# Development of Low Maintenance, Field Ruggedized $SO_3$ CEM

## Final Report

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## DISCLAIMER

# ABSTRACT

A prototype semi-continuous monitor and associated particulate-free sample extraction probe have been developed for measuring the concentrations of $SO_3$ and $H_2SO_4$ in industrial flue gases. The monitor provides two measurements per hour for concentrations above 1 ppmv. The probe provides the capability of continuous operation while avoiding passing the sample through a layer of particulate and can be used as a probe for conventional controlled condensation measurements of $SO_3$ and $H_2SO_4$ emissions.

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# INTRODUCTION

This the final report on the project "Development of A Low Maintenance, Field Ruggedized SO3 CEM Suitable for Unattended Plant Use", funded by the U.S. Department of Energy's National Energy Technology Laboratory under DOE Cooperative Agreement No. DE-FC26-02NT41593 to Southern Research Institute (Southern). The objective of this project was the development of a robust, automated CEM system to quantify $SO_3$/sulfuric acid vapors and aerosols present in coal-fired boiler flue gas streams.

# EXECUTIVE SUMMARY

Improvements in control technology for coal-fired boilers are substantially reducing nitrogen and sulfur oxide emissions. Further reductions of nitrogen oxides to decrease ozone precursors and ambient fine particulate matter precursors are projected to require the widespread installation of SCR (selective catalytic reduction) systems preceding wet FGD (flue gas desulfurization) scrubbers. SCR technology has a problematic side effect of catalytic enhancement of $SO_2$ oxidation to $SO_3$, which in turn can negatively affect particulate collection, ash disposal, air preheater performance, and/or general maintenance. The increased $SO_3$ formation results in increased particulate emissions due to sulfuric acid aerosol formation within (or near) the wet scrubber or, if a wet scrubber is not present, in the near-stack plume. Plumes containing these condensation aerosols are quite visible and persist over long distances in part due to their particle size and in part due to the retention of substantial fractions of water (sulfuric acid aggressively scavenges water). After wet scrubbers, the low temperature, saturated stack gases can have negligible plume rise. Relative to plumes formed from hotter stack gas, which rise to high elevations because of temperature-related buoyancy, reduced plume rise can result in localized high ground-level concentrations of stack gas constituents. Aside from adding reactive acid gases to the environment, $SO_3$/sulfuric acid emissions increase fine particle emissions and impair visibility. Physiological responses such as eye irritation and breathing difficulty have been reported for episodes involving highly visible ground-level plumes containing sulfuric acid aerosols. An accurate and reliable sulfuric acid monitor would greatly facilitate studies and implementation of controls for sulfuric acid emissions.

A prototype $SO_3$ monitor was developed cooperatively by Southern Research Institute (SRI), AMETEK Process Instruments, and Bob Saltzman Associates, Inc. The monitor is based on the manual controlled condensation method (CCRM) developed by Cheney and Homolya. The controlled condensation method is generally recognized as the most reliable method for measuring $SO_3$/ $H_2SO_4$ at the levels encountered at power plants.

This project addressed the major requirements for a field-useable monitor: a sample extraction system that separates $SO_3/H_2SO_4$ vapor from in-stack particulate matter and transports it efficiently as a vapor to a rugged, low maintenance external sensor. The detector system was an extension of a field-proven AMETEK product, the Model 4660, originally developed to measure low-level $H_2S$ in refinery fuel gas, natural gas, and for emissions monitoring. The detection method is a turbidity measurement of a barium sulfate suspension formed from the reaction of barium chloride and sulfate ions from the collected $SO_3/H_2SO_4$ sample and is based on the detection method for airborne sulfate particulate matter. Because of proven performance in similar applications, a commercially-available probe, the Apogee Scientific QSIS, was purchased and modified to include injection of hot dilution gas for heating the sample gas in order to vaporize any condensed $H_2SO_4$. The monitor can be expected to perform well for $SO_3/H_2SO_4$ concentrations down to 2.5 ppm at a measurement frequency of two samples per hour.

The monitor was tested at the pilot-scale Combustion Research Facility (CRF) at Southern Research Institute in Birmingham, Alabama. Due to various problems, but mainly time delays due to difficulties with AMETEK's development of a functioning condenser and condenser wash system, testing of the final system on actual flue gas was limited to a series of experiments done with the CRF fired by natural gas with $SO_3$ being injected from two catalytic generators rather than a coal-fired test. The agreement between the monitor and the CCRM results in these tests was generally good and encouraging.

