

DOE/PC/90363-T2

DEVELOPMENT OF ADVANCED NO<sub>x</sub> CONTROL CONCEPTS  
FOR COAL-FIRED UTILITY BOILERS

DOE Contract No. DE-AC22-90PC90363

Period of Performance: September 26, 1990 to October 26, 1992

DOE/PC/90363--T2

DE92 010009

**Quarterly Technical Progress Report No. 2**

Period Covered by Report: January 1 to March 31, 1991

prepared by:

J. Newhall  
G. England  
W.R. Seeker

Energy and Environmental Research Corporation  
18 Mason  
Irvine, California 92718

Date Submitted: December 23, 1991

prepared for:

Mr. Charles E. Schmidt  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, Pennsylvania 15236-0940

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**MASTER**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## TABLE OF CONTENTS

PART I. Fundamental Studies Test Plan

PART II. Quality Assurance Project Plan

**DEVELOPMENT OF ADVANCED NO<sub>x</sub> CONTROL CONCEPTS  
FOR COAL-FIRED UTILITY BOILERS**

**FUNDAMENTAL STUDIES TEST PLAN**

**Prepared for**

**Mr. Charles E. Schmidt  
U. S. Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, Pennsylvania 15236-0940**

**Contract No. DE-AC22-90PC90363**

**Prepared by**

**G.C. England  
J.L. Newhall  
W.R. Secker**

**Energy and Environmental Research Corporation  
18 Mason  
Irvine, CA 92714**

**December 23, 1991**

## TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1.0	SUMMARY .....	1-1
2.0	INTRODUCTION .....	2-1
3.0	OVERVIEW OF FUNDAMENTAL TESTING .....	3-1
3.1	Lab-Scale Fundamental Tests .....	3-1
	3.1.1 Evaluation of NO <sub>2</sub> Scrubbing .....	3-2
	3.1.2 Lab-Scale Characterization of the Methanol Injection Step .....	3-4
	3.1.3 Lab-Scale Test Schedule .....	3-4
3.2	Fundamental Pilot-Scale Tests .....	3-7
4.0	TEST MATRICES AND MEASUREMENTS .....	4-1

## LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
3-1	Lab-scale scrubbing studies experimental setup . . . . .	3-3
3-2	Methanol injection lab-scale studies test setup . . . . .	3-5
3-3	Schedule for lab-scale fundamental tests . . . . .	3-6
3-4	Boiler simulation furnace schematic . . . . .	3-8
3-5	Schedule for pilot-scale fundamental tests . . . . .	3-10

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
4-1a	Lab-scale scrubbing studies test matrix . . . . .	4-2
4-1b	Test matrix for the lab-scale methanol injection tests . . . . .	4-3
4-2a	Test matrix for contacting studies . . . . .	4-4
4-2b	Test matrix for pilot-scale advanced reburning experiments . . . . .	4-6
4-2c	Test matrix for methanol injection studies at the BSF . . . . .	4-7

This test plan describes the test activities to be conducted in the Fundamental Studies phase of the program entitled "Development of Advanced NO<sub>x</sub> Control Concepts for Coal-Fired Utility Boilers" currently being performed by Energy and Environmental Research Corporation (EER) for the Department of Energy. The overall objective of this project is to demonstrate the effectiveness of advanced NO<sub>x</sub> control concepts for removing NO<sub>x</sub> from coal-fired flue gas at a large enough scale and over a sufficiently broad range of conditions to provide all the information needed to conduct a full-scale demonstration in a coal-fired utility boiler. Technology objectives are to achieve 70% reduction in NO<sub>x</sub> emissions at 20% of the cost of selective catalytic reduction (SCR), without significant adverse impacts on boiler efficiency, operational complexity, or environmental impacts. A secondary goal is to reduce NO<sub>x</sub> emissions to 60 ppm at half of the cost of SCR for ozone non-attainment areas.

CombiNO<sub>x</sub> involves the use of hybrid NO<sub>x</sub> control technologies which act synergistically when applied together. The initial approach involves the use of advanced reburning, itself a hybrid technology combining reburning with selective non-catalytic reduction (SNCR), in combination with methanol injection at lower temperatures. The methanol converts NO to NO<sub>2</sub> which is subsequently removed in a conventional SO<sub>2</sub> scrubber. This technology has been dubbed CombiNO<sub>x</sub>. The program is being conducted in five tasks:

- Task 1 – Program Definition
- Task 2 – Design and Construct Test Unit
- Task 3 – Experimental Program and Data Reduction
- Task 4 – Conceptual Design and Economics
- Task 5 – Test Unit Restoration

Task 3 – Experimental Program and Data Reduction is divided into two primary subtasks: Fundamental Studies and Process Testing. Both Fundamental and Process Studies will be performed to characterize all features of the CombiNO<sub>x</sub> process. The goals of the Fundamental Tests are to better understand the controlling parameters of the CombiNO<sub>x</sub> process and to generate a data base consisting of NO reduction achieved as a function of various operational parameters. In the process design phase of the program, subcontractor Research Cottrell will perform pilot

scale scrubbing tests, and finally, an integration of all of the CombiNOx processes (including the scrubbing step) will be demonstrated at EER's 10 MMBtu/hr tower furnace at the Test Site in California. Historically, the tower furnace has simulated behavior in full scale boilers, so this phase will address scale-up phenomena such as surface to volume ratio.

This test plan presents the approach for the Fundamental Studies subtask. Lab-scale studies will be performed to characterize the methanol injection and NO<sub>2</sub> scrubbing steps. The first series of experiments will focus on the NO<sub>2</sub> scrubbing step, to determine how well various scrubbing solutions remove NO<sub>2</sub> in the presence of SO<sub>2</sub>. The second series of tests will focus on the conversion of NO to NO<sub>2</sub>.

In parallel to the lab-scale tests, pilot-scale tests will also be performed to investigate the CombiNOx process. The pilot-scale experiments will be performed in the Boiler Simulation Furnace (BSF) which has a nominal firing rate of 1x10<sup>6</sup> Btu/hr. Previous research has suggested that injection of a SNCR agent into a region wherein CO is oxidizing improves the performance of the agent. At the BSF, initial tests will be performed to understand the role of contacting between the SNCR agent and oxidizing CO. The alternatives to be considered are: 1) utilizing reburning to generate a CO rich region and injecting the agent into the reburning zone with an oxidant and, 2) premixing the agent with CO and injecting the mixture into a fuel lean region of the furnace. Second, a parametric study will be performed to understand the impact of controlling parameters on advanced gas and advanced coal reburning performance. Next, the methanol injection step will be characterized. The results of the lab-scale tests will be available at this time. Finally, after all of the components of CombiNOx have been evaluated individually, they will be integrated (except for the scrubbing step) and demonstrated.

## INTRODUCTION

Energy and Environmental Research Corporation (EER) is currently conducting a test program to develop an advanced NO<sub>x</sub> control method utilizing reburning, promoted selective non-catalytic agent injection, and methanol injection. The study will consist of fundamental and process testing over a large enough range of operating parameters to significantly reduce the risk of a full scale demonstration project. The test plan for the fundamental testing phase of the program is presented here.

Pilot scale fundamental testing will take place at the pilot-scale Boiler Simulation Furnace (BSF). A series of lab-scale tests to better understand the methanol injection and NO<sub>2</sub> scrubbing steps will be performed also. These tests will commence in the Spring of 1991 and be completed in January of 1992, at which time the process testing will be planned.



### 3.0

## OVERVIEW OF FUNDAMENTAL TESTING

Previous data suggest that if a selective non-catalytic reduction (SNCR) agent is introduced into a flue gas region where an appropriate amount of CO is oxidizing, performance of the agent is enhanced – the temperature window broadens and the NO reduction improves. Additionally, the optimum agent injection temperature decreases as the amount of oxidizing CO increases. This feature may result in a process that has a degree of flexibility in terms of full-scale application. In a boiler, the flue gas temperatures of interest to SNCR generally occur in the vicinity of the convective pass where access may be limited. The ability to vary the CO concentration such that the temperature at the access area is optimum for SNCR is an attractive benefit. A key feature of the CombiNOx process is the addition of the SNCR agent into CO rich zones to take advantage of the promotion effect.

The other main component of the CombiNOx process is the methanol injection step. It has been found at bench scale that if methanol is injected into the flue gas at appropriate temperatures, it will convert NO to NO<sub>2</sub>. Although the total NO<sub>x</sub> is not reduced, it is possible to remove NO<sub>2</sub> in a conventional SO<sub>2</sub> scrubber. Clearly, this step of the CombiNOx process would only be retrofitted on a boiler that already uses an SO<sub>2</sub> scrubber, since the cost of a scrubber would not allow us to meet our economic goals for the process. Thus CombiNOx may be thought of as promoted SNCR combined with conversion of NO to NO<sub>2</sub> which is subsequently removed.

### 3.1

#### Lab-Scale Fundamental Tests

The lab-scale work may be broken down into two test series. The purpose of the first test series is to determine whether or not the type of scrubber developed by Research Cottrell will be effective for removing NO<sub>2</sub> (without deleterious effects on the SO<sub>2</sub> removal). In this test series, it will be determined whether or not the scrubber will work with only a minor change to the scrubbing solution and not require significant changes to the hardware or operating conditions. As a result, the first test series will experiment with different additives to conventional scrubbing solutions to try to achieve good removal efficiencies. The purpose of the second test series will be to develop an empirical understanding of the conversion of NO by methanol to NO<sub>2</sub>, or in other words, to generate a data base characterizing the reaction.

### 3.1.1 Evaluation of NO<sub>2</sub> Scrubbing

The goal of the lab-scale scrubbing tests is to find a scrubbing solution that will:

- Capture a high percentage of NO<sub>2</sub> and SO<sub>2</sub> in the flue gas;
- Have a substantial capacity for NO<sub>2</sub> and SO<sub>2</sub>;
- Be inexpensive;
- Produce a waste that is at least as disposable as what is now produced;
- Not convert NO<sub>2</sub> to N<sub>2</sub>O.

The experimental set-up is shown in Figure 3-1. The test is essentially a batch process in which a simulated flue gas, consisting of known quantities of N<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub> and NO<sub>2</sub>, is flowed through a bubbler in a constant temperature bath where it contacts the scrubbing solution. After leaving the scrubber, the water is removed from the clean flue gas in a water trap and the sample is sent to the NO<sub>x</sub> and SO<sub>2</sub> analyzers. The effect of moisture in the flue gas will be evaluated by adding a known amount of water just upstream of the scrubber. The effect of scrubbing temperature on removal efficiency and capacity may be assessed by varying the temperature of the bath that the bubbler sits in. Since liquid-gas contact times are relatively long in this experimental set-up compared to actual scrubbers, the results represent chemical interactions in the absence of contacting time limitations.

From the initial and scrubbed levels of NO<sub>2</sub> and SO<sub>2</sub>, the removal efficiency of the scrubbing solution may be evaluated. Since it is a batch process with a fixed amount of the scrubbing solution, the length of time that removal takes place tells us how much capacity the particular scrubbing solution has for either NO<sub>2</sub> or SO<sub>2</sub>. After candidate scrubbing solutions have been identified, the disposal problem will be addressed. The scrubbing liquid will be recovered after testing, and analyzed to determine if there are any undesirable byproducts of the process. Finally, after the experiments are completed, an attempt will be made to model the results, so that in the future, the model may be used to predict the performance of a given scrubbing solution.

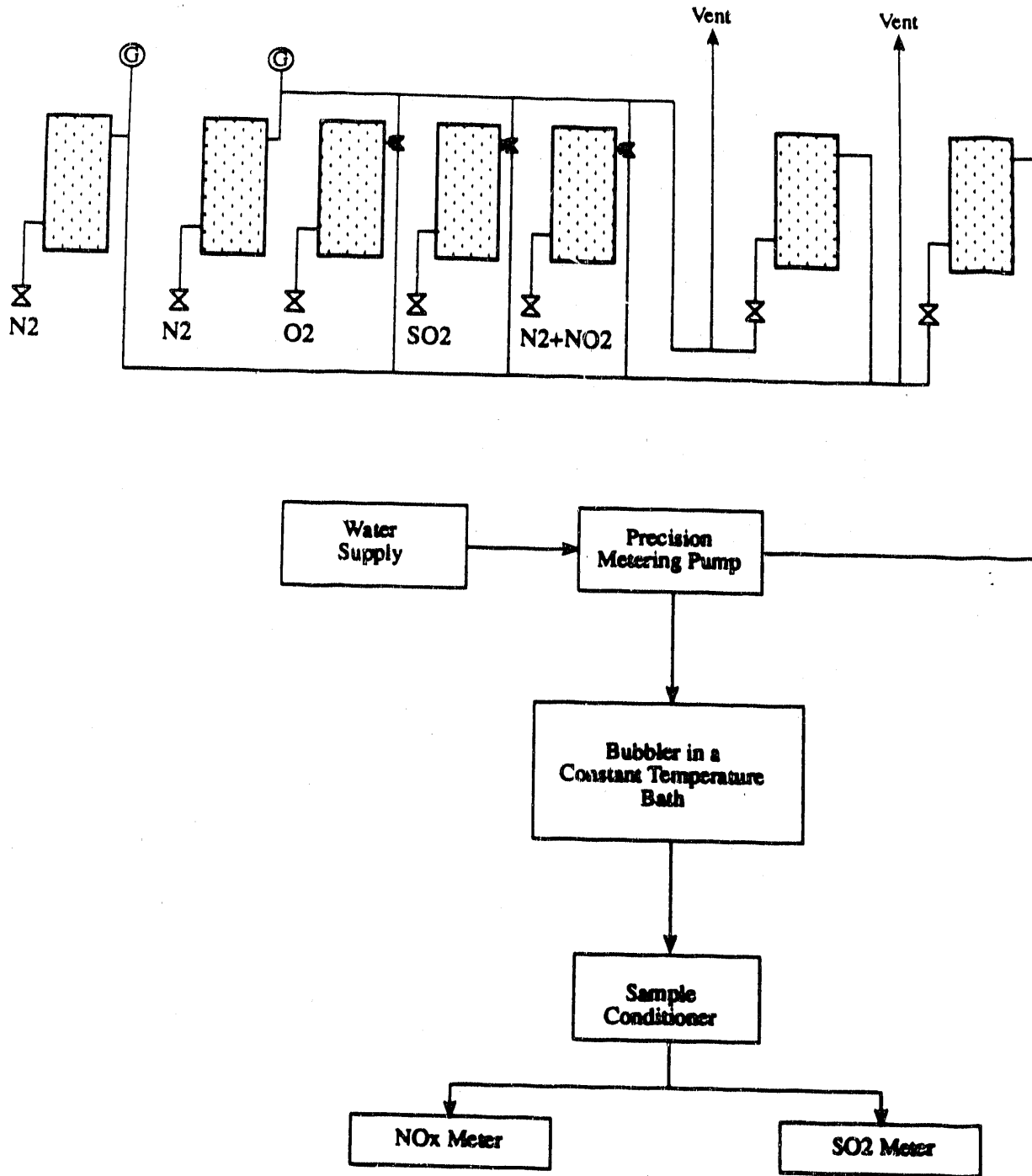


Figure 3-1. Lab-scale scrubbing studies experimental setup.

### 3.1.2 Lab-Scale Characterization of the Methanol Injection Step

The methanol injection step of the CombiNO<sub>x</sub> process serves to convert NO to NO<sub>2</sub>. The lab-scale tests are designed to generate a data base to define the:

- optimum methanol injection temperature for a given flue gas composition;
- impact of amount of methanol injected on the NO conversion efficiency;
- impact of the above on the formation of byproducts such as CO and formaldehyde.

The experimental setup is shown in Figure 3-2. A gas blending system similar to that used in the scrubbing experiments will be employed to generate a simulated flue gas. Methanol will be added to the dry flue gas via a saturator using N<sub>2</sub> as the carrier gas. The amount of methanol may be adjusted by varying the bath temperature. Knowledge of the vapor pressure of methanol will allow the amount of methanol added to be calculated. If desired, a known amount of water may be added to the simulated flue gas via a precision metering pump.

The mixture is rapidly heated to a set temperature in a quartz tube reactor where it remains for a finite, variable length of time. It is assumed that the temperature rise is an ideal step function. Finally, the flue gas passes through a water trap on its way to the NO<sub>x</sub>, SO<sub>2</sub>, O<sub>2</sub>, and CO analyzers. The NO<sub>x</sub> analyzer will be operated in NO mode only. The final NO level will be compared to the initial NO level to determine the conversion efficiency.

