any time to require strict performance by Buyer *of any of the provisions* herein shall not waive or diminish Seller's right thereafter to demand strict compliance therewith or with any other provision. Waiver of any default shall *not waive any other default*.

16. **Applicable Law.** The rights and duties of the parties shall be governed by the laws of the State of Ohio.

17. ***Hold Harmless/Nuclear Energy.*** *In the event this purchase order is for work to* be performed, or goods in the nature of or concerning nuclear materials to be delivered by Seller on Buyer's premises, or the premises of a customer of the Buyer, which premises are or concern a nuclear facility, the Buyer hereby assumes the entire responsibility and liability for, and indemnities and holds Seller harmless from, any all damage or injury of any kind and any and all associated losses, claims, demands or expense whatsoever caused by, resulting from or occurring in connection with the hazardous properties of nuclear material or arising out of the furnishing by Seller of goods in connection with the execution of the work provided for in this contract. *Buyer agrees to carry property damage* and bodily injury insurance at its own expense with a recognized underwriter with limits sufficient by reasonable commercial standard to cover any and all of the above risks, to name Seller as an insured party, and assume Seller's defenses. Buyer hereby waives any and all claims of any kind against Seller and waives its own and its insurer's right of subrogation *against Seller for any loss resulting from any such risks*.

140 SHELDON ROAD/BEREA, OHIO 44017/PHONE OR TELECOPY: 216-243-0700/TELEX: 098-5590

GLOSSARY

Term	Identification
AC	Activated carbon
AMC	Army Material Command
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulfate
CAMBL	Continuous Automated Multi-Base Line
COD	Chemical oxygen demand
DBP	Dibutylphthalate
DEG	Diethylene glycol
DEGDN	Diethylene glycol dinitrate
DNG	Dinitroglycerin
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
FAD	Forced air dry
GC	Gas chromatography
HETP	Height-equivalent-theoretical-platee
HNO_3	Nitric acid
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
HSO_3^-	Bisulfite ion
HTSS	High temperature separation of the sulfate
IC	Ion chromatography
LC	Liquid chromatography
L/G	Liquid-to-gas ratio
LTSS	Low temperature separation of the sulfate
MHF	Multiple hearth furnace
MRT	Membrane Research and Technology, Inc.
N_2	Nitrogen
NAC/SAC	Nitric acid concentrator/sulfuric acid concentrator
$NaHSO_3$	Sodium bisulfite
Na_2S	Sodium sulfide
Na_2SO_3	Sodium sulfite
Na_2SO_4	Sodium sulfate
$Na_2S_2O_5$	Sodium metabisulfite
NG	Nitroglycerin
NO_x	Nitric oxide
HNO_3	Nitric acid
OVA	Organic vapor analyzer
PE	Process Engineering
PHA	Preliminary Hazards Analysis
PS&ER	Production Support and Equipment Replacement
RAAP	Radford Army Ammunition Plant
RBC	Rotating biological contactor
ROM	Rough Order of Magnitude
SAR	Sulfuric acid regeneration
SO_2	Sulfur dioxide

SO_4^{2-}	Sulfate ion
$S_2O_5^-$	Thionate/thionite ion
SRP	Sulfite Recovery Process
TEG	Triethylene glycol
TNT	Trinitrotoluene
VOC	Volatile organic compound

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