## BACKGROUND

Over the last decade, regulatory pressures and economics have led to improvements in control technology and combustion practices and to the use of low-sulfur coals. The net result of these advances is a substantial reduction of nitrogen and sulfur oxides emissions from coal-fired boilers. Further reductions of these oxide precursors of ambient fine particulate matter are projected to require the widespread installation of SCR (selective catalytic reduction) systems preceding wet FGD (flue gas desulfurization) scrubbers. A significant advantage of coupling these two control technologies is that they can provide low NOx and $SO_2$ emissions with higher-sulfur fuels. However, exploratory research of SCR and wet FGD technologies and some full-scale installations have revealed some important side effects of this coupling, which involve substantial operational and particulate emissions problems.[1]

The problematic contribution of SCR technology is the catalytic enhancement of $SO_2$ oxidation to $SO_3$, which in turn can negatively affect the performance and operability of particulate collectors, result in plugging and loss of efficiency of air preheaters, and/or cause corrsosion and other general maintenance problems. As would be expected, increased $SO_3$ formation results in increased particulate emissions due to sulfuric acid aerosol formation within (or near) the wet scrubber or, if a wet scrubber is not present, in the near-stack plume. Plumes containing these condensation aerosols are quite visible and persist over long distances in part due to their particle size and in part due to the retention of substantial fractions of water (sulfuric acid aggressively scavenges water). After wet scrubbers, the low temperature, saturated stack gases can have negligible plume rise. Relative to plumes formed from hotter stack gas, which rise to high elevations because of temperature-related buoyancy, reduced plume rise leads to localized high ground-level concentrations of stack gas constituents. Aside from adding reactive acid gases to the environment, $SO_3$/sulfuric acid emissions increase fine particle emissions and impair visibility. Physiological responses such as eye irritation and breathing difficulty have been reported for episodes involving highly visible ground-level plumes containing sulfuric acid aerosols.

### Historical Experience With $SO_3$

The origin of sulfuric acid is a small fraction of the sulfur in the fuel being oxidized beyond $SO_2$ to $SO_3$, which subsequently reacts with water vapor to form $H_2SO_4$.[2] Almost all of the sulfur is oxidized to $SO_2$ in the combustion zone. Thermodynamically, the most stable species in the combustion zone is $SO_2$, changing to sulfur (VI) species ($SO_3$) below 650°C. $SO_2$ remains the predominant sulfur species emitted due to kinetic factors that limit the key oxidation step from $SO_2$ to $SO_3$. As the gas temperature falls, rapid shifts in the equilibria occur from $SO_3$ between the economizer and air preheater, to sulfuric acid vapor between the air preheater and the stack or wet scrubber (if present), and diluted liquid sulfuric acid in the wet scrubber and stack effluent. The dew point for acid condensation for typical gas compositions varies from about 200°F at 0.1 ppm acid to over 300°F at 50 ppm.

In addition to fuel sulfur and excess combustion air levels, the rate of formation of $SO_3$ depends upon catalytic oxidation associated with some compounds originating with the fuel and metal heat-transfer surfaces. Reported ranges for conversion of $SO_2$ to $SO_3$ in coal-fired boilers extend from 1% to 5% of the $SO_2$.[2] For utility boilers burning eastern 3%-sulfur coals that produce $SO_2$ levels over 2000 ppm, then 20 to 100 ppm of $SO_3$ would be expected. A significant portion of this $SO_3$ is removed in passage through the air preheater due to condensation and/or reaction at the colder sections. Based upon empirical data at 18 conventional pulverized-coal-fired boilers, a proposed prediction method for estimating sulfuric acid emissions concluded that combined $SO_3/H_2SO_4$ at preheater outlets averages 0.4% of $SO_2$ levels when burning eastern bituminous coals, 0.1% when burning western bituminous and 0.05% when burning Powder River Basin coal.[2] Within that data set variations were high, corresponding to a range for the eastern bituminous coals of 4 to 16 ppm of $SO_3$ emitted. Levels outside this range cannot be ruled out because of the uncertainty associated with the subtleties of catalytic oxidation in boilers or varying losses in the air preheater and indeed have been observed at several sites by SRI personnel over three decades of investigations.

Electrical utility plant operators have long dealt with the presence of sulfuric acid. Some acid levels have been found to be beneficial because the acid is adsorbed by fly ash and reduces resistivity, resulting in better ESP performance. Typically the flue gas temperature is maintained high enough (>270°F) to limit levels of condensed-phase acid, thus limiting corrosion rates and maintaining dry particulate properties, and passing more acid to condense in the plume. Each 1 ppm of sulfuric acid corresponds to a mass concentration of 4 $mg/m^3$ at standard conditions, but at moisture levels of coal flue gas, temperatures below 200°F cause significant amounts of $H_2O$ to accompany condensed acid.