### 3.1.3 Lab-Scale Test Schedule

The test schedule for the lab-scale tests is shown in Figure 3-3. The experimental setup for the scrubbing studies will be done in the month of April. Approximately seven weeks of tests will be performed commencing at the beginning of May. Modeling of the results will be done in August for three to four weeks. The experimental setup for the methanol injection tests take the first two weeks of September, while the tests will last until the middle of November, 1991.

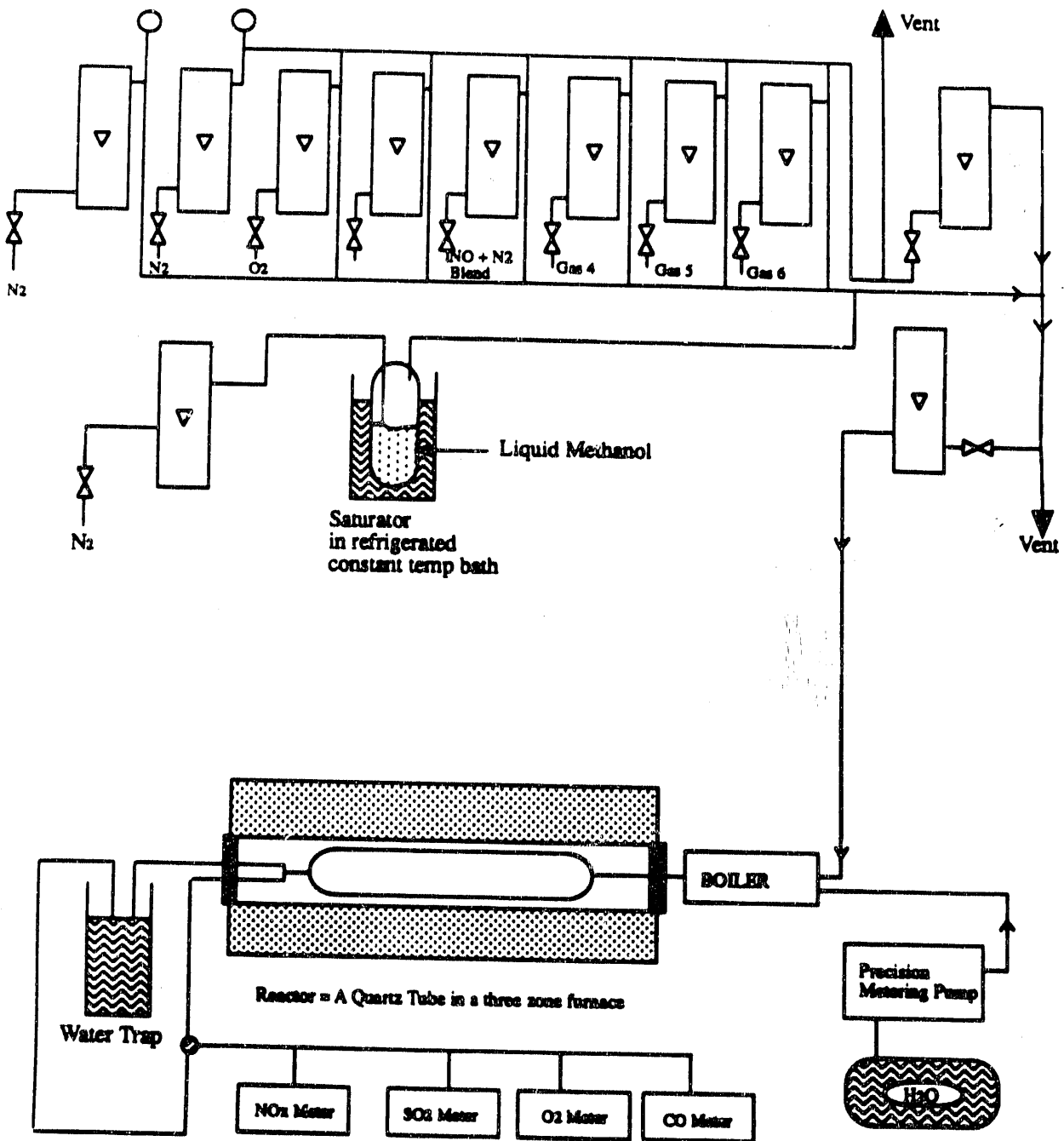


Figure 3-2. Methanol injection lab-scale studies test setup.

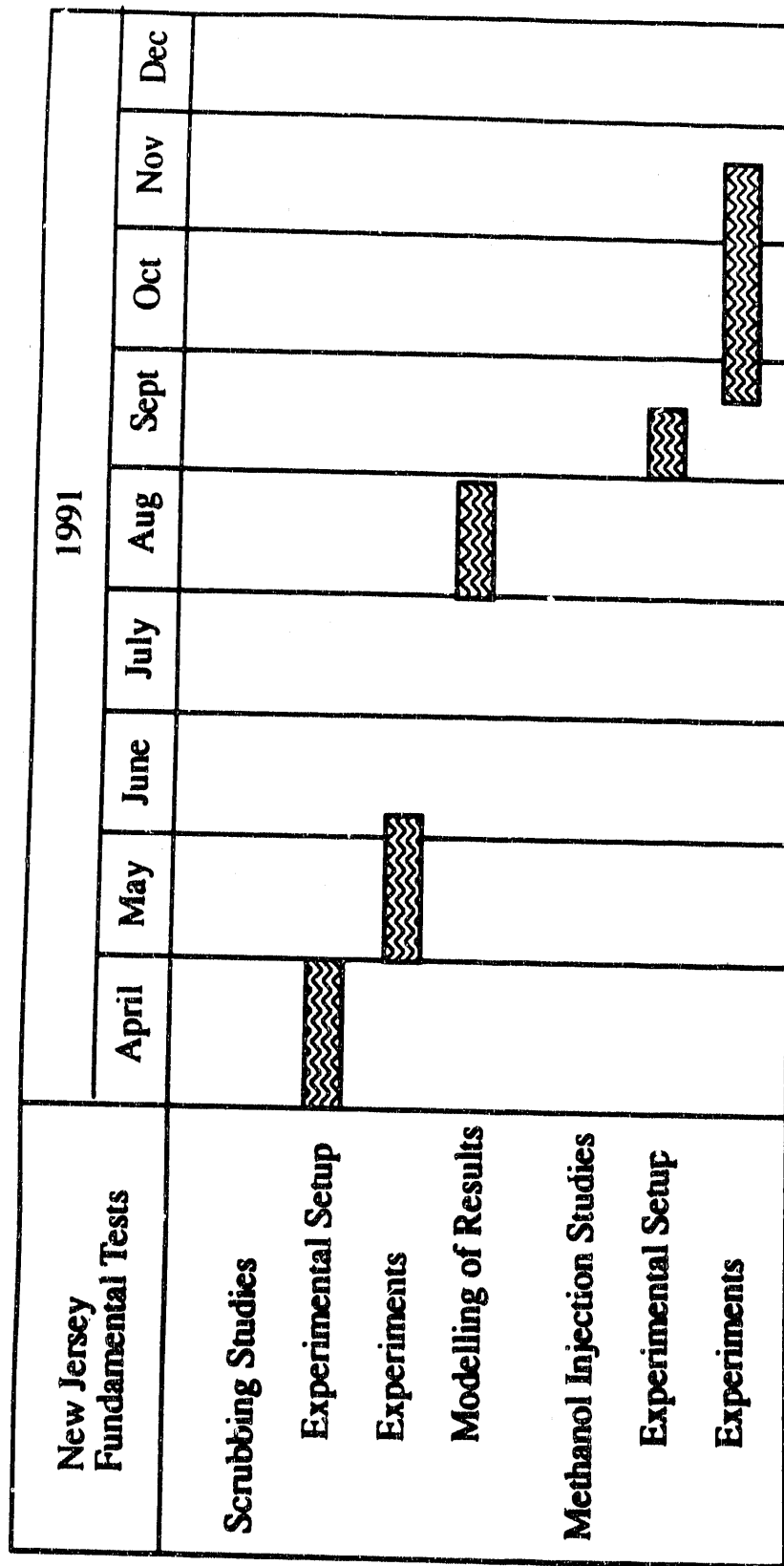


Figure 3-3. Schedule for lab-scale Fundamental Tests.

### 3.2

#### Fundamental Pilot -Scale Tests

The Boiler Simulation Furnace (BSF) will be used to study the CombiNOx process. The BSF is a 1 Million Btu/hr down-fired furnace that stands approximately 25 feet high. A schematic of the facility is given in Figure 3-4. The vertical section generally represents the radiant furnace while the horizontal "S" shaped ducting simulates the convective pass. Here, banks of air cooled fouling probes are employed to simulate heat transfer surfaces in the convective section of the boiler. Both flue gas temperature and probe temperatures may be adjusted independently. Numerous ports are located in the vertical section of the furnace to insert cooling rods and in addition, eight square water cooled panels are available (one for each section of the radiant furnace) if desired. The potential for cooling flexibility in the radiant furnace allows, the temperature profile of most full scale boilers to be easily duplicated. For this project, the quench rate will be in the range of coal-fired utility boilers.

All of the steps of the CombiNOx process will be investigated in the fundamental tests here except for the NO<sub>2</sub> scrubbing step. The specific goals of the fundamental tests at the BSF will be to:

1. Understand the role of contacting oxidizing CO with the SNCR agent;
2. Determine the impact of the reburn zone stoichiometry (when reburning is used to generate CO for promotion) on NO reduction performance;
3. Define the relationship between SNCR agent injection temperature and NO reduction performance;
4. Understand the impact of burnout air injection location and temperature on NO reduction performance;
5. Characterize the methanol injection step.
6. Identify the parameters controlling undesirable emissions such as N<sub>2</sub>O and formaldehyde.

The first step is to determine the best way to take advantage of the CO promotion effect on SNCR efficiency. As mentioned previously, the possibilities identified are: 1) perform reburning to generate CO, and 2) inject CO with the SNCR agent. For the reburning method, (advanced reburning) the effect of amount of reburning or the amount of CO present in the furnace on NO

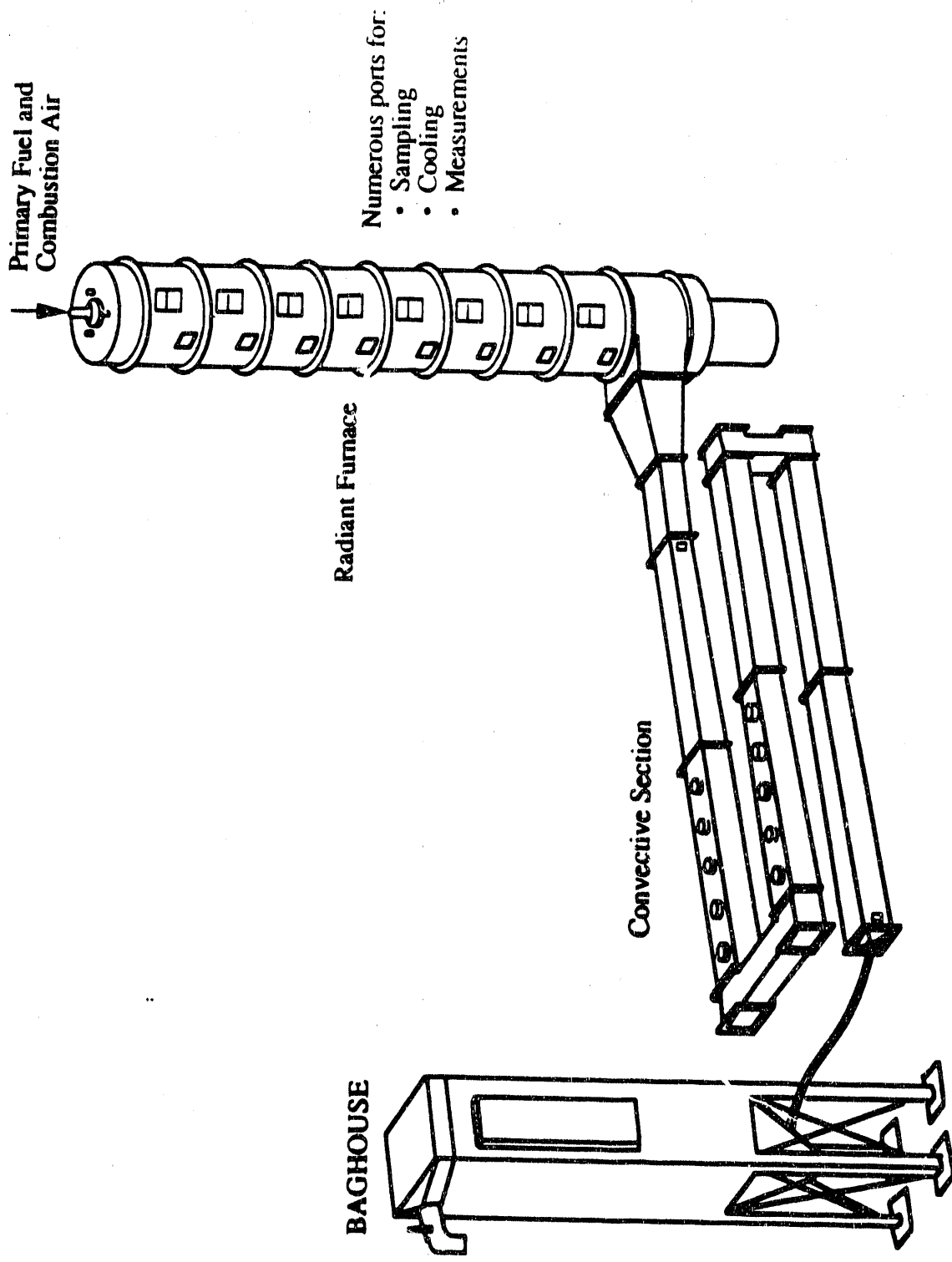


Figure 3-4. Boiler Simulation Furnace schematic.



removal efficiency will be measured. The impact of burnout air injection location will be explored. At issue is whether the burnout air required for CO oxidation needs to be available upstream of the SNCR agent, or if it is better to inject it with the agent or even downstream of it. Both natural gas reburning and coal reburning will be tested.

For the method of promotion utilizing co-injection of CO and the agent, the effect of furnace stoichiometry and amount of CO injected will be examined. Finally, for each promotion method, the relationship between stoichiometry (CO concentration) and optimum agent injection temperature will be noted.

The next series of experiments planned will essentially be a scale-up of the lab scale methanol injection tests discussed in the previous section. A key concern in these tests is accurate measurement of NO in the presence of large amounts of NO<sub>2</sub>. Parameters to be varied include methanol to NO ratio, methanol injection temperature, fuel type and initial NO level. In addition, the effect of ammonia concentration in the flue gas on methanol injection performance will be checked.

Finally, after all of the CombiNOx steps have been tested individually, the processes will be integrated and performed simultaneously. An estimate of emissions of undesirables such as formaldehyde (which may be a byproduct of the methanol injection step), ammonia and N<sub>2</sub>O will be monitored for each parametric variation. In this way, the controlling parameters leading to their possible emission may be understood and potentially corrected. The schedule for the proposed tests is presented in Figure 3-5. It is estimated that the fundamental tests at the BSF will be completed by the end of January, 1992. As may be seen testing breaks have been scheduled to allow for sufficient data analysis and formulation of a plan to proceed.

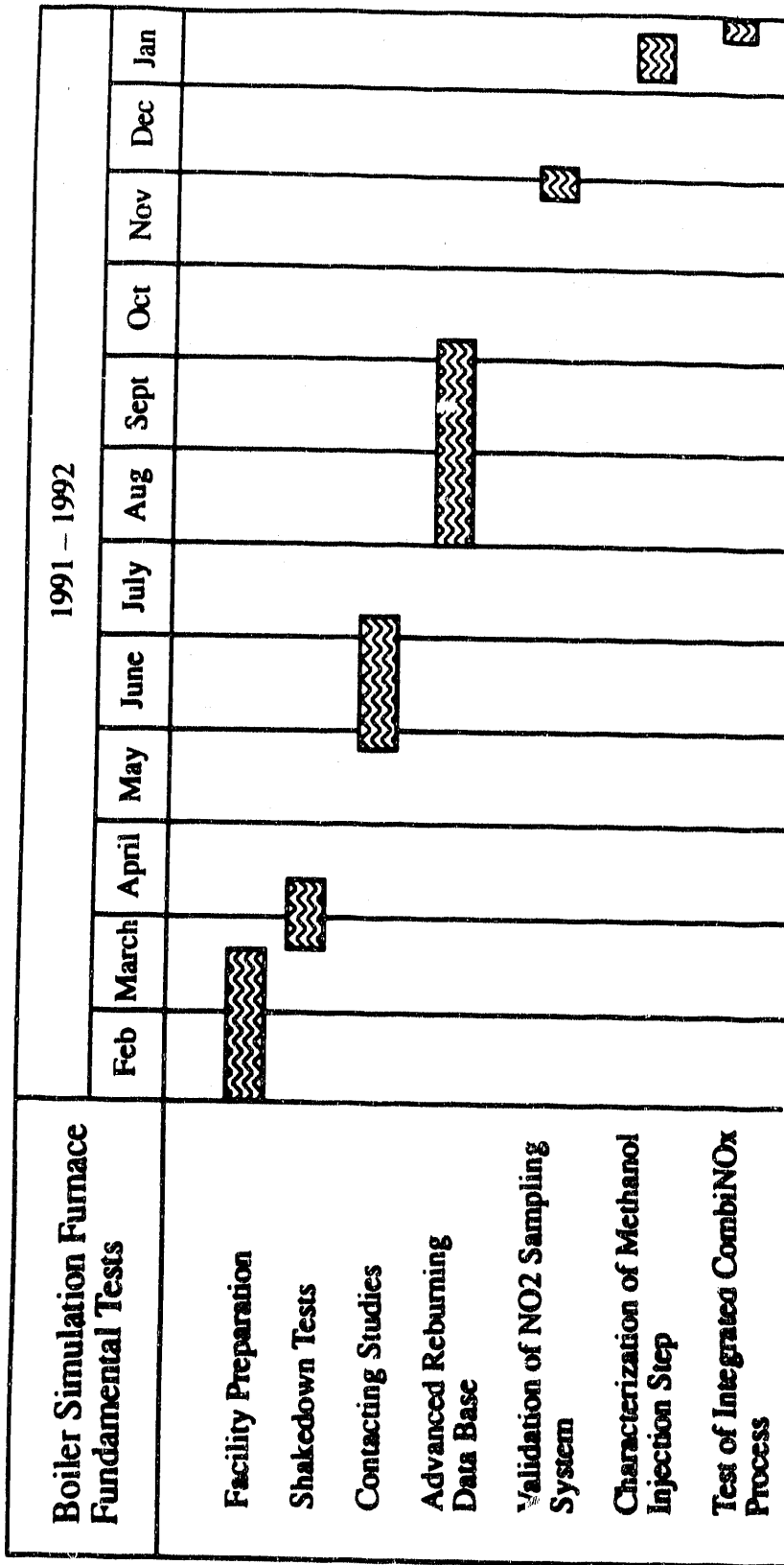


Figure 3-5. Schedule for pilot-scale Fundamental Tests.

## 4.0 TEST MATRICES AND MEASUREMENTS

The preliminary detailed test matrices for the lab-scale and pilot-scale Fundamental Studies are presented in Tables 4-1 and 4-2.

### *NO<sub>2</sub> Scrubbing Studies*

In the NO<sub>2</sub> scrubbing studies, the single most important parameter to be varied is the scrubbing solution. The process will be deductive – the initial scrubbing solution tested will be calcium hydroxide and each subsequent solution will be identified after observing the results of the previous test. Other parameters of interest include the bath temperature and moisture content of the gas to be scrubbed. The matrix is presented in Table 4-1a.

### *Lab Scale Methanol Injection Studies*

The test matrix for the methanol injection characterization tests is shown in Table 4-1b. As may be seen, seven parameters will be varied. Generally, removal efficiency of NO<sub>x</sub> reduction technologies improves as initial NO increases. The magnitude of this effect on the methanol injection step will be documented at this scale for three different initial NO levels: 50, 100 and 200 ppm. For each of these initial NO levels, the reaction temperature (which will simulate injection temperature at the BSF) will be varied over a wide range. Finally, for each of these reaction temperatures, the amount of methanol injected will be varied, resulting in a total of approximately 250 data points. The effect of ammonia slip, flue gas oxygen content, moisture content, and reactor residence time will also be examined. Emissions of NO, CO, formaldehyde and N<sub>2</sub>O will be recorded.

### *Pilot-Scale Contact Studies at the BSF*

At the BSF, the first series of tests will focus on the effect of how CO promotion is accomplished. As discussed earlier, oxidation of CO in close proximity to the SNCR agent may enhance the process. The two methods of promotion to be evaluated are: 1) co-injection of the CO and SNCR agent into a fuel lean environment and 2) advanced reburning in which the agent is injected near or at the reburning zone. The test matrix is presented in Table 4-2a.

These tests will be conducted with natural gas fired at 1 MMBtu/hr. The SNCR agent will be ammonia in gas phase to remove droplet evaporation effects. Gas reburning will be simulated

TABLE 4-1a. LAB-SCALE SCRUBBING STUDIES TEST MATRIX

Test Series	Scrubbing Solution	Bath Temp (°F)	Gas Flow (cc/min)	Gas Moisture (cc/min)
1	Vary	135	3660	none
2	Optimum	109	3660	none
3	Vary	135	3660	0.72

TABLE 4-1b. TEST MATRIX FOR THE LAB-SCALE METHANOL INJECTION TESTS

Test Series	Initial NO (ppm)	Temperature (°F)	Methanol (ppm)	Oxygen (%)	Water Vapor (%)	Ammonia (ppm)	Residence Time (s)
1	50, 100, and 200	752	Vary from 29 to 1390 for each reactor temp	20	1	none	0.21
		1090		"	"	"	"
		1141		"	"	"	"
		1283		"	"	"	"
		1375		"	"	"	"
		1468		"	"	"	"
		1465		"	"	"	"
		1692		"	"	"	"
2	50 50	Vary from 1094 to 1742	116 116	20 20	1 1	0 400	Vary from 0.2 to 0.8
		Vary from 1270 to 1650	116	Vary from 0 to 8	0	0	Vary from 0 to 0.4

TABLE 4-2a. TEST MATRIX FOR CONTACTING STUDIES

Natural gas – 1 MM Btu/hr  
 SNCR Agent – Gaseous Ammonia  
 NSR – moles NH<sub>3</sub>/moles NO = 1.5

Test Number	Initial SR	Final SR	CO Promotion Method	CO – ppm Meas @ 1600F	NH <sub>3</sub> Injection Temp (°F)
1	1.2	1.2	none	low	vary
2	1.02	1.02	co-injection	high	vary
3	1.2	1.2	co-injection	high	vary
4	1.2	1.2	co-injection	low	vary
5	1.09	1.09	co-injection	low	vary
6	1.02	1.02	simulated AGR	low	vary
7	0.99	1.2	simulated AGR	high	vary
8	1.02	1.2	simulated AGR	low	vary
9	0.99	1.02	simulated AGR	high	vary

by reducing the initial stoichiometry. The parameters of interest are: initial stoichiometry, final stoichiometry (simulated reburning cases only), CO level and ammonia injection temperature. Emissions measurements to be made include O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>x</sub>, and N<sub>2</sub>O. Also, a suction pyrometer will be used to measure injection temperatures.

#### *Pilot-Scale Advanced Gas and Coal Reburning Studies*

The test matrix for the advanced reburning tests is given in Table 4-2b. For these tests, coal will be fired as the main fuel, and both natural gas and coal will be used as the reburning fuel. The SNCR agent will be an approximately 15% aqueous solution of urea. The injection nozzle used will be a twin fluid 180° nozzle with good atomization properties. The solution and atomizing medium flows will remain constant so that droplet atomization will not be a variable. Atomizing fluids that will be tested include air, oxygen and nitrogen (simulates steam in a full scale application). To minimize the amount of reburning fuel used, the initial stoichiometry will be 1.13, lower than the final stoichiometry of 1.20.

For both natural gas and coal advanced reburning, the impact of variations in reburn zone stoichiometry, agent injection temperature and burnout air injection temperature will be measured, and an optimum found. The nitrogen stoichiometric ratio (moles of N in urea : moles of NO) or NSR will be maintained at 1.5 for all tests except for the final test which will use the optimum operating conditions found in the foregoing tests where the NSR will be varied. Measurements that will be made include: O<sub>2</sub>, CO (both at the exhaust and in the reburning zone), CO<sub>2</sub>, NO, NO<sub>x</sub>, N<sub>2</sub>O, and ammonia slip.

#### *Pilot Scale Methanol Injection Characterization Tests*

In the final tests series at the BSF, the methanol injection step will be characterized at a larger scale than the New Jersey tests, and all of the individual parts of the CombiNO<sub>x</sub> process will be integrated. The test matrix is shown in Table 4-2c. In the first nine tests, either coal or natural gas will be fired at a final stoichiometry of 1.2. Because the two fuels will be compared, when coal is fired, enough gas reburning will be performed to reduce the NO level upstream of the methanol injection step to 400 ppm. Similarly, when natural gas is burned, ammonia will be doped in with the combustion air to increase the NO level to 400 ppm. Concentrations of O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O and formaldehyde will be routinely measured. In addition, in the ammonia doping case, ammonia emissions will be quantified.

TABLE 4-2b. TEST MATRIX FOR PILOT-SCALE ADVANCED REBURNING EXPERIMENTS

SNCR Agent - Urea  
 Urea Solution Flow Rate - 20 gm/min  
 Urea Atomization Flow Rate - 5.3 scfm

Test Number	Main Fuel	Reburn Fuel	SR1	SR2	SR3	NSR	Urea Inj Temp (°F)	Urea Atmz. Fluid	Burnout Air Inj Temp (°F)	Comments
1	Nat Gas	-	1.2	1.2	1.2	1.5	vary	N2	-	Effect of NG Effect of urea injection temp
2	Coal	Nat Gas	1.13	vary	1.2	1.5	1800	N2	1600	Effect of SR2
3	Coal	Nat Gas	1.13	1.02	1.02	1.5	vary	N2, O2, air	-	Effect of urea inj temp Effect of atomization agent
4	Coal	Nat Gas	1.13	1.02	1.2	1.5	vary	N2, O2, air	1600	Effect of urea inj temp Effect of atomization agent
5	Coal	Nat Gas	1.13	1.02	1.2	1.5	1800	N2	vary	Effect of BOA inj temp
6	Coal	Coal	1.13	vary	1.2	1.5	1800	N2	1600	Effect of SR2
7	Coal	Coal	1.13	1.01	1.01	1.5	vary	N2, O2, air	-	Effect of urea inj temp Effect of atomization agent
8	Coal	Coal	1.13	1.01	1.2	1.5	vary	N2, O2, air	1600	Effect of urea inj temp Effect of atomization agent
9	Coal	Coal	1.13	1.01	1.2	1.5	1800	N2	vary	Effect of BOA inj temp
10	Coal	Nat Gas	1.13	1.02	1.2	1,2,3	1800	N2	1600	Effect of NSR



TABLE 4-2c. TEST MATRIX FOR METHANOL INJECTION STUDIES AT THE BSF

Test Number	Fuel	SR	Initial NO ppm (0% O <sub>2</sub> )	Methanol Form	Meth/NO Ratio	Methanol Inj Temp (°F)	Gases Doped	Comments
1	Coal	1.2	400	Gaseous	1.5	vary	none	Gas return to get 400 ppm
2	Coal	1.2	400	Gaseous	1,2,3	optimum	none	Effect of Meth/NO ratio
3	Coal	1.2	400	Gaseous	1.5	vary	100 ppm NH <sub>3</sub>	Effect of Ammonia Slip
4	Coal	1.2	400	25% Solution	1.5	vary	none	Effect of aqueous solution
5	Coal	1.2	400	Liquid	1.5	vary	none	Effect of liquid methanol
6	Nat Gas	1.2	400	Gaseous	1.5	vary	none	Effect if NG is the fuel
7	Nat Gas	1.2	400	Gaseous	1.5	vary	SO <sub>2</sub>	SO <sub>2</sub> to match coal level
8	Nat Gas	1.2	200	Gaseous	1.5	vary	none	Effect of initial NO
9	Nat Gas	1.2	400	Gaseous	1.5	vary	SO <sub>2</sub> + ash	SO <sub>2</sub> + ash to match coal
10	Optimized gas CombiNO <sub>x</sub> (coal main fuel, advanced gas reburning + methanol injection)							
11	Optimized coal CombiNO <sub>x</sub> (coal main fuel, advanced coal reburning + methanol injection)							

Some of the parameters that will be considered in the first nine tests are: initial NO, Methanol : NO molar ratio, and methanol injection temperature. Since there are previous lab scale data suggesting that ammonia slip reduces the effectiveness of the methanol, Test 3 will involve methanol injection during ammonia slip conditions. All of the tests will be performed with a gaseous mixture of methanol and nitrogen except for Tests 4 and 5, which will show the effect of aqueous and liquid methanol injection, respectively.

Finally, previous lab scale data have shown that the presence of SO<sub>2</sub> is detrimental to the methanol process. If these data are validated (the natural gas tests show better conversion of NO to NO<sub>2</sub> than the coal tests, with different optimum methanol injection temperatures), the natural gas will be doped with sufficient SO<sub>2</sub> to match the SO<sub>2</sub> emissions in the coal tests, and methanol injection temperature will be varied (Test 7). If these data still do not agree with the coal data, ash and SO<sub>2</sub> will be added (Test 8), to determine if the ash in the coal alters the performance of the methanol.

In tests ten and eleven, the integrated CombiNOx process will be performed. For both the coal and natural gas versions of CombiNOx, the optimum advanced reburning and methanol injection conditions will be used. The effect of varying the urea and methanol injection temperatures will be evaluated.

DEVELOPMENT OF ADVANCED NO<sub>x</sub> CONTROL  
CONCEPTS FOR COAL-FIRED UTILITY BOILERS

DOE Contract No. DE-AC22-90PC90363

Revision

QUALITY ASSURANCE PROJECT PLAN

Prepared for

U.S. Department of Energy  
Pittsburgh Energy Technology Center  
P.O. Box 10940  
Pittsburgh, Pennsylvania 15236-0940

Prepared by

Energy and Environmental Research Corporation  
18 Mason  
Irvine, Ca. 92714

Approved by:

WRS W.R. Seeker, EER Project Manager

JC J. Cole, EER QA/QC Officer

\_\_\_\_\_ C. Schmidt, DOE Project Manager

September, 1991

## TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1.0 INTRODUCTION . . . . .	1-1
2.0 PROJECT DESCRIPTION . . . . .	2-1
3.0 PROJECT ORGANIZATION AND RESPONSIBILITY . . . . .	3-1
4.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVES, AND COMPARABILITY . . . . .	4-1
5.0 SAMPLING PROCEDURES . . . . .	5-1
5.1 <u>Continuous Monitoring Instrumentation</u> . . . . .	5-1
5.2 <u>N<sub>2</sub>O</u> . . . . .	5-7
5.3 <u>NH<sub>3</sub></u> . . . . .	5-7
5.4 <u>In-Furnace Gas Temperature</u> . . . . .	5-7
5.5 <u>Formaldehyde</u> . . . . .	5-8
6.0 SAMPLE CUSTODY . . . . .	6-1
6.1 <u>Sample Acquisition and Sample Tracking</u> . . . . .	6-1
6.2 <u>Laboratory Custody Procedures</u> . . . . .	6-2
6.3 <u>Reagents, Filters and Materials</u> . . . . .	6-6
7.0 CALIBRATION PROCEDURES AND FREQUENCY . . . . .	7-1
8.0 ANALYTICAL PROCEDURES . . . . .	8-1
8.1 <u>Continuous Monitoring Instrumentation</u> . . . . .	8-1
8.2 <u>N<sub>2</sub>O</u> . . . . .	8-4
8.3 <u>NH<sub>3</sub></u> . . . . .	8-4
8.4 <u>Formaldehyde</u> . . . . .	8-4
9.0 DATA REDUCTION, VALIDATION AND REPORTING . . . . .	9-1
9.1 <u>Data Reduction, Validation and Reporting Procedures</u> . . . . .	9-1
9.2 <u>Equations Used to Calculate Results</u> . . . . .	9-3

TABLE OF CONTENTS (CONTINUED)