Sulfuric acid in electrical power plant emissions is not regulated. Emissions in the condensed phase at stack conditions are reported based upon estimation procedures as part of the Toxic Release Inventory (TRI) system. Generally speaking, procedures utilized for particulate emission measurements exclude sulfuric acid. Nevertheless, it is clear that $SO_3$ in the vapor phase at stack conditions is condensed in the near stack plume and contributes to ambient fine particulate levels and plume opacity. For example, one investigation compared particulate size distribution and mass of the aerosol in stacks to those in the "plumes" by developing a dilution-based plume simulator. In measurements using this technique at one plant, the particulate mass below 2 µm of 2 mg/dncm in the stack became 41 mg/dncm in the "plume" due to condensation and/or homogeneous nucleation of $H_2SO_4$.[3] The condensed $H_2SO_4$ particles that formed had diameters of about 0.075 µm. During these tests there was no visible stack plume because particles with size below 0.1 µm are inefficient light scatterers, but condensed size distributions vary, and it is common for plants using high-sulfur coal to have persistent plumes with significant visibility.[4]

### $SO_3$ impacts of SCR and Wet Scrubber FGD

SCR technology and its utilization have developed with realization that catalytic oxidation of $SO_2$ to $SO_3$ accompanies $NO_X$ reduction. In Japan and Europe commercial installations of the 1980s encountered conversion rates of 1 to 2% of the $SO_2$.[5] These plants burn fuels with lower sulfur contents than those burned by many plants in the US. In an investigation of SCR with high sulfur coal that was performed in DOE's Clean Coal Program, $SO_2$ oxidation across catalysts varied from negligible to 1.5%. There was a large variation of oxidation rate from catalyst to catalyst by different manufacturers but the investigators concluded that this resulted from different choices by each manufacturer involving tradeoffs with design and operating parameters.[6]

SCR specialists project that the envelope of observed characteristics will expand substantially with growth in the near future of SCR utilization with US coals. From previous experience changes caused by variation of coal chemistry are expected.[5] In addition, variation of choices made concerning SCR design parameters to match unit-specific circumstances will contribute to the range of $SO_2$ oxidation rates and resulting $SO_3$ levels.

Implementation of SCR is typically expected to double levels of sulfuric acid approaching air preheaters, 1% added to 1% of $SO_2$ levels (from a net concentration of 1% of that of $SO_2$ to 2% of that of $SO_2$) with more significant changes at some plants. Some of this added $SO_3$ will react with $NH_3$ slip in the air preheater and deposit downstream, but the amount removed by that path must be limited and carefully controlled, by controlling $NH_3$ slip, to prevent fouling problems in the air preheater.[7] Consideration of potential effects of ammonia reaction with sulfuric acid on particulate control leads to concern for accumulation of ammonium bisulfate (with fly ash) on ESP collection plates and corona electrodes due to its low melting point. There is also concern for potential degradation of ESP performance as the result of high levels of ultrafine particles, resulting from gas phase reactions between $SO_3$ and $NH_3$, that have a strong effect on space charge. Clearly, $SO_3$ oxidation across SCR will affect several areas of plant operation.

Like SCR units, Wet FGD scrubbers may affect the state and effects of the $SO_3$ downstream of the control device – in this case, in the plume. A recent investigation found acid removal efficiency at one site to vary between 30 and 80% with no apparent reason for the variations.[8] Much, if not most, particulate matter formed by condensation is believed to be submicron particle size, and wet scrubbers have low collection efficiency in that size regime. This low collection, coupled with the reduced dispersion described above for wet scrubber plumes, can lead to localized high concentrations of acidic particulate emissions (mass concentrations in the range of 50 $mg/m^3$ are projected).

### $SO_3$/ $H_2SO_4$ Measurement And Monitoring

Method 8, the EPA promulgated method for measuring emissions of sulfuric acid mist[9], has a lower detection limit of about 50 $mg/m^3$, thus it lacks the sensitivity needed for measurements at electric utility plants. The manual controlled condensation method (CCRM) developed by Cheney and Homolya[10] is generally recognized as the most reliable method for measuring $SO_3$/ $H_2SO_4$ at the levels encountered at power plants.[10, 11] In the CCRM, a sample gas stream is conveyed through a heated quartz-lined probe, through a quartz fiber filter and then through a condenser in which the acid vapor is removed. The probe and filter holder are held at a temperature at or above 550 °F to ensure that the $SO_3$/ $H_2SO_4$ in the sample is entirely in vapor form before reaching the filter. The condenser is maintained at a temperature above the moisture dew point but well below the sulfuric acid dew point so that all of the acid is collected in it. A second filter downstream of the condenser ensures that any aerosolized acid is retained for analysis with that collected in the condenser itself. After each sample is collected, the condensor is washed to recover the collocted acid. The amount of acid collected is later quantified in the laboratory by titration. Over the past few years several improvements have been made to the method as it is applied to coal-fired utility installations.[8,12] The changes deal with minimizing problems arising from the acid vapor being adsorbed on or reacting with ash collected on the filter upstream of the condenser or the filter medium itself, together with the problem of ensuring that any sulfuric acid mist in the sampled gas is completely volatilized in the probe. The first problem is significant upstream of PCDs and the second is especially important downstream of a scrubber where the $H_2SO_4$ is, for practical purposes, entirely in the condensed phase. Both problems must be addressed in automated as well as manual systems. The CCRM as described above was used as a manual reference measurement for comparison with the results of automated measurements with the instrument developed here.

An accurate and reliable sulfuric acid monitor would greatly facilitate studies and implementation of controls for sulfuric acid emissions. Several monitors have been developed over the years, some using colorimetric methods (*e.g.* the Severn Science Ltd. System), spectroscopic techniques (*e.g.* the tunable diode laser system first developed by Laser Analytics), and a conductivity cell system developed by the U.S. EPA.[13] There is interest in use of FTIR but low sensitivity appears to be a continuing problem to the successful development of this technology for $SO_3$ measurement. Physical Sciences Incorporated has announced the intention to develop an IR spectroscopic-based analyzer.[14] The Severn Science system is the only one of these that has survived as a commercially available instrument. Field experience by SRI indicated that it showed promise but was not suitable for unattended operation beyond a day.[15]

## TECHNICAL APPROACH

The development for this project addresses the major requirements for a field-useable monitor: a sample extraction system that separates $SO_3$ vapor from instack PM and transports it efficiently as vapor to a rugged, low maintenance external sensor.

The major tasks of this project can be summarized as follows. AMETEK, our subcontractor and partner in this effort, was to design the detector portion of the $SO_3$ Analyzer and fabricate and deliver a field worthy prototype analyzer (Task1) for interfacing to a sample extraction and transport system (SETS) developed by SRI (Task 2). The completed prototype system would undergo short-term tests in SRI Pilot-Scale Combustion Research Facility in conjunction with experimental burns under SRI's multipollutant research program (Task 3). During this period, operational lessons learned would be applied to unspecified but anticipated instrumental refinements (Task 4) and the updated instrument subjected to long-term tests at a high sulfur coal-fired plant with periodic comparative measurements taken using the manual controlled condensation $SO_3$ method as a reference (Task 5).

The proposed detector system was an extension of a field-proven AMETEK product, the Model 4660, originally developed to measure low-level $H_2S$ in refinery fuel gas, natural gas and for emissions monitoring. The detection method is a turbidity measurement of a barium sulfate suspension formed from the reaction of barium chloride and sulfate ions from the collected $SO_3/H_2SO_4$ sample and is based on the detection method for airborne sulfate particulate matter outlined in "Methods of Air Sampling and Analysis"[16] with references to ASTM, EPA and USPHS methods. The Task 2 sample extraction and transport system likewise is an extension of designs used for other sampling systems by SRI. The SETS design has a common core configuration with adaptations for the different conditions at the required sample locations. One aspect of the design that we judged an important addition was a provision to generate and add to the sample a field "spike" of vapor phase sulfuric acid for QA purposes. An apparatus was designed for this at SRI using catalytic oxidation of $SO_2$ in air to generate the $SO_3$ spike, and AMETEK used this design to construct a laboratory $SO_3$ generator to test their prototype detector.

## SUMMARY OF DEVELOPMENT OF THE MONITOR

### $SO_3$ Analyzer design finalization and fabrication.

The proposed analysis system, shown in the Figure 1, used discrete sampling with a scrubbing column (successfully used in the AMETEK 4660 $H_2S$ analysis system). AMETEK assembled a breadboard system using a packed bubbler collection cell like that used in their existing sampler to evaluate adaptations to the current application. After laboratory evaluation of the breadboard, the design was to be incorporated into the fieldable prototype which is the Task 1 deliverable. The water in the column is drained into a special cell with a magnetic stirrer, and the $BaCl_2$ solution is injected into the water. After 30 seconds of stirring, the turbidity measurement is made with the stirrer turned off. Figure 1 also shows this timing sequence. This breadboard analysis system was tested for sequencing, stability, leaks, etc., and calibrated based on volumetric dilutions of 96% $H_2SO_4$. Good sensitivity and linearity were observed as expected. In preliminary laboratory testing at the AMETEK Process and Analytical Division Newark, DE, plant, it was determined that the equivalent of 10 ppm of gas phase $H_2SO_4$ dissolved in water could be measured within ± 0.5 ppm with this detection technique (based on a 2 liters/min. gas flow rate for 5 minutes into 50 mL of water).

AMETEK used the SRI catalytic oxidation design to construct a laboratory $SO_3$ generator to test their breadboard detector configuration, but encountered a number of operational problems, including erratic $SO_3$ generation and erratic collection efficiency by the sampler. They reported that: “Providing a reliable standard for the analysis system turned out to be a major obstacle in the development and testing of the system. Our attempts to use catalytic conversion of 50 ppm $SO_2$ to $SO_3$ was particularly time consuming, unreliable and frustrating.” It was later found during discussions with the catalyst vendor that SO3 generators of this type cannot be turned on and off at will, but require hours to days to reach steady state conditions and must be operated continuously if steady state concentrations are required. This makes them much less desirable as a means of providing spikes for QA purposes as originally proposed.