<u>Section</u>	<u>Page</u>
9.3 <u>Daily Table of Data and Results</u> . . . . .	9-4
9.4 <u>Bi-Weekly Report</u> . . . . .	9-12
10.0 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY . . . . .	10-1
10.1 <u>Quality Control Check Procedures</u> . . . . .	10-2
10.1.1 <u>Calibration standards and devices</u> . . . . .	10-3
10.1.2 <u>Quality Control Samples</u> . . . . .	10-3
10.1.3 <u>Replicates</u> . . . . .	10-3
10.1.4 <u>Control Charts</u> . . . . .	10-3
10.2 Specific Checks and Frequency . . . . .	10-4
11.0 PREVENTIVE MAINTENANCE . . . . .	11-1
12.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT . . . . .	12-1

## LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
2-1	Program structure . . . . .	2-4
2-2	Program schedule and major milestones . . . . .	2-7
3-1	EER technical organization and project team organization . . . . .	3-3
5-1	Continuous monitoring sampling system . . . . .	5-4
5-2	SO <sub>2</sub> continuous monitoring system . . . . .	5-5
5-3	NO and NO <sub>2</sub> continuous monitoring system . . . . .	5-6
6-1	EER sample label . . . . .	6-3
6-2	Lab sample tracking report . . . . .	6-5
9-1	Data reduction, validation and reporting scheme . . . . .	9-2
9-2	Gas concentration calculation . . . . .	9-4
9-3	Summary of results SO <sub>3</sub> as H <sub>2</sub> SO <sub>4</sub> . . . . .	9-5
9-4	Calculation of NH <sub>3</sub> results . . . . .	9-7
9-5	Calculation of formaldehyde concentration . . . . .	9-8
9-6	Daily table of data and results . . . . .	9-9
9-7	Bi-weekly report format . . . . .	9-13

LIST OF TABLES

<u>Table</u>		<u>Page</u>
4-1	Program objectives for measurement precision, accuracy and completeness . . . . .	4-2
5-1	Sampling procedures . . . . .	5-2
7-1	Calibration procedures . . . . .	7-2
8-1	Analytical procedures . . . . .	8-2
8-2	Continuous Gas Analysis Instruments . . . . .	8-3
10-1	Quality control checks . . . . .	10-5
11-1	Preventive maintenance procedures . . . . .	11-2
11-2	Critical spare parts . . . . .	11-4

## 1.0 INTRODUCTION

The measurements to be performed in this program will be used to assess the potential application of COMBINOX. COMBINOX is a hybrid  $\text{NO}_x$  control scheme. It is the integration of three separate control technologies:

- Gas reburning
- Enhanced selective non-catalytic reduction
- Methanol injection

The measurements will determine the effectiveness on COMBINOX for removing  $\text{NO}_x$  from coal-fired utility boiler, including emissions of  $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$  and other pollutants. EER management recognizes that the collection and analysis of quality data is key to the success of this program and will take all the necessary steps to insure that the data quality is commensurate with the program objective.

This document is EER's Quality Assurance Program Plan for the subject program. It details the sampling and analytical procedures to be utilized along with quality control and quality assurance procedures, measurement precision and accuracy goals, and procedures for QA/QC reporting and corrective action.



## 2.0 PROJECT DESCRIPTION

The overall objective of this program is to demonstrate the effectiveness of the COMBINOX process at a large enough scale and over a sufficiently broad range of conditions to provide all of the information needed to conduct a full-scale demonstration in a coal fired utility boiler. Thus, this program will: 1) demonstrate that the controlling process variables are known, 2) provide a process design basis for the application of COMBINOX to coal fired boilers, 3) demonstrate to boiler owners and operators that the process is unlikely to have any adverse impacts upon boiler operation or life, and 4) provide sufficient confidence that when applied at full-scale the technology will be capable of meeting the following two technical performance goals:

- $\text{NO}_x$  emissions must be reduced by 70 percent at 20 percent of the cost of selective catalytic reduction (SCR). In ozone non-attainment areas,  $\text{NO}_x$  emissions must be reduced to less than 60 ppm at 50 percent of the cost of SCR.
- The application of COMBINOX must avoid reduction in boiler efficiency, it must not significantly increase the operational complexity of the boiler and must not introduce any adverse environmental impacts.

The program consists of 5 major tasks and subtasks, as shown in Figure 2-1.

Task 1, program definitions consists of two subtasks: Task 1.1, project work plan, and Task 1.2, QA/QC plan. The purpose of Task 1.1 was to prepare a detailed project work plan covering the entire period of performance of the contract (this task has been completed and submitted to DOE). The work plan describes in detail the activities needed to achieve the program goals and objectives.

The purpose of Task 1.2 is to prepare this QA/QC plan. The QA/QC plan describes a series of procedures that must be followed to ensure that the work

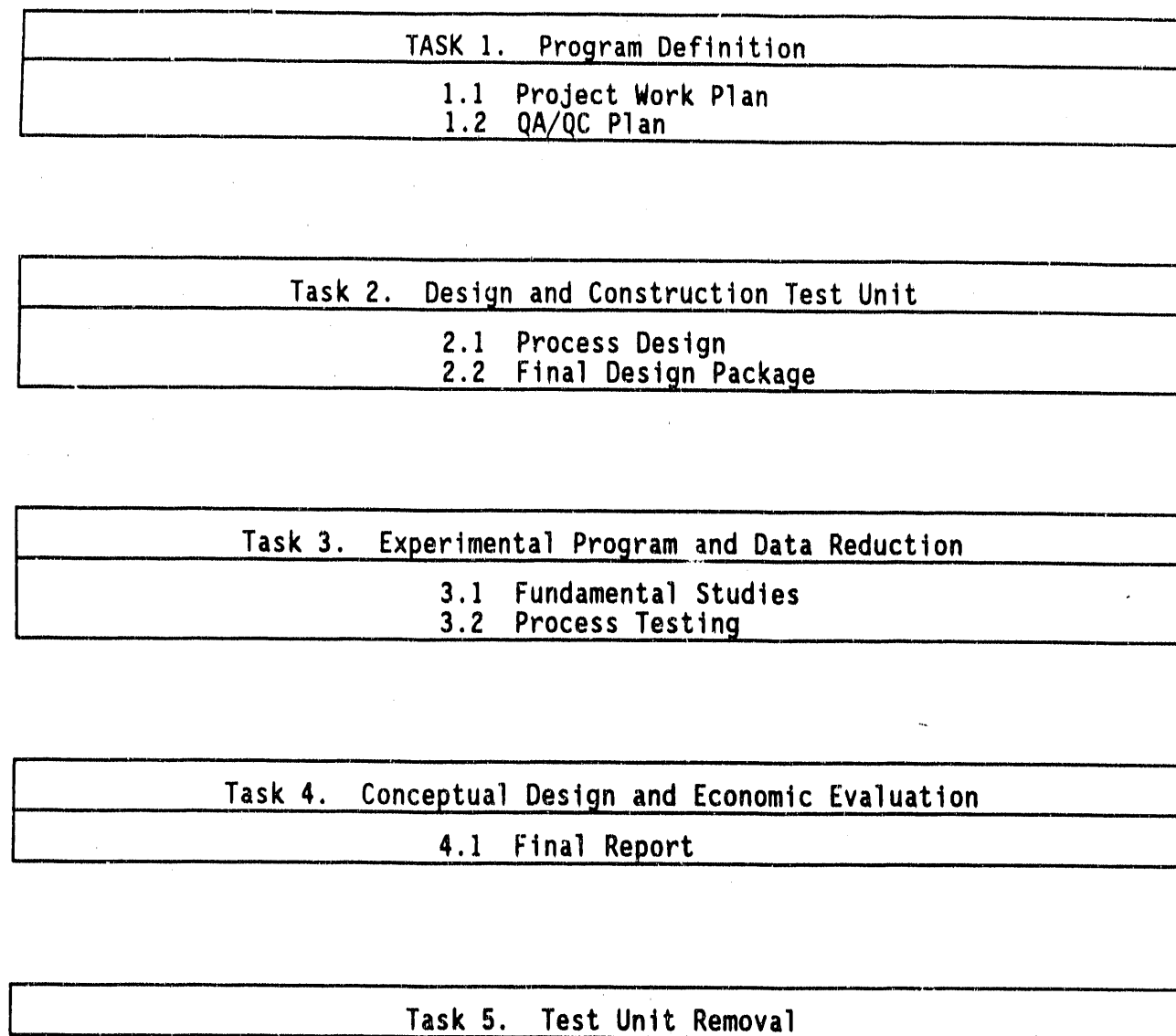


Figure 2-1. Program structure.

is performed in a manner that is consistent with the technical approach and the scope of work and which also satisfies DOE's QA/QC requirements.

The studies that will be carried out during Task 3 will be conducted at two scales: 1.0 and 10MM Btu/hr. Since all the major facilities are in existence, there will be no need for facility design and construction. However, minor modifications will be made (Task 2) to accommodate the injection of Methanol and reducing agents and evaluate NO<sub>2</sub> capture in both wet and dry SO<sub>2</sub> scrubbing systems.

The 1.0 MMBtu/hr Boiler Simulation Furnace (BSF) which will be used in Task 3.1 was designed to produce variable combustion conditions in order to simulate a wide variety of coal combustor firing schemes. There was no attempt to simulate directly the hardware of each of these types of firing systems; instead the BSF design simulates a fire-side environment that is typical of these various systems. In particular, the unit was designed to simulate the time\temperature\stoichiometry history of a range of coal-fired utility boilers. The furnace was designed to operate over a wide range of combustion conditions typical of current commercial practice.

The BSF has the following features:

- Nominal firing rate of 1.0 MMBtu/hr;
- Capability of firing sulfur-doped gases;
- Sorbent injection locations at 15 different points within the furnace profile;
- A low NO<sub>x</sub> distributed mixing burner (DMB) employed as the main burner;

- Adjustable temperature profile via load and cooling panels over ranges appropriate for all time/temperature conditions of U.S. designed boilers.

The equipment used at the BSF includes a full set of instrumentation devoted to both the monitoring of emissions and the system operating conditions. The emission monitoring system includes measurements of parameters such as CO, CO<sub>2</sub>, NO, NO<sub>2</sub> and O<sub>2</sub>. The process monitoring systems include a full array of gas flow sensors, coal feed rate monitors, and furnace thermal profile monitors.

The Tower Furnace which will be used in Task 3.2 is designed to simulate a wide range of flue gas conditions which are representative of those existing in pre-NSPS boilers firing medium-to-high sulphur coals. This test furnace has a nominal firing rate of  $10 \times 10^6$  Btu/hr. The tower furnace was designed as a research facility for the evaluation and development of in-furnace sorbent injection for SO<sub>2</sub> control. The furnace is down-fired vertically through a single multi-variable swirl burner, and is equipped to fire natural gas, fuel oil, emulsion, and /or pulverized coal. The main body of the furnace is a refractory lined, water-cooled steel shell, 4 ft. x 4 ft. in internal cross-section, and is approximately 30 ft. tall. Flue gases exiting the furnace pass through a series of water-cooled tube banks, and ultimately arrives at a recuperative heat exchanger which provides preheated combustion air. The first tube banks are fixed, and simulate typical boiler superheat and reheat sections, while the downstream tube banks are removable to facilitate the control of flue gas temperature and temperature quench rate.

A complete monitoring system is available for the reburning tower that provides a complete analysis of both emissions and systems operating conditions. Again the full complement of instrumentation is available including CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub> and O<sub>2</sub>.

All information is accessed through a computer based data acquisition system, which performs on-line data reduction and tabulation of all desired input and output conditions. Since the basic reburning system is already installed on

the facility, only agent and methanol injection systems will need to be designed in Task 2.

In addition to the furnaces described above, testing in Task 3 will be performed at the Whitehouse Facility in New Jersey to study  $\text{NO}_2$  scrubbing at bench scale.

Pilot scale studies will be performed at Research Cottrell's Wet Scrubber Test System. Their boiler is a Scotch double water wall design, fired with propane, rated at a 2 MMBtu/hr and capable of generating flue gas at 500 cfm. By injecting  $\text{NH}_3$  and  $\text{SO}_2$  into the combustion air, the levels of  $\text{NO}_x$  and  $\text{SO}_x$  in the flue gas that this boiler produces can be adjusted to match those of a coal fired boiler.

The principal modification required by the Research Cottrell unit will be the installation of new duct work between the boiler and the scrubber. This is needed to accommodate the selective agent injection system and the methanol injection system. Also required will be the agent injection and methanol injection system.

Task 3 is divided into two sub-tasks, Task 3.1, Fundamental Testing and 3.2, Process Testing. Fundamental Testing will include a study of the promoted selective non-catalytic reduction (SNCR) process at the BSF. Parameters to be evaluated for optimum performance are injection configuration, injection temperature, and stoichiometries.

In parallel to the BSF tests, the final step of the COMBINOX process-methanol injection to convert  $\text{NO}$  to  $\text{NO}_2$  and its subsequent removal in an  $\text{SO}_2$  scrubber - will be optimized. At EER's Whitehouse Facility, the following tasks will be performed:

- Bench-scale investigation of  $\text{SO}_2/\text{NO}_2$  removal using limestone.
- Define the kinetics of  $\text{NO}$  to  $\text{NO}_2$  conversion via  $\text{CH}_3\text{OH}$  oxidation.

- Measurement of possible  $N_2O$ ,  $CH_2O$ ,  $CH_3OH$  byproducts.
- Measurement of  $NO$  to  $NO_2$  conversion,  $NH_3$  removal and  $CO$  production.
- Measurements of  $N_2O$ ,  $CH_2O$  and  $CH_3OH$  byproducts in the presence of ammonia.

This step of the process will be studied at pilot scale at Research Cottrell's Facility.

Finally, in Task 3.2, all of the COMBINOX steps will be integrated, and fine tuning of the process will be done on the tower furnace. Since the tower furnace has historically been able to match full scale data, this task will provide scaleup information.

Task 4 will focus on the conceptual design for the application of COMBINOX to a 500 MWe boiler. The conceptual design and economic evaluation shall be based on a complete integrated plant.

The primary effort of Task 5 will be associated with removal of waste products accumulated during the program due to the dry scrubber residue and other aspects of the testing.

The program schedule is presented in Figure 2-2. It is based on initiation of the program on October 1, 1990. The final report will be submitted in October 1992.

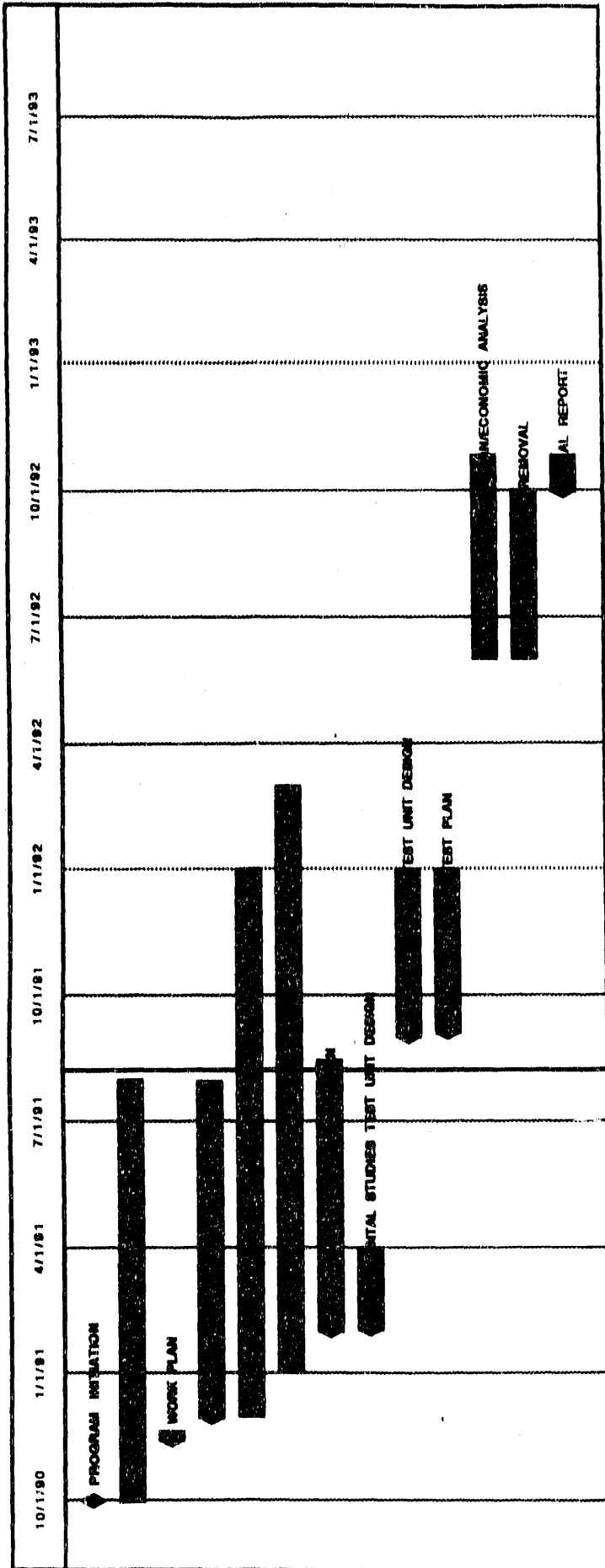


Figure 2-2. Program schedule and major milestones.

### 3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Figure 3-1 shows the organization for the program. The program will be managed by Dr. W. R. Seeker, the Senior Vice President of the Environmental Systems Division of EER. Dr. Seeker is internationally known for his work in a wide range of combustion studies focused on environmental issues. Dr. Seeker has successfully managed numerous large-scale programs, making him an ideal candidate to manage the proposed program effort. He has been with EER Corporation for over ten years and has managed and been directly involved with programs involving similar activities.

Mr. G. C. England, who is Vice President within the Environmental Systems Division, will act as Principal Investigator for the program. Mr. England has over thirteen years of experience at EER and is well known for his studies in  $\text{NO}_x$  formation and control.

Mr. S.L. Chen will direct the test planning and execution operations of this program. Mr. Chen will be aided in the evaluation and design of the COMBINOX process by Ms. J. Newhall.

The engineering design activities will be directed by Mr. T. M. Sommer, Vice President of the Engineering Services Division of EER.

Three senior scientist engineers at EER will serve as corporate consultants and directors on this program. These personnel include Dr. R. K. Lyon inventor of the Exxon Thermal De $\text{NO}_x$  process. Dr. Lyon has developed a number of  $\text{NO}_x$  reduction concepts while at EER, many of which have been evaluated and are an important aspect of the subject program activity. Dr. D. W. Pershing, who is a staff consultant at EER as well as being Dean of Engineering at University of Utah, has been involved with  $\text{NO}_x$  control strategies for over 20 years. Dr. Roy Payne will serve as the final program consultant. Dr. Payne is Senior Vice President of the Process Research Division of EER and has recently completed design studies of gas reburning/sorbent injection for the DOE/GRI Clean Coal



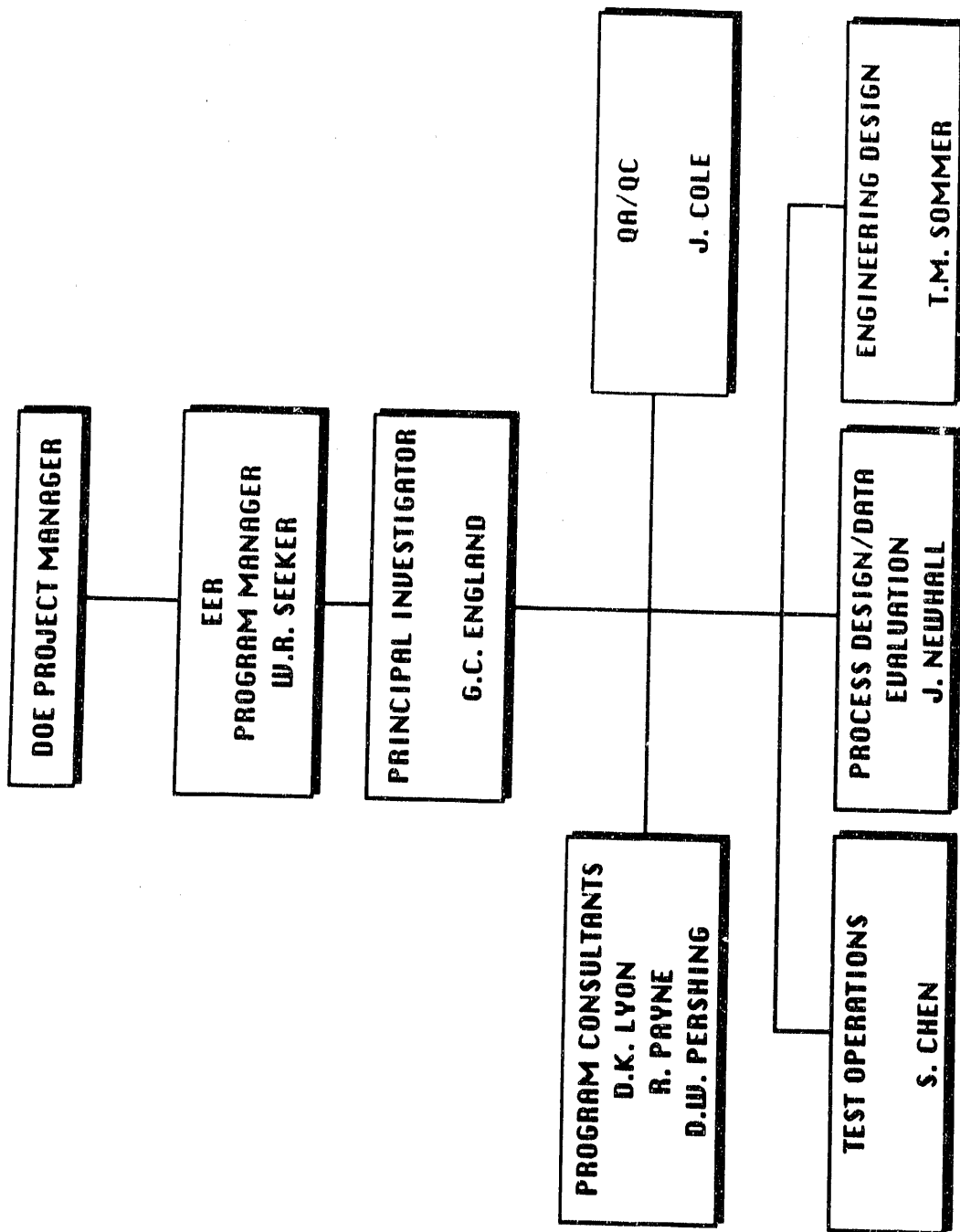


Figure 3-1. EER technical organization and project team organization.

Program. He is familiar with all aspects of scaling and retrofitting reburning technologies to existing coal fired units.

Finally, the team has an independent Quality Assurance/Quality Control Officer who is well experienced in the implementation of QA/QC protocol. Mr. J. A. Cole, who is in the Process Research Division, will serve as the Quality Assurance Officer and directly assist the Program Manager in quality assurance areas. His sole responsibility on this program is to ensure that the program is being conducted and documented at the highest level of quality, consistent with protocol developed over a number of years of similar studies.

#### 4.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY.

The program QA objectives for precision, accuracy, and completeness are listed in Table 4-1 for each major measurement. The QA objectives are based on the program requirements and the precision and accuracy levels achievable by the selected measurement methods. The results of previous methods validation studies and EER's experience were used to determine the anticipated precision and accuracy limits for each method.

The values for precision shown in Table 4-1 are defined as the relative standard deviation (ratio of the standard deviation to the mean of replicate measurements expressed as percentage). Accuracy is the percent difference between the measured value and a known or standard value. Completeness is the percentage of valid data obtained compared to the total amount of data planned to be obtained.

Table 4-1 also shows references to standard measurement procedures or measurement validation studies, and the experimental conditions under which each measurement will be performed. EER will present results in a format and in consistent units to allow direct comparability to the referenced and other studies. EER will ensure that data are representative of the experimental conditions being measured.

TABLE 4-1. PROGRAM OBJECTIVES FOR MEASUREMENT PRECISION, ACCURACY AND COMPLETENESS.

MEASUREMENT PARAMETER (Method)	REFERENCE	EXPERIMENTAL CONDITIONS	PRECISION RELATIVE STANDARD DEVIATION	ACCURACY	COMPLETENESS
Fuel Flowrate	Brooks Catalog	Natural Gas	2%	2%	100%
Combustion Air Flowrate (Laminar Flow Elements)	Meriam Handbook	Ambient Air	2%	2%	100%
Combustion Air Temperature	Omega Handbook	Ambient Air	2%	2%	100%
Exhaust Gas Composition: NO, NO <sub>2</sub> (Chemiluminescent)	EPA Method 7E	Exhaust	+/-3%	+/-5%	100%
O <sub>2</sub> (Paramagnetic)	EPA Method 3A	Exhaust	+/-3%	+/-5%	100%
CO (Infrared)	EPA Method 10	Exhaust	+/-2%	+/-5%	100%
CO <sub>2</sub> (Infrared)	EPA Method 3A	Exhaust	+/-2%	+/-5%	100%
SO <sub>2</sub> (Ultraviolet)	EPA Method 6C	Exhaust	+/-3%	+/-5%	100%
SO <sub>3</sub> (Controlled Condensation)	EPA Method 8 40CFR60 APPA	Exhaust	+/-10%	+/-10%	100%
N <sub>2</sub> O GC/ECD	Geo. Res. Ltrs Vol 15, No. 12, 1988	Exhaust	+/-5%	+/-5%	100%
NDIR	Montgomery, Muzio Samuelson: JAPCA, 39, 721(1989)	Exhaust	+/-5%	+/-5%	100%
Formaldehyde	CARB Method 430	Exhaust	+/-10%	+/-10%	100%
NH <sub>3</sub> , (Water-Quenched probe specific ion electrode)	EER HCN/NH <sub>3</sub> Procedure 8/83 Rev 2	Exhaust	+/-10%	+/-10%	100%
Furnace Gas Temperature (suction pyrometer)	Industrial Flames Vol 1, "Measurements in Flames" International Flame Research Foundation, 1972	Furnace Gas	5%	5%	100%

## 5.0 SAMPLING PROCEDURES

Sampling procedures for each measurement are summarized in Table 5-1. This Table includes sampling location selection criteria, sampling procedures, and sampling frequency. Standard EPA procedures are used where appropriate. Procedures not following standard procedures are described below.

Reagents to be used in the measurement conform to the specifications of the reference methods. Reagent grade chemicals are used exclusively. Clean sample containers are used to collect samples, with each container prepared by rinsing in appropriate solutions. Samples are analyzed as rapidly as possible.

Sampling procedures for the continuous monitoring instrumentation,  $N_2O$ ,  $NH_3$  and in-furnace gas measurements are described in the following sub-sections.

### 5.1 Continuous Monitoring Instrumentation

Figure 5-1 shows a schematic diagram of EER's continuous monitoring system for  $NO$ ,  $CO$ ,  $CO_2$  and  $O_2$ . This system is specifically designed to monitor emissions from sources such as combustion exhaust and has been used in previous test programs. All components in contact with the sample are stainless steel or teflon to insure sample integrity and corrosion resistance. The gas sample is provided to the instruments by a sample conditioning system consisting of a pump, moisture condenser and particulate filters. Figure 5-2 shows a diagram of the continuous monitoring system for  $SO_2$ . A phase discrimination probe is used to separate the majority of the particulate from the sample gas stream. This design is used due to the high reactivity of the particulate with  $SO_2$  during sorbent injection tests. The gas sample then passes through a heated sample line to a heated filter, Perma Pure drier, sample pump, and final filter before entering the analyzer. Figure 5-3 shows the continuous monitoring system for  $NO_2$ . A heated stainless steel glass lined probe is used to draw emission gas from the exhaust. To avoid  $NO_2$  condensation in a chiller, the sample is passed through a Perma Pure drier. Next, since  $NH_3$  can be oxidized inside the converter, the sample passes through an ammonia scrubber. Finally, the sample passes through

TABLE 5-1. SAMPLING PROCEDURES

MEASUREMENT PARAMETER	SAMPLING LOCATION SELECTING CRITERIA	SAMPLING PROCEDURE	SAMPLING FREQUENCY	REFERENCE
Fuel Flowrate/Distribution	Based on Burner Design	Volume flow measurement	Continuous	Brooks Catalog
Combustion Air Flow	Based on Burner Design	Laminar flow meter	Continuous	Meriam Flow Meters
Combustion Air Temperature	Based on Burner Design	In-Line Thermocouple	Continuous	Omega Handbook
Exhaust Gas Composition:	Downstream of burnout	EPA Method 7E	Continuous	40CFR60 APP A
NO, NO <sub>2</sub>	air injection,	EPA Method 3A	"	"
O <sub>2</sub>	upstream of	EPA Method 10	"	"
CO	convective banks to	EPA Method 3A	"	"
CO <sub>2</sub>	avoid leakage	EPA Method 6C	"	"
SO <sub>2</sub>	"	EPA Method 8	At Selected Conditions	"
SO <sub>3</sub>	"	GC/ECD and	Selected Conditions	Geo. Res. Ltrs. Vol 15, No. 12, 1988
N <sub>2</sub> O	"	continuous NDIR	Continuous	Montgomery et al., JAPCA 39, 721 (1989)
Formaldehyde	Downstream of methanol injection point	CARB Method 430	At Selected Conditions	CARB Method 430
NH <sub>3</sub>	With continuous emissions measurements	Water-Cooled Probe Impinger Collection (see text)	At Selected Conditions	EER HCN/NH <sub>3</sub> Procedure 8/83, Rev. 2
Furnace Gas Temperature	Selected Locations throughout Furnace	Suction Pyrometer (see text)	At Selected Conditions	"Industrial Flames Vol. I, Measurements in Flames" International Flame Research Foundation, 1972

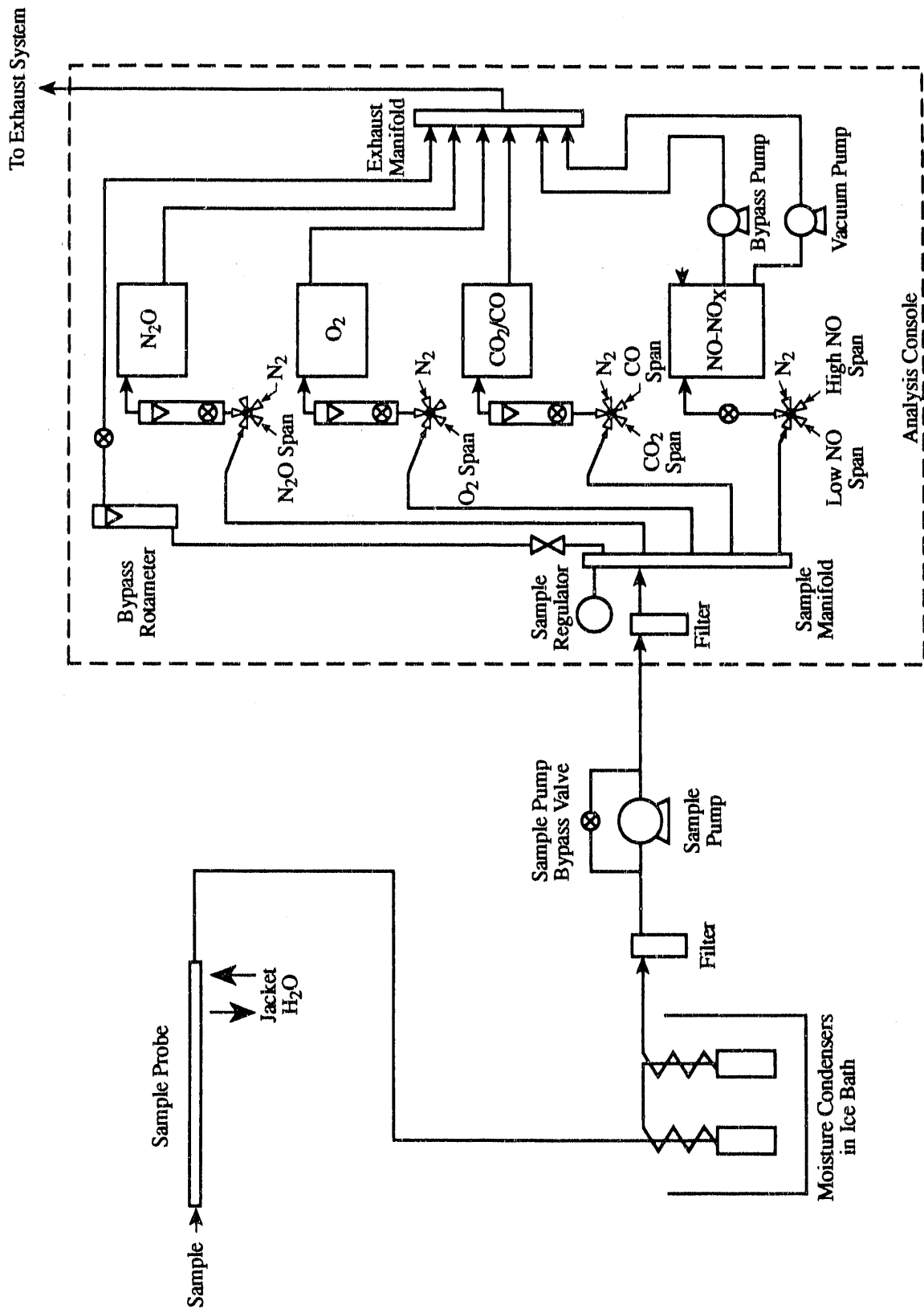


Figure 5-1. Continuous Monitoring Sampling System.