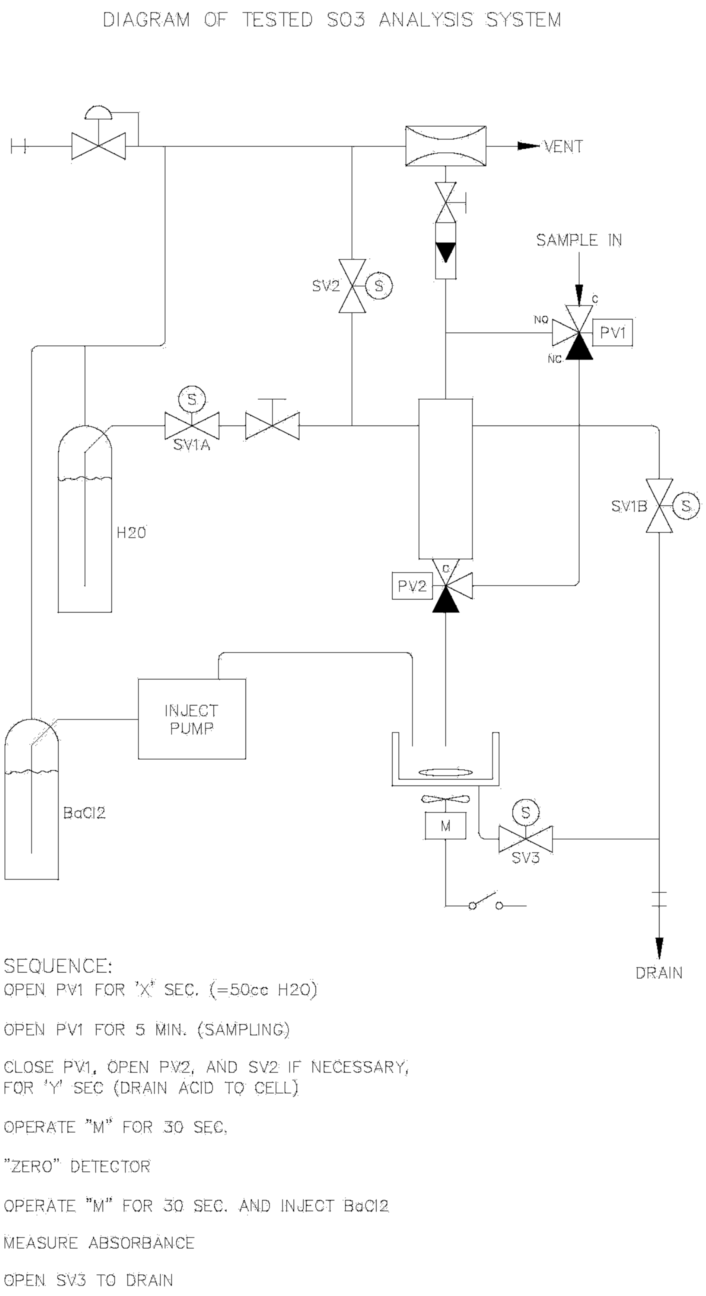


DIAGRAM OF TESTED SO3 ANALYSIS SYSTEM

SEQUENCE:

OPEN PV1 FOR 'X' SEC. (=50cc H2O)

OPEN PV1 FOR 5 MIN. (SAMPLING)

CLOSE PV1, OPEN PV2, AND SV2 IF NECESSARY,
FOR 'Y' SEC (DRAIN ACID TO CELL)

OPERATE "M" FOR 30 SEC.