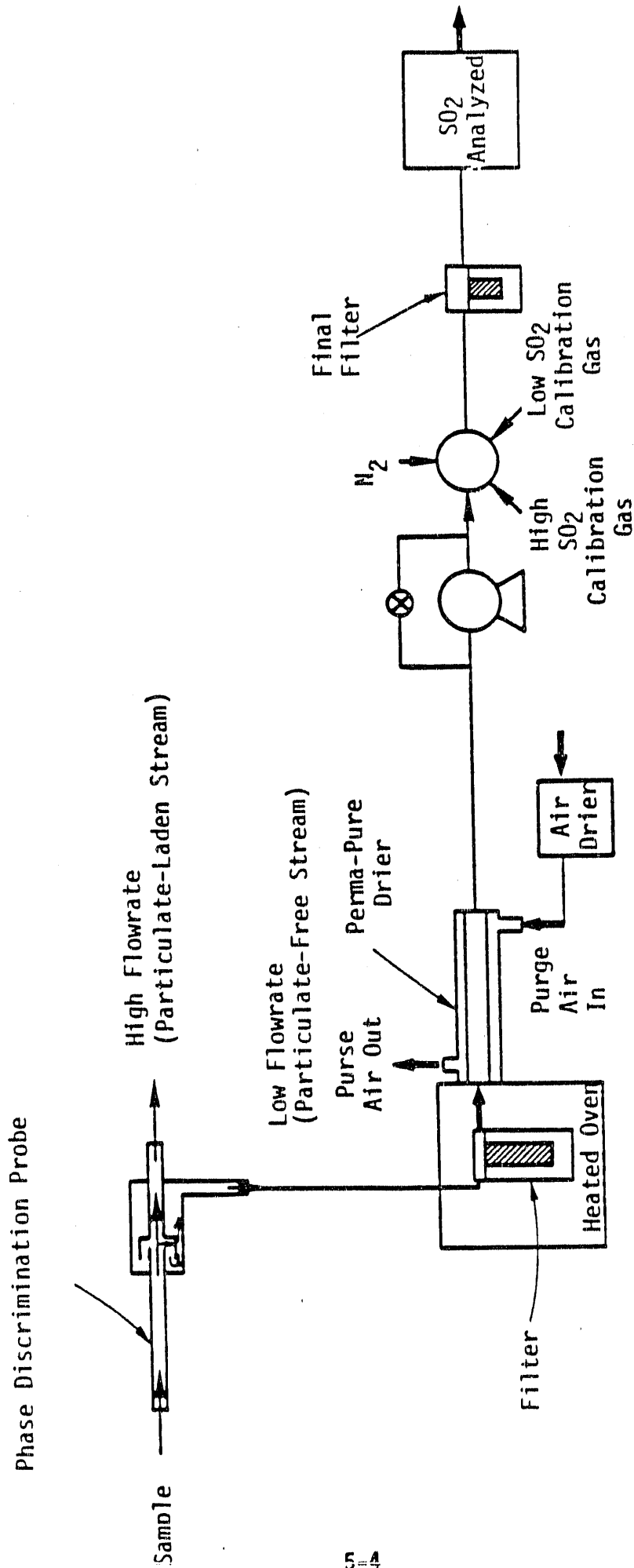


Figure 5-2. SO<sub>2</sub> Continuous Monitoring System.



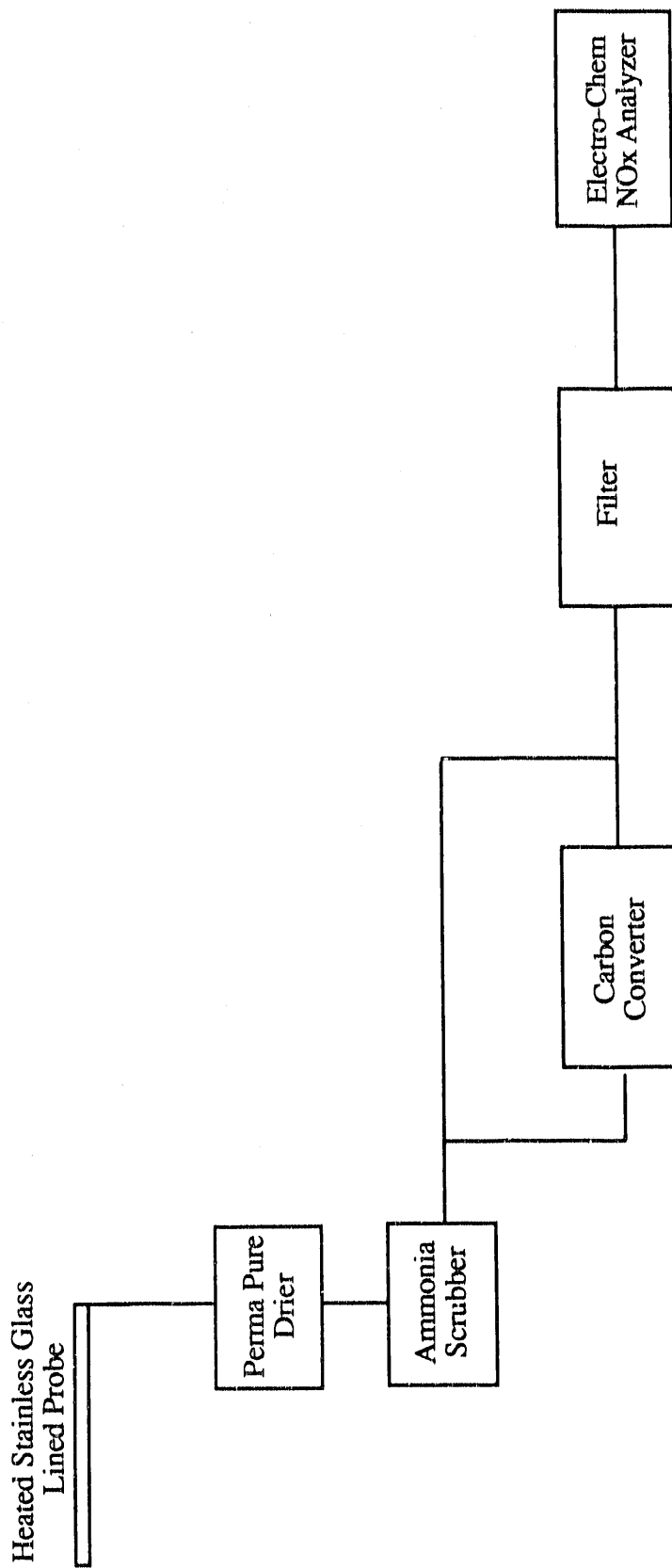


Figure 5-3. NO and NO2 continuous monitoring system.

a carbon converter (converting  $\text{NO}_2$  to  $\text{NO}$ ), the sample pump and filter before reaching the analyzer.

## 5.2 $\text{N}_2\text{O}$

$\text{N}_2\text{O}$  will initially be measured by two different methods: a manual method, and a continuous method. The manual method will be used to check the continuous method. If the results from the continuous system are valid, the manual method as described by Kramlich, Muzio et al.<sup>1</sup> will be discontinued. In the manual method, the  $\text{N}_2\text{O}$  sample is collected using a water-cooled probe for sample gas temperatures higher than 400°F. The sample is collected in a glass sampling vial. The vial is filled with 25 cc of 1N sodium hydroxide to avoid the sampling artifact (reference). A gas-tight syringe is then used to withdraw a gas sample for direct injection into the gas chromatograph. The actual  $\text{N}_2\text{O}$  analysis is described in Section 8.0, Analytical Procedures. The continuous  $\text{N}_2\text{O}$  analyzer uses the same dry flue gas sample that is extracted for the  $\text{O}_2$ ,  $\text{CO}/\text{CO}_2$  and  $\text{NO}/\text{NO}_2$ . The Siemens continuous analyzer employs the non dispersive infrared absorption technique to quantify  $\text{NO}/\text{NO}_x$  levels.

## 5.3 $\text{NH}_3$

To measure  $\text{NH}_3$ , flue gas is collected in a gas washing unit which consists of impingers in series with a fritted gas bubbler. The presence of sulfide ions can interfere with the specific ion electrode detection of  $\text{NH}_3$  by forming an insoluble layer of silver sulfide on the electrode membrane surface. Therefore the impingers and bubblers contain an absorbing solution of lead carbonate and sodium carbonate to precipitate sulfide ions as lead sulfide.

## 5.4 In-Furnace Gas Temperature

High temperature gas measurements within furnaces are subject to large inaccuracies due to the effects of thermocouple radiation loss. Therefore in-

---

<sup>1</sup>Geo. Res. Ltrs. Vol. 15, No. 12, 1988

furnace gas temperatures will be measured using a suction pyrometer. The suction pyrometer consists of a high temperature thermocouple in a porous ceramic radiation shield. A high flow rate of furnace gas is drawn through the shield and over the thermocouple to increase conductive heat transfer to the thermocouple and reduce radiation loss. As the gas flow rate is increased, the temperature increases to a constant value, indicating no additional reductions in radiations loss. Therefore during the measurements, sufficient gas flow rate will be verified by increasing the flow rate until a constant temperature is obtained.

### 5.5 Formaldehyde

Gaseous emissions containing formaldehyde are drawn through two midget impingers containing an aqueous acidic solution of 2,4-dinitrophenyl hydrazine (DNPH). Formaldehyde reacts with DNPH by nucleophilic addition on the carbonyl followed by 1,2-elimination of water and the formation of 2,4-dinitrophenyl hydrazone.

## 6.0 SAMPLE CUSTODY

Most of the Measurements in this program involve the use of continuous instruments or other measurement methods which do not require custody procedures. Those measurements requiring sample custody procedures include the following:

MEASUREMENT	SAMPLE
SO <sub>3</sub>	Liquid
N <sub>2</sub> O	Gas
Formaldehyde	Impinger Liquid
NH <sub>3</sub>	Impinger Liquid

This program involves measuring process performance in laboratory research furnaces. Thus it is not expected that any samples will be needed for legal purposes. If such samples are required, EER will utilize the "Chain of Custody" procedures as defined by EPA Office of Enforcement. Otherwise, EER will utilize the procedures in Section 3.3 of Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III - Stationary Source Specific Methods. EPA-600/4-77-027b, August 1979.

### 6.1 Sample Acquisition and Sample Tracking

The test engineer/technician responsible for sample acquisition will maintain a detailed log of testing activities including the details of sample acquisition. As a minimum, the log will itemize the following for each sample:

1. Sample identification number;
2. Location and time of sample extraction;
3. Test conditions and all other factors defining the test conditions;
4. Sampling method and procedures reference;
5. Processing or preserving of sample conducted in the field.

The test log will be used by the project engineer to evaluate test results.

The test engineer/technician will also prepare the following two documents:

- Sample Label - The sample label shown in Figure 6-1 will be completed filled-out and attached to each sample by the test engineer/technician prior to transfer of custody.
- Lab Sample Tracking Report - The test engineer will prepare a Lab Sample Tracking Report for each batch of samples delivered to the laboratory. The format for this document is shown in Figure 6-2. It specifies the analytical procedures to be conducted by the laboratory. The Lab Sample Tracking Report will be returned to the responsible person (listed on the form) along with the test results.

The test engineer/technician will ensure that all information on these forms and the test log is accurate and consistent.

## 6.2 Laboratory Custody Procedures

The procedures to be followed for handling, storage and shipping samples are listed below. EER's chemist will be responsible for carrying out these procedures.

1. When samples are received in the laboratory, they are identified by a unique numbering code.
2. This unique number is recorded in a sample log along with date, location of sample, and other related information. Samples are preserved as required by procedure.
3. Samples are segregated into those to be analyzed at the test site laboratory and those to be sent to outside laboratories.
4. Those analyses which require immediate attention are started at this point.

**E  
E  
R**

No 145033

Date \_\_\_\_\_  
Time \_\_\_\_\_  
Test No. \_\_\_\_\_

Site \_\_\_\_\_  
Location \_\_\_\_\_  
Sample Description \_\_\_\_\_  
\_\_\_\_\_

18 Mason      Irvine, CA 92714      (714) 859-8851

Figure 6-1. EER sample label.



5. All samples are packaged consistent with the physical abuse they may receive during shipment. Samples are shipped and packed in a manner which insures that the handling requirements are met and maintained throughout the entire time of shipment.
6. An inventory of samples by ID number and analysis is recorded in the Sample Shipment Letter. A separate form is prepared for each shipment container. One copy of the Sample Shipment Letter is included in the shipping box, one copy is sent to the project manager, and one to the shipping designation. The original is maintained at the field facility.
7. Upon delivery for shipment, the test engineer telephones the outside laboratory and informs them of the estimated time of arrival of the samples, the carrier, the number of shipping containers, and whether the samples will be held for pickup or will be delivered.
8. When the outside laboratory receives the shipment, they sign and date the letter, note any discrepancies on it and forward a copy of the letter to the project manager.

### 6.3 Reagents, Filters and Materials

All reagent chemicals, filters and materials which will become parts of a sample will be dated upon receipt and properly stored in compliance with safety regulations. A material log-book will be maintained in the laboratory. Entries will document the log number of the reagent, stock solution or filter, the concentration of the solution, date of preparation (and the expiration date if appropriate, etc) and name of technician who prepared the stock solution. A label inscribed with the above information will also be affixed to the material.



## 7.0 CALIBRATION PROCEDURES AND FREQUENCY

Calibration procedures and frequency for each measurement system are listed in Table 7-1. As shown in the table, standard calibration procedures will be used for each system. Each system will be calibrated at the frequency shown in the table to insure the accuracy of the measurements are traceable to the calibration standards.

TABLE 7-1. CALIBRATION PROCEDURES.

MEASUREMENT PARAMETER	CALIBRATION PROCEDURE	CALIBRATION FREQUENCY	CALIBRATION STANDARD	REFERENCE
Fuel Flowrate/Distribution	Compare with EPA Method 2 or dry gas meter	Bi-annually	Calibrated dry gas meter	Meriam Catalog
Combustion Air Flowrate/Distribution	Laminar flowmeter sent back to Meriam for calibration	Annually		
Combustion Air Temperature	Compare to standard thermometer	Monthly	ASTM Thermometer	Omega Handbook
Exhaust Gas Composition				
NO, NO <sub>2</sub>			Span Gases	EPA Method 7E
O <sub>2</sub>			"	EPA Method 3A
CO			"	EPA Method 10
CO <sub>2</sub>	Compare to Standard Compressed Gas	Daily	"	EPA Method 3A
SO <sub>2</sub>			"	EPA Method 6C
SO <sub>3</sub>	Compare to standard Acid	As Required	"	EPA Method 8 40CFR60 App A
Formaldehyde	Compare to Standard	As Required	"	CARB Method 430
N <sub>2</sub> O (manual)	Lab prepared sample	As Required	"	Geophysical Research Letters, Vol. 15, No. 12, 1988
(continuous)	Compare to span gas	As Required	"	Montgomery et al., JAPCA 39, 721 (1989)
Gas Meter	Compare to wet test meter	Before and after each test series	Wet Test Meter ASTM Thermometer	Federal Register, Vol. 42, No. 197, October 10, 1979 pp. 58602-58663
Balance	Compare to standard weights	Daily	Class 5 weights	
NH <sub>3</sub>	Standard Solution	As Required	Gravimetrically prepare standard solutions	EER HCN/NH <sub>3</sub> Procedure 8/83, Rev. 2
Furnace Gas Temperature	Compare to Standard Thermocouple	Monthly	Nbs Standard Thermocouple	"Industrial Flames, Vol I, Measurements in Flames" International Flame Research Foundation

## 8.0 ANALYTICAL PROCEDURES

Analytical procedures for each measurement are listed in Table 8-1. EPA standard procedures are used, where appropriate. Where possible, the remaining measurements use other standard procedures, as shown in the table. Non-standard procedures are described in the following sections.

### 8.1 Continuous Monitoring Instrumentation

Continuous monitoring instrumentation to be used to analyze NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>, SO<sub>2</sub> and N<sub>2</sub>O, is described in Table 8-2. These instruments were specially selected to provide the highest sensitivity and minimum interferences possible. Test data from the instrument will be continuously recorded with a strip chart recorder to provide permanent documentation of test results. As previously mentioned, the continuous N<sub>2</sub>O data will initially be validated by manual testing before it is used exclusively.

The principal instrument employed to measure oxides of nitrogen is the chemiluminescent analyzer. The chemiluminescent analyzer measures nitric oxide (NO). To measure the NO<sub>2</sub> in the gaseous sample, a convertor must be employed to reduce the NO<sub>2</sub> to NO. The sample exiting the convertor consists of NO from two sources: (1) the NO entering the convertor (2) the NO<sub>2</sub> converted in the convertor. Hence, in this mode the instruments measures the total oxides of nitrogen (NO<sub>x</sub>). By routing the gaseous sample around the convertor the NO<sub>2</sub> is not converted and the instruments measures only NO in the unconverted sample. By taking the difference between the concentrations of NO measured in both modes ( $[NO_x] - [NO]$ ), the concentration of NO<sub>2</sub> is established.

The convertor must be located prior to the water trap (which is employed in the CMS system to remove water, since the analyzer requires dry clean sample gas). In this manner water soluble NO<sub>2</sub> is reduced to NO before the extraction of water. A carbon converter is the most reliable and rugged of those available. Also, since the operating temperature of carbon converter is low (180°F), no

TABLE 8-1. ANALYTICAL PROCEDURES.

MEASURED PARAMETER	ANALYTICAL PROCEDURE	REFERENCE
Combustion Air Flowrate/Distribution	Pressure differential across laminar flow elements	Meriam Catalog
Combustion Air Temperature	Thermocouple	Omega Handbook
Exhaust Gas Composition:		
NO, NO <sub>2</sub>	Gas Phase Chemiluminescent Analyzer	Teco Model 10 Operating Manual
O <sub>2</sub>	Paramagnetic Analysis	Taylor OA 570 Operating Manual
CO, CO <sub>2</sub>	Infrared Analysis	Anarad AR 500 Operating Manual
SO <sub>2</sub>	Ultraviolet Analysis	DuPont 400 Operating Manual
Exhaust Gas Composition (Continued)		
SO <sub>3</sub>	Barium Perchlorate Titration using a thorim indicator	EPA Method 8
N <sub>2</sub> O	Gas Chromatography/ECD (manual method) Nondispersive Infrared absorption (continuous method)	Geophys. Res. Ltrs. Vol 15, #12, May 1988 Siemens 5E Operating Manual
Formaldehyde	HPLC check-analyze deriv.	CARB Method 430
NH <sub>3</sub>	Specific Ion Electrode	EER HCN/NH <sub>3</sub> Procedure 8/83 Rev. 2
Furnace Gas Temperature	Suction Pyrometer	Industrial Flames, Vol I, "Measurements in Flames" International Flame Research Foundation

TABLE 8-2. CONTINUOUS GAS ANALYSIS INSTRUMENTS

GAS MEASURED	DETECTION PRINCIPLE	MANUFACTURER	MODEL No.	RANGE
NO, NO <sub>2</sub>	Chemiluminescent	Thermo Electron Corp. (TECO)	10 AR	0-1000 ppm
CO	Nondispersive Infrared (NDIR)	Anarad, Inc.	AR500R	0-500 ppm
CO <sub>2</sub>	Nondispersive Infrared (NDIR)	Anarad, Inc.	AR500R	0-25%
O <sub>2</sub>	Paramagnetic	Taylor Servomex	OA-272	0-10%
SO <sub>2</sub>	Nondispersive Ultraviolet (NDUV)	DuPont	400	0-5000 ppm
N <sub>2</sub> O	Nondispersive Infrared (NDIR)	Siemens	7MB1120-1RD20-0BA0	0-100

oxidation of HCN and  $\text{NH}_3$  and reduction of  $\text{N}_2\text{O}$  to NO will occur inside the convertor, i.e, the convertor is selective only toward  $\text{NO}_2$ .

## 8.2 $\text{N}_2\text{O}$

The manual  $\text{N}_2\text{O}$  samples are analyzed by gas chromatography using an electron capture detector. The gas chromatograph is operated with an argon/5 percent methane carrier gas and separation is achieved using a 2 m x 3 mm (o.d.) Porasil B column. Results are presented as  $\text{N}_2\text{O}$  concentrations in ppm by volume. The method is calibrated by analyzing standard mixtures of  $\text{N}_2\text{O}$  in  $\text{N}_2$ . The continuous  $\text{N}_2\text{O}$  analysis method is nondispersive infrared absorption.

## 8.3 $\text{NH}_3$

The  $\text{NH}_3$  sample is analyzed by specific ion electrodes immediately after sampling to avoid complexation of cyanide ions with lead ions in the sample solutions. An Orion Model 95-10 ammonia electrode is first used to detect  $\text{NH}_3$  after the PH of the solution has been adjusted to 13 to convert the ammonium ions to  $\text{NH}_3$  gas. Electrical potentials generated within the electrodes are proportional to the  $\text{NH}_3$  concentrations and are measured with an Orion Model 901 Digital Analyzer. Calibration curves are developed using standard solutions to relate electrical potential to species concentrations.

## 8.4 Formaldehyde

Formaldehyde measurement is based on high performance liquid chromatography (HPLC), with on ultraviolet (UV) absorption detector operated at 360 nm. Separation is achieved by using a C-18 reverse phase (RP) column (30 in x 3.9 mm ID). Analysis will be performed by an outside laboratory.

## 9.0 DATA REDUCTION, VALIDATION AND REPORTING

### 9.1 Data Reduction, Validation and Reporting Procedures

Results of the measurements in this program will be obtained from manual calculations using the measurement data. Figure 9-1 shows the general reporting scheme for each measurement from collection of raw data to validation and reporting of results. Following the sampling and analysis portion of each measurement, results are calculated manually for each measurement using equations described below. The preliminary results are then subjected to an independent check to verify the following:

- Accuracy
- Proper sampling and analytical procedures
- Representative experimental condition

Data obtained with improper sampling or analytical procedures, or under non-representative conditions are then invalidated if the results cannot be corrected. Results passing the checks are correlated with other results to identify potential outliers. Results not correlating with existing data are subjected to a double check of calculation and measurement procedures. The results are then subjected to an outlier test using the Dixon criteria at the 5 percent significance level as described in EPA-600/9-76-005, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1, Principles", EPA, EMSC, March 1976.

Measurements passing the above checks are validated and added to the data base. Specific criteria used to validate data are the following:

1. Measurement performed under representative experimental conditions.
2. Proper sampling and analytical procedures utilized.
3. All calculations independently checked.

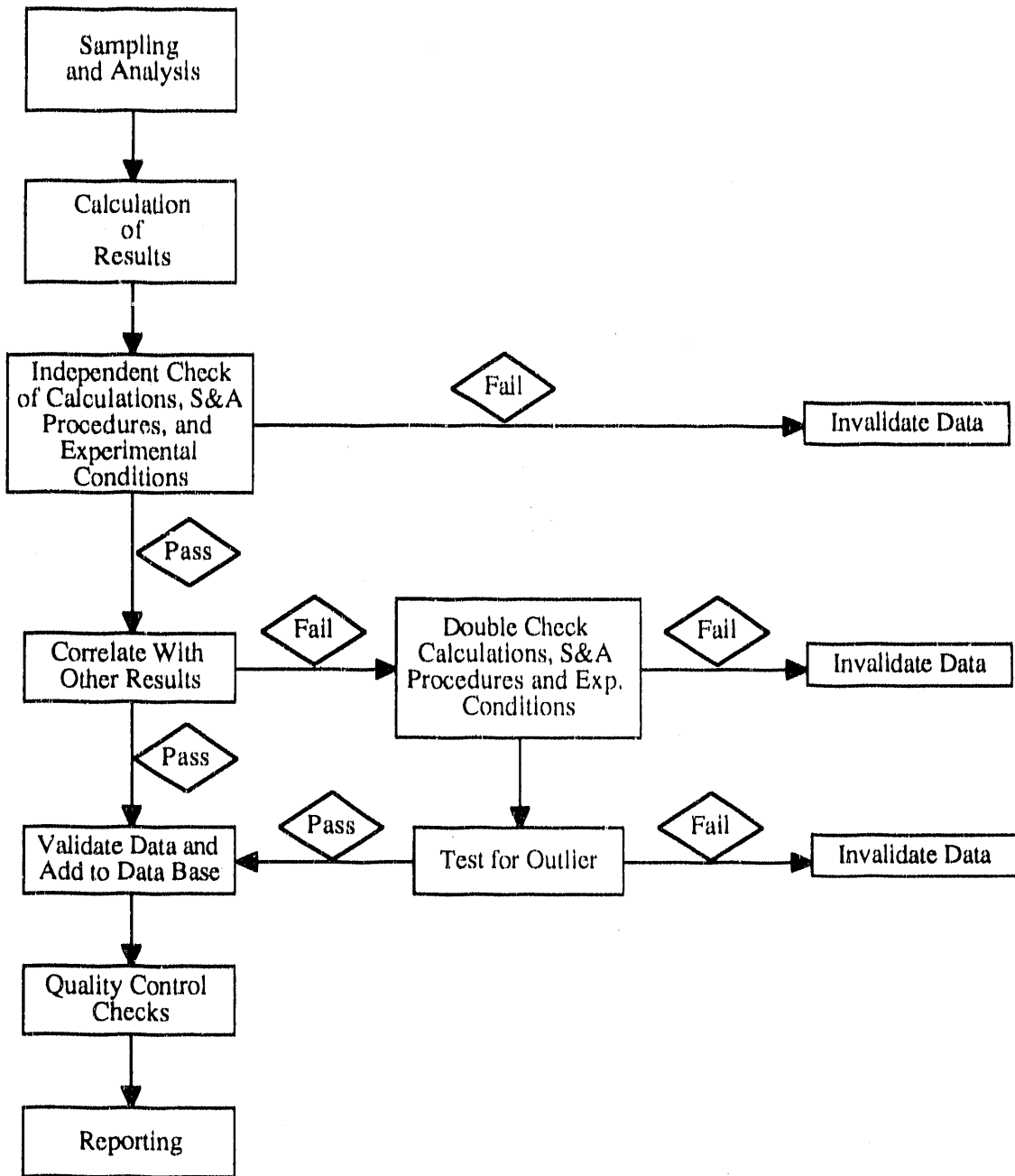


Figure 9-1. Data reduction, validation, and reporting scheme.



4. Data correlate within  $\pm 2$  standard deviation with existing data.
5. Data not correlating with existing data don't pass outlier test.

Key individuals responsible for data handling are the same individuals discussed in Section 3.0, Project Organization and Responsibility. The Task Managers will be responsible for the collection, reduction, and validation of data. The Program Manager will be responsible for insuring that the measurements fulfill the program objectives. The Quality Assurance Officer will be responsible for verifying that the specific data handling procedures are followed and that the results meet the validation criteria.

## 9.2 Equations Used to Calculate Results

Equations used to calculate results for each of the measurements are discussed below. Many of the results are obtained directly from the measurements and thus will not require calculations.

1. Fuel Flowrate/Distribution

Flue flowrate is obtained directly from the rotameter

2. Combustion Air Flowrate/Distribution

Combustion air flowrate is read directly from rotameters or is calculated from pressure drop measured across laminar flow elements based on equations:

$$Q = K \left( \frac{P}{T} \right)^{1/2}$$

3. Combustion Air, Furnace Gas, and Exhaust Gas Temperatures

Temperatures are measured by thermocouples and provide results in units of degrees centigrade which can then be converted to other temperature scales, as required.

4. Exhaust Gas Composition - NO, NO<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>  
The above gas compositions are measured as chart divisions on a strip chart recorder. The measured divisions are converted to concentration (ppm or %) based on calibrations with concentration based on the measured oxygen concentration. Figure 9-2 shows an example of the form and equations used to perform these calculation.
  
5. Exhaust Gas Composition: SO<sub>3</sub>  
SO<sub>3</sub> results are determined from the titration of the collected SO<sub>3</sub> and the measured gas volume. Figure 9-3 shows the form and equations used to calculate SO<sub>3</sub> results.
  
6. Exhaust Gas Composition: N<sub>2</sub>O  
N<sub>2</sub>O is measured by electron capture detector, with data obtained as peak areas from an automatic integrator. Results are converted to concentration (ppm) based on a ratio of peak areas of the sample to a calibration standard.
  
7. In Furnace NH<sub>3</sub>  
NH<sub>3</sub> is measured by specific ion electrodes with results as ppm, liquid based on calibration standards. Results are converted to gas concentrations using the form and equations shown in Figure 9-4.
  
8. Formaldehyde  
Formaldehyde is measured by high performance liquid Chromatograph. Results are converted to gas concentration using the form and equations shown in Figure 9-5.

### 9.3 Daily Table of Data and Results

Figure 9-6 shows the daily data sheet. At the end of each daily test all the raw data such as natural gas, air, sorbent, methanol flowrates, injection temperatures, flue gas composition and pollutant concentrations etc. will be

GAS CONCENTRATION CALCULATION

DATE: \_\_\_\_\_ PLANT: \_\_\_\_\_  
 TEST NO. \_\_\_\_\_ SAMPLING LOCATION: \_\_\_\_\_  
 TIME STARTED: \_\_\_\_\_ DATA COLLECTED BY: \_\_\_\_\_  
 TIME ENDED: \_\_\_\_\_

	NO <sub>x</sub>	CO	CO <sub>2</sub>	O <sub>2</sub>
SPAN GAS CONCENTRATION, G <sub>s</sub> (ppm or %)	ppm	ppm	%	%
INITIAL ZERO RESPONSE, Z <sub>i</sub> (Div.)				
INITIAL SPAN RESPONSE, S <sub>i</sub> (Div.)				
FINAL ZERO RESPONSE, Z <sub>f</sub> (Div.)				
FINAL SPAN RESPONSE, S <sub>f</sub> (Div.)				
AVG. ZERO RESPONSE, Z <sub>avg</sub> . (Div.) = (Z <sub>i</sub> + Z <sub>f</sub> ) / 2				
AVG. SPAN RESPONSE, S <sub>avg</sub> . (Div.) = (S <sub>i</sub> + S <sub>f</sub> ) / 2				
AVG. GAS RESPONSE, D <sub>avg</sub> . (Div.)				
ACTUAL GAS CONCENTRATION, G <sub>a</sub> (ppm or %) = (D <sub>avg</sub> - Z <sub>avg</sub> ) * G <sub>s</sub> / (S <sub>avg</sub> - Z <sub>avg</sub> )	ppm	ppm	%	%
GAS CONCENTRATION CORRECTED TO 3% O <sub>2</sub> , G <sub>c</sub> (ppm or %) = G <sub>a</sub> *18/(21-%O <sub>2</sub> )	ppm	ppm	%	%

Figure 9-2. Gas concentration calculation.

SUMMARY OF RESULTS: SO3 AS H2SO4

Date	Sampling Location	Run No.	Corrected Sample Volume Vmstd (ft <sup>3</sup> )	Titrant Volume Vt (ml)	Total Solution Volume Vsoln (ml)	Aliquot Volume Va (ml)	Titrant Normality N	H2SO4 Concentration (lb/ft <sup>3</sup> )	H2SO4 Concentration (ppm)

$$\text{H2SO4 (lb/ft}^3\text{)} = (1.081\text{E-4}) * \text{N} * (\text{Vt} - \text{Vtb}) * (\text{Vsoln}/\text{Va}) / \text{Vmstd}$$

$$\text{H2SO4 (ppm)} = \text{H2SO4 (lb/ft}^3\text{)} * (384.8 \text{ ft}^3/\text{mole}) * (\text{mole}/98\text{lb}) * 10,000$$

Figure 9-3. Summary of results SO<sub>3</sub> as H<sub>2</sub>SO<sub>4</sub>.