"ZERO" DETECTOR

OPERATE "M" FOR 30 SEC. AND INJECT BaCl2

MEASURE ABSORBANCE

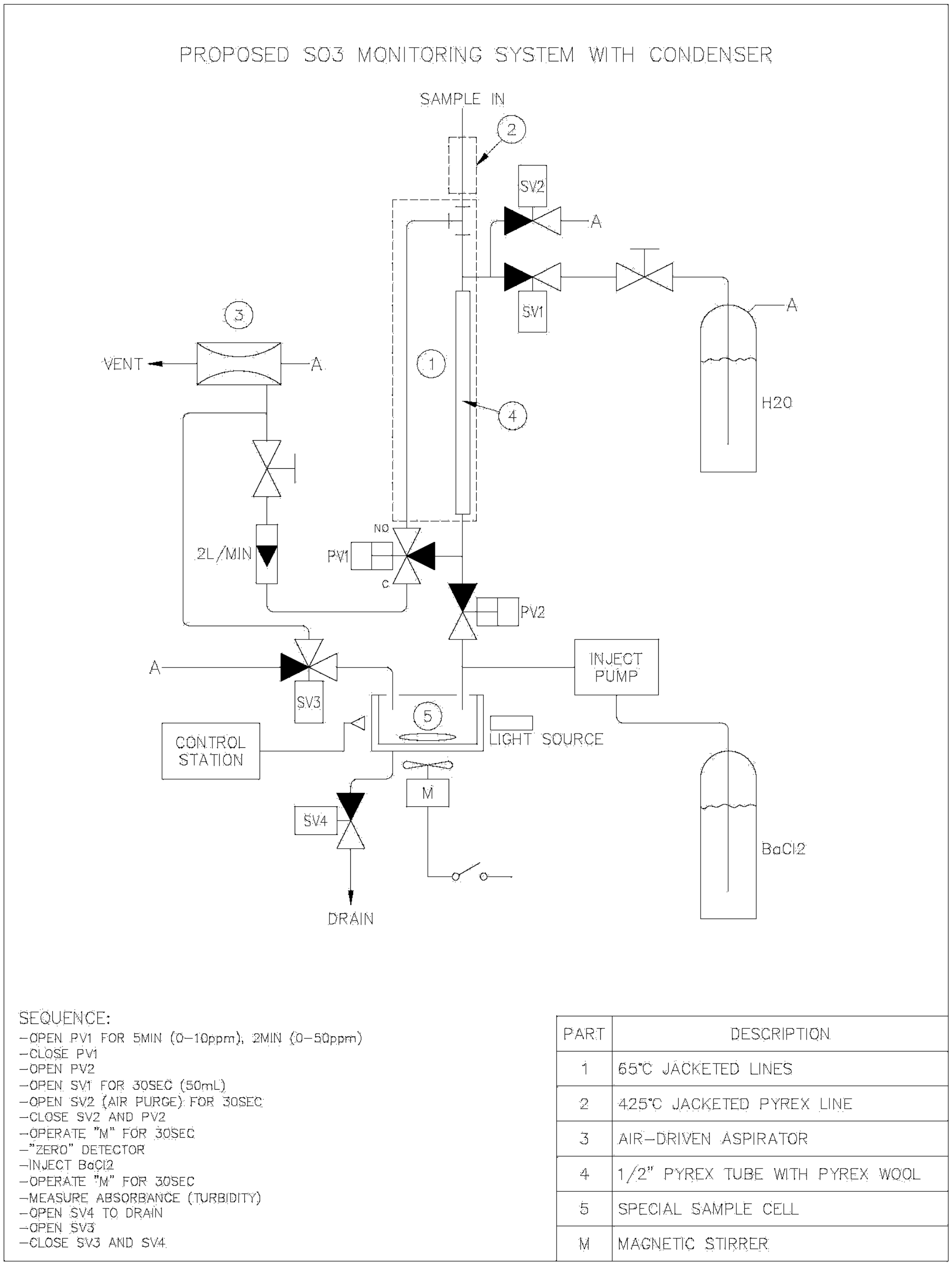
OPEN SV3 TO DRAIN

**Figure 1. Block diagram of initial prototype $SO_3$ detector.**

After switching to a liquid phase spike technique of injecting a very low flow of dilute $H_2SO_4$ into the gas stream using a low flow peristaltic pump, AMETEK was able to achieve consistent and reproducible measurements of $H_2SO_4$ concentrations. While the erratic behavior of the previous spiking system was clearly part of the earlier inconsistent results, AMETEK also noted ill effects due to holdup on the collector and condensation on cold spots in the inlet lines. They concluded that the packed tower scrubbing collector system design should be replaced by a collector using the controlled condensation principle, and provided a schematic design of a detector with these changes as shown in Figure 2.

A revised breadboard version of the modified system was constructed by AMETEK's original consultant, Bob Saltzman, now working directly under contract to Southern Research. This breadboard system was challenged with test streams spiked with known amounts of $H_2SO_4$ to simulate stack-level sample atmospheres. The liquid phase spike technique of injecting a very low flow of dilute $H_2SO_4$ into the gas stream by a low flow peristaltic pump was used for these tests. AMETEK felt this technique had previously achieved consistent and reproducible measurements of $H_2SO_4$ concentrations. Unfortunately, the spiking results showed some promise but were again compromised by problems with the laboratory $SO_3$ generator used at that site. Figure 3 shows the result of the series of spike tests. Although the testers attempted to deliver a consistent spike equivalent to a typical acid concentration (50 or 10 ppm), the monitor reading swung between episodes of low response and readings over three times the spike value. This effect is symptomatic of acid condensation on cold spots in the inlet lines followed by release in a burst as the line heat raises the cold spot above the dew point and the condensate is evaporated. The average sample points in Figure 3 correspond to a cumulative average of the monitor response from the beginning of the test sequence, which may somewhat simulate the averaging effect of hold-up and reemission of the acid spike. The average sample is not far from the constant input concentration at both spike levels, which gave some encouragement that the monitor may respond reasonably to a stable acid generator test system.

Upon completion of the tests described above, a field-usable prototype monitor was designed and constructed under the direction of Bob Saltzman Associates, Inc. The general layout of the monitor is illustrated below in Figure 4. The unit was fabricated on two panels which could be mounted separately for ease of use in the field.