Date			
Sample Number			
Sample Volume (ft <sup>3</sup> )			
Average Meter Temperature, Tm (°R)			
Barometric Pressure, Pbar ("Hg)			
Average Orifice Pressure, ΔH ("H2O)			
Standard Gas Sample Volume:			
$V_{mstdl} = (17.64)(28.32) * V_m / T_m * (P_{bar} + \Delta H / 13.6)$			
NH4+ (ppm, liquid)			
$NH4+ \text{ (ul gas)} = mgNH4+ * 24.04 / 18 * 1000$			
$NH3 \text{ (ppm gas)} = ulNH4+ / V_{mstdl}$			

Figure 9-4. Calculation of NH3 results.

CARB METHOD 0.430 FORMALDEHYDE EMISSIONS

DATA ENTER	SYMBOL	UNITS	DATA #1	DATA #2	DATA #3
RUN NUMBER			#1	#2	#3
AVERAGE STACK TEMPERATURE	F <sub>s</sub>	deg. F			
AVERAGE PROBE TEMPERATURE	F <sub>m</sub>	deg. F			
BAROMETRIC PRESSURE	P <sub>bar</sub>	in. HG			
METER CALIBRATION FACTOR	Y				
GAS SAMPLE VOLUME	V <sub>m</sub>	Litres			
MASS OF FORMALDEHYDE IN SAMPLE	W <sub>f</sub>	ug			
DRY GAS FLOW RATE	Q <sub>dg</sub>	cubft/min			
CALCULATED DATA					
RUN NUMBER					
AV. STACK. TEMP	T <sub>s</sub>	deg. R			
AV. PROBE. TEMP	T <sub>m</sub>	deg. R			
GAS SAMPLE VOLUME AT STANDARD CONDITIONS					
	V <sub>mstd</sub>	cub. ft			
FORMALDEHYDE CONCENTRATION					
	C <sub>e</sub>	gr/dscf			
	C <sub>m</sub>	mg/dscm			
	F <sub>ppm</sub>	ppm			
FORMALDEHYDE MASS FLOWRATE					
	M <sub>ff</sub>	lb/hr			

Figure 9-5. Calculation of formaldehyde concentration.

Input	units	Data	Data	Data	Data
Date					
Test Number					
Sorbent					
Sorbent inject temp	deg F				
Solution flow rate	grams/min				
% Sorbent in soln	%w/w				
M.wt of sorbent	gm/gmol				
Methanol inject temp	deg F				
MeOH Soln flow rate	grams/min				
% MeOH in soln	%w/w				
Natural gas flowrate	%				
Burnout.air inj.temp	deg F				
Burnout.air flow	cfh psig				
Atomization N2 flow	cfh psig				
Reb.gas inj.temp	deg F				
Reburnig gas flow	cfh psig				
Combustion air flow	scfm				
O2 baseline	%v/v				
NO baseline (NO1)	ppm				
NO2 baseline	ppm				
CO baseline	ppm				
O2 sorbent	%v/v				
NO sorbent (NOf)	ppm				
NO2 sorbent	ppm				
CO sorbent	ppm				
NH3	ppm				
N2O	ppm				
SO3	ppm				
Formaldehyde	ppm				

Figure 9-6. Daily table of data and results.

Facility:BSF  
 Project:CombiNOx  
 Page 2 of 3

Calculated	Units	Data	Data	Data	Data
Date					
Test Number					
Sorbent flow rate	grams/min	0	0	0	0
Sorbent flow rate	gmole/min	ERR	ERR	ERR	ERR
MeOH flow rate	gmole/min	0	0	0	0
MeOH flow rate	grams/min	0	0	0	0
Burnout air flow	scfm	0	0	0	0
Total input air	scfm	0	0	0	0
Atomization N2 flow	scfm	0	0	0	0
Reburnig gas flow	scfm	0	0	0	0
Combustion gas flow	scfm	0	0	0	0
Total gas flow	scfm	0	0	0	0
Total gas flow	lbmol/min	0	ERR	0	0
Total O2 supplied	lbmol/min	0	0	0	0
Total N2 supplied	lbmol/min	0	0	0	0
Firing rate	MMBtu/hr	0.000			

Figure 9-6. (Continued).



Flue gas	Units	Data	Data	Data	Data
Theoretical					
Date					
Test Number					
CO2	lbmol/min	0	ERR	0	ERR
O2	lbmol/min	0	ERR	0	ERR
N2	lbmol/min	0	ERR	0	0
H2O	lbmol/min	0	ERR	0	ERR
NO	lbmol/min	ERR	ERR	ERR	ERR
Tot	lbmol/min	ERR	ERR	ERR	ERR
CO2	scfm	0	ERR	0	ERR
O2	scfm	0	ERR	0	ERR
N2	scfm	0	ERR	0	0
H2O	scfm	0	ERR	0	ERR
NO	scfm	ERR	ERR	ERR	ERR
Tot wet	scfm	ERR	ERR	ERR	ERR
Tot dry	scfm	ERR	ERR	ERR	ERR
CO2	%v/v,dry	ERR	ERR	ERR	ERR
O2	%v/v,dry	ERR	ERR	ERR	ERR
N2	%v/v,dry	ERR	ERR	ERR	ERR
NO	%v/v,dry	0	0	0	0
Tot dry	%v/v,dry	ERR	ERR	ERR	ERR
Nsorbent/NOi	mole/mole	ERR	ERR	ERR	ERR
NOf/NOi	%ppm/ppm	ERR	ERR	ERR	ERR
Nsorbent/Methanol	mole/mole				
Comments					

Figure 9-6. (Continued).

loaded into a Lotus 123 spread sheet (as shown in Figure 9-6). Any missing data such as  $\text{NH}_3$  slip concentration or  $\text{N}_2\text{O}$  concentration that requires either in house or outside analysis will be recorded, as data becomes available. Also, each given test is indicated by a date and a test number which will be recorded in the table and the raw data log book for reference. Figure 9-6 will progressively develop throughout the test program.

#### 9.4 Bi-weekly Report

At the request of DOE a report will be submitted to DOE at the end of each two week reporting period. This bi-monthly report will be presented in the format given in Figure 9-7.

Date:  
Report No.:  
Report Period:

**CONTRACT TITLE AND NUMBER:**

Development of advanced NO<sub>x</sub> control concepts for Coal-Fired Utility Boilers  
Contract No. DE-AC22-90PC90363.

**CONTRACTOR NAME:** Energy and Environmental Research Corporation  
18 Mason, Irvine, CA 92718

**CONTRACT PERIOD:** October 1990 - October 1992

1. **CONTRACT OBJECTIVE:**
2. **TECHNICAL APPROACH:**
3. **CONTRACT STATUS:**

---

**ACTIVITIES:** These includes an outline of tests performed during this period.

**SIGNIFICANT RESULTS:** Results of above tests, a brief description with graphs and tables( as required).

**PROBLEMS:** Any problems encountered, such as instrument failure, etc..

**CORRECTIVE ACTIONS:** Actions taken to remedy the problem or problems, described above.

**PLANS:** Plans for next reporting period/future.

Figure 9-7. Bi-Weekly Report Format.

## 10.0 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

EER will conduct an internal quality control program which will include the following items:

- Training program
- Routine Calibrations and Maintenance
- Periodic Quality Control Checks

The project engineer will conduct a training program for the engineers and technicians who will be responsible for data organization. This will include review and discussion of the quality assurance program plan and hands on experience with all measurement systems.

The engineers/technicians responsible for data collection will also be responsible for routine calibration and maintenance of all instruments and measurement systems. Specific calibration procedures and frequency are discussed in Sections 7.0.

The project engineer will also administer a program of quality control checks. The following subsection discusses the type of checks which will be conducted and subsection 10.2 lists the specific checks and frequency for each measurement.

### 10.1 Quality Control Check Procedures

The following quality control checks will be used:

1. Calibration Standards and Devices
  - equipment checks
  - reagents
  - zero and span gases

## 2. Quality Control Samples

- blanks
- spiked samples
- surrogate samples

## 3. Replicates

## 4. Control Charts

### 10.1.1 Calibration Standards and Devices

Periodic equipment checks will be made to ensure that all measurement systems are operational within the manufacturer's or QA specifications. This will include direct inspection of critical components such as probe tips for damage.

All reagents and other materials used in evaluating sample composition will be checked for conformance with required grades and/or accuracy. The EER chemist will maintain a log of all reagents. The log will document the reagent supplier, purchase date, composition, grade and accuracy, and expiration date. This information will also be recorded on the reagent container. Prior to using reagent, the chemist will check the information against the specific requirements for its intended use. No reagents will be used after the expiration date. The composition, concentration or other characteristics of key reagents will be checked independently.

Zero and span gases will be purchased by a reputable supplier and certified to be accurate within the QA requirements. A log will be maintained documenting each gas. The following information will be recorded: bottle number, reported composition, gas supplier, purchase date and expiration date. Two levels of accuracy for span gases will be used. For tests requiring consistent data for determination of trends, span gases will be accurate to about  $\pm 5$  percent. The concentration of each new span gas will be directly compared with old span gases

to ensure consistency. For tests requiring determination of absolute levels for standard setting or similar data uses, the gases will meet the EPA Protocol and the overall gas measurements system accuracy will be compared to EPA reference methods.

#### 10.1.2 Quality Control Samples

Quality Control samples will be used on a blind and known basis. Blanks are samples which contain none of the material to be measured. Examples include unused filters and collecting solutions. Spiked samples are samples which are assembled to contain specific and known concentrations of the material to be measured. Blind and spiked samples will be included along with regular samples on a blind basis. The technician/chemist conducting the analysis will not be able to distinguish between these samples and normal samples. He will report these results in the normal manner.

Surrogate samples are samples which have been prepared to simulate real samples but which do not necessarily have known composition. Surrogate samples will be used to check-out the performance of some measurement systems after calibration to confirm satisfactory operation. The repeatability in measuring the surrogate samples is one index of precision.

#### 10.1.3 Replicates

Replicates are redundant measurements where the test conditions are maintained constant. To establish initial repeatability of the measurement methods, triplicate measurements will be conducted at a baseline condition. A representative number of test conditions will be repeated for all measurements to establish the overall repeatability and precision of the entire experiment, not just specific measurement systems.

#### 10.1.4 Control Charts

Control charts will be prepared to include the results of blind blank and spiked samples, known surrogate samples, and replicates. The control charts will be used to provide an on-going indication of precision and accuracy. They will also identify any degradation of the measurement systems or procedures necessitating corrective action.

#### 10.2 Specific Checks and Frequency

Table 10-1 lists the specific quality control checks and frequency for each measurement.

TABLE 10-1. QUALITY CONTROL CHECKS

MEASURED PARAMETER (Method)	QUALITY CONTROL CHECKS	FREQUENCY
Exhaust Gas Composition: NO, NO <sub>2</sub> (Chemiluminescence) O <sub>2</sub> (Paramagnetic) CO (Infrared) CO <sub>2</sub> (Infrared) SO <sub>2</sub> Hydrocarbons (Heated Flame Ionization) Formaldehyde SO <sub>3</sub> (Controlled Condensation) N <sub>2</sub> O (Gas Chromatography/ECD)	Check out instruments and align electronics EPA Reference Methods Blank Blank Blank and Spiked Samples	Weekly Once During Program Each Test Each Test Quarterly
NH <sub>3</sub> (Water-Quenched probe, specific ion electrode) Furnace Gas temperature Furnace Gas Temperature (Suction Pyrometer) Fuel Flow/Distribution (weight feeders) Combustion Air Flowrate Distribution (Laminar flow elements or rotameters) Combustion Air Temperature (Thermocouple) Sorbent Flowrate (Volumetric Feeder)	Blanks Check out T.C. and shields and leak check Check out T.C. and shields and leak check Back calculate from fuel composition, air flowrate and excess O <sub>2</sub> Back calculate from fuel composition and flowrate and excess O <sub>2</sub> EPA Method 2 Check ambient and heat balance on preheater Check out equipment	Each Test Each Test Each test Each Test Each Test If calculation indicates a problem Each Test Each Test



## 11.0 PREVENTIVE MAINTENANCE

Proper equipment is essential to obtain quality measurements. During this program EER will utilize our standard procedures for routine preventive maintenance and an inventory of critical spare parts to insure quality data are collected and minimize a loss of data due to equipment malfunctions. Tables 11-1 and 11-2 list standard maintenance procedures and critical spare parts for the measurement systems. In addition to these routine procedures, EER personnel continually monitor equipment performance to detect and allow correction of equipment problems.

TABLE 11-1. PREVENTIVE MAINTENANCE PROCEDURES.

EQUIPMENT	PROCEDURE	FREQUENCY
CONTINUOUS MONITORING INSTRUMENTATION:		
Calibration Gases	Verify Pressure >100 psig	Daily
Instrument Operating Conditions	Verify to Manufacturer's Specifications	Daily
Leak Check Sample System	Vacuum and Pressure Component Check	Daily
Clean Probe Filter Tips	Reverse Gas Purge with Compressed Air	Daily
Sample Probes	Balance Sample Flow in each Probe	Daily
Filters	Change	Weekly, or as required
Sample Flowrate	Verify Constant	Daily
System Vacuum/Pressure	Verify Constant	Daily
Heater and Chiller Temperatures	Verify Within Specifications	Daily
NO <sub>x</sub> Vacuum Pump Oil	Change	Monthly
MANUAL SAMPLING EQUIPMENT:		
Sample System	Leak Check	Before and After Each Test Run
Sample Nozzle	Inspect for Damage Measure	Daily Before and After Each Test Run
Pitot	Inspect for Damage	Daily

TABLE 11-1. (Continued)

EQUIPMENT	PROCEDURE	FREQUENCY
Pump Oil Level	Check Change	Daily Semiannually
Manometer	Inspect Fluid for Contamination	Daily
Sample lines, Electrical Lines, Thermocouple Lines	Inspect for Kinks, Wear, Shorts	Weekly
Meter	Calibrate  Clean and Inspect	Before and After each Test Series  Semiannually
Pump	Inspect	Semiannually
All Components	Clean	Weekly, or as Required
LABORATORY EQUIPMENT		
Balances	Calibration Check Service and Calibration by Manufacturer	Daily Semiannually
Instrumentation	Service Combustors, Scrubbers, Filters, Columns	As Specified by Manufacturer

TABLE 11-2. CRITICAL SPARE PARTS.

Continuous Monitoring Instrumentation	Manual Sampling Equipment	Laboratory Equipment
Filters Probe Filter Frits Sample Pump Pump Valves, Diaphragm Back Pressure Regulator NO <sub>x</sub> Sample Capillary Infrared Sample Cells Valves, Flowmeters Misc. Tubing and Fittings	Sample Pump Nozzles Pump Oil Manometer Oil Fuses Glass Probe Liners Nozzle "O" Rings Sample Filters Thermocouples and Lead Wire Glassware Reagents	Reagents GC Columns Glassware Instrument Spare Parts: Combustion Tubes Filters Scrubbers

## 12.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The project engineer will be responsible for preparing the following quality assurance reports:

- Quality Assurance Program Plan
- Quarterly Quality Assurance Reports
- Final Quality Assurance Report

Within 150 days after project initiation, the project engineer will prepare Revision 1 to this Quality Assurance Plan and submit it to DOE. In the event that the quality assurance goals and/or requirements for this program change, the Quality Assurance Officer will review subsequent revisions to the plan prior to submission to the DOE program officer.

The Quality Assurance Officer will monitor QA/QC activities and prepare brief quarterly reports summarizing the following:

1. Percentage of duplication or replication of determinations.
2. Instrument or equipment downtime.
3. Percentage of voided samples versus total samples.
4. Quality costs (prevention, appraisal, and correction costs).
5. Interlaboratory test results and, where applicable, intralaboratory test results (precision and accuracy).
6. Status of solutions to major quality problems.

To minimize errors in transmission, translation and interpretation, the data in these reports will be obtained from source documents wherever possible. The data will be presented in a precise and simple format so that QA/QC

performance for the quarter can be directly compared with previous performance and program QA/QC requirements as specified in the Quality Assurance Project Plan. The quarterly reports will be submitted to the EER Program Manager and the EPA Project Officer.

At the completion of the program, a Final Quality Assurance Report will be prepared as part of the Program Final Report. It will include the same information as the quarterly reports, but will apply to the entire program.

**END**

**DATE  
FILMED**

**4 / 27 / 92**