SEQUENCE:
- OPEN PV1 FOR 5MIN (0–10ppm), 2MIN (0–50ppm)
- CLOSE PV1
- OPEN PV2
- OPEN SV1 FOR 30SEC (50mL)
- OPEN SV2 (AIR PURGE) FOR 30SEC
- CLOSE SV2 AND PV2
- OPERATE "M" FOR 30SEC
- "ZERO" DETECTOR
- INJECT BaCl2
- OPERATE "M" FOR 30SEC
- MEASURE ABSORBANCE (TURBIDITY)
- OPEN SV4 TO DRAIN
- OPEN SV3
- CLOSE SV3 AND SV4

| PART | DESCRIPTION |
|---|---|
| 1 | 65°C JACKETED LINES |
| 2 | 425°C JACKETED PYREX LINE |
| 3 | AIR–DRIVEN ASPIRATOR |
| 4 | 1/2" PYREX TUBE WITH PYREX WOOL |
| 5 | SPECIAL SAMPLE CELL |
| M | MAGNETIC STIRRER |

**Figure 2. Block diagram of modified $SO_3$ detector design**.

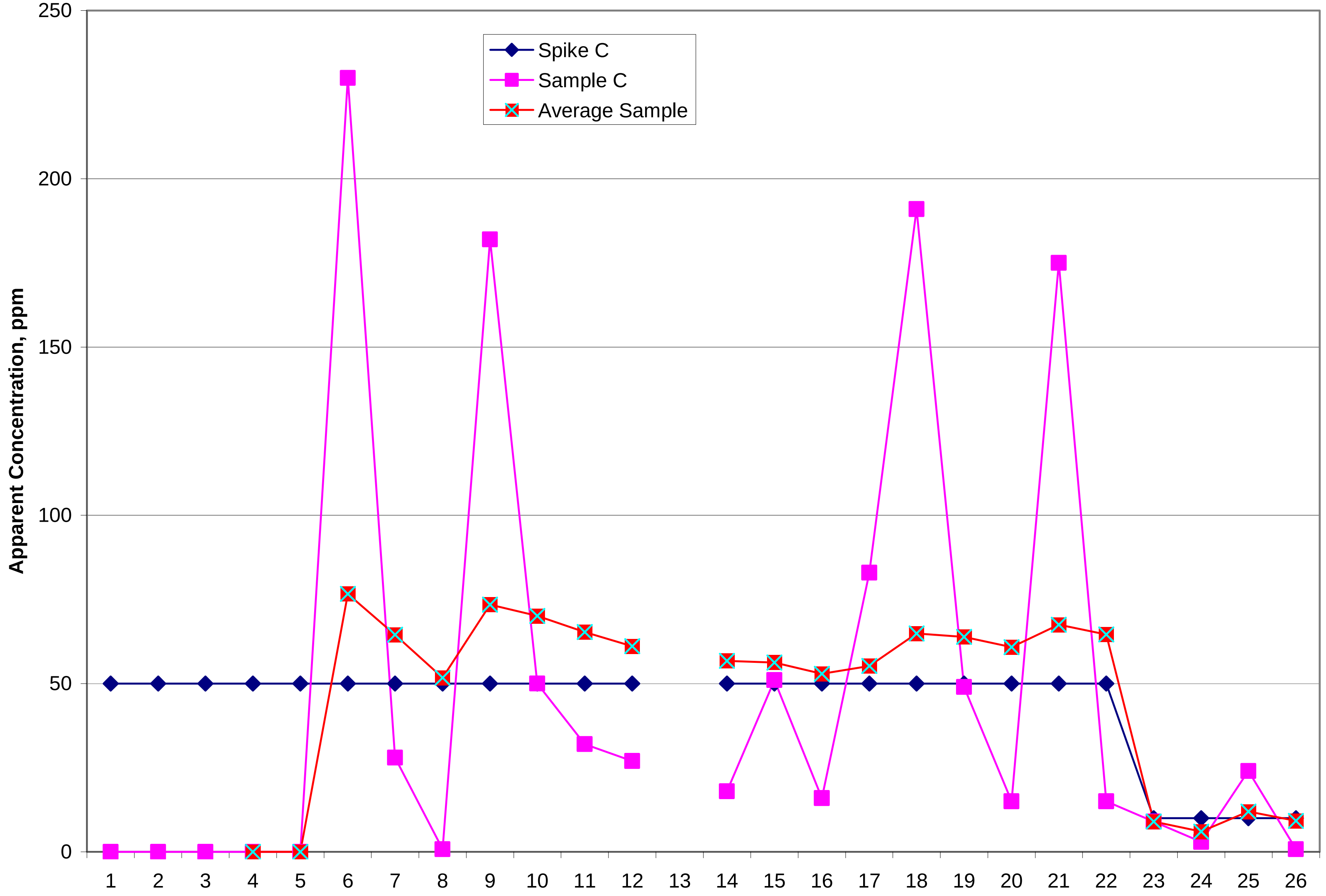


**Figure 3. Apparent monitor response to acid spike tests.**

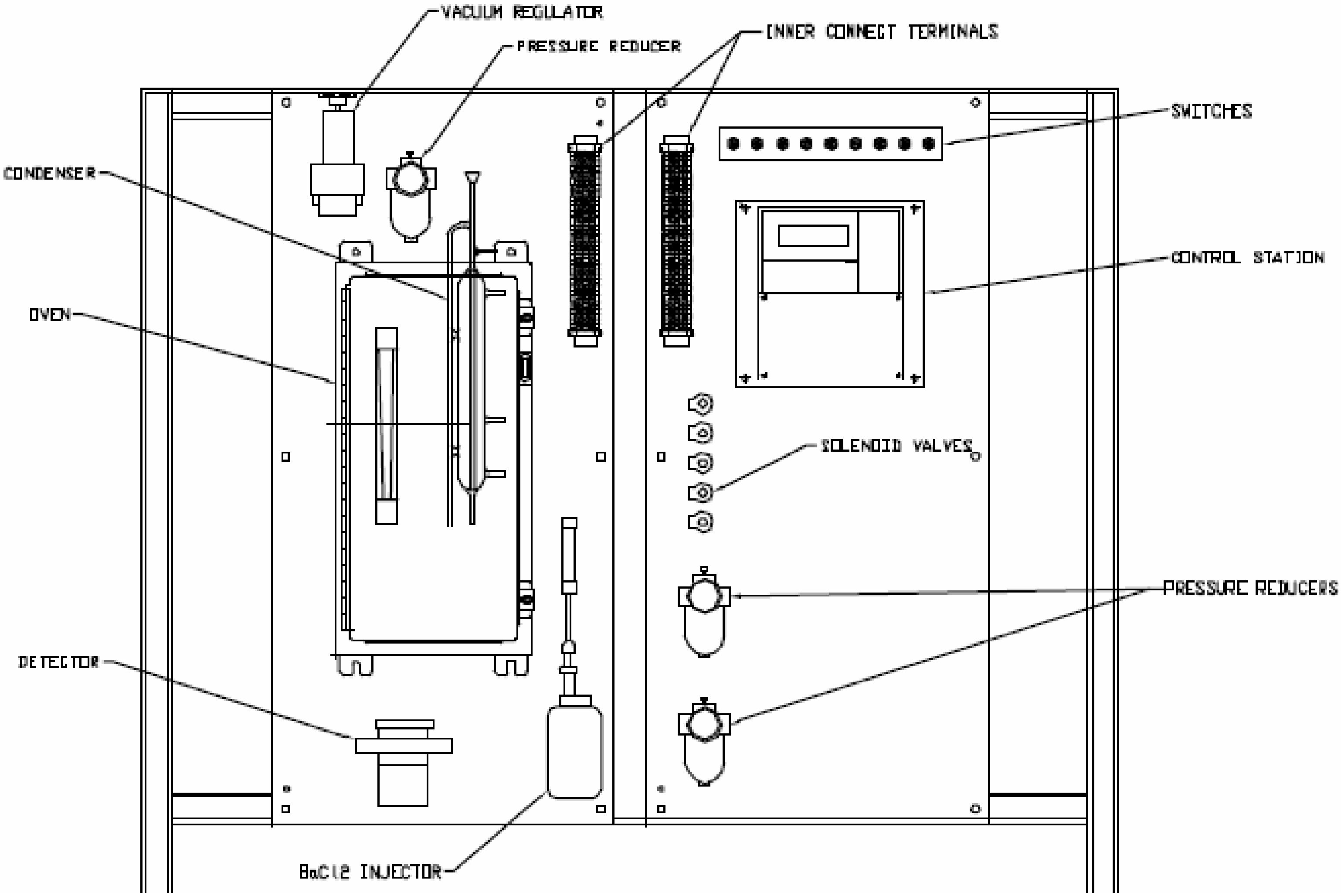


**Figure 4. Layout of the Final Prototype AMETEK $SO_3$ monitor.**

Design and fabrication of sample extraction and transport system(s) by SRI.

A conceptual design for the base SETS system was presented at the project kickoff meeting. The sample extraction and transport system (SETS) must extract and maintain or heat the flue gas to >550°F, transport, separate $SO_3$ from PM, deliver $SO_3$ to the AMETEK analyzer, and return excess flue gas and PM to the duct. As illustrated in Figure 5, extraction and heating of the sample gas was to be accomplished primarily by the injection of very hot dilution gas ($\approx$ 1:1) near the probe entrance as well as from contact heating. Flow through the SETS was to be driven by an eductor, with the analyzer extracting about 2 slpm hot sample gas from through an annular filter upstream of the eductor. The original conceptual design of the probe called for essentially all surfaces in contact with the sample gas to be quartz lined; while others were to be Hastelloy C276 or Teflon as appropriate for temperature. Because of proven performance in similar applications, a conceptually-similar commercially-available probe, the Apogee Scientific QSIS, was purchased and modified to include the hot dilution gas injection for heating the sample gas. The QSIS probe and filter element are fabricated from stainless steel with a proprietary coating applied to all surfaces to minimize reactions with the sample gas.

The QSIS probe is an inertial separation probe manufactured by Apogee Scientific primarily for use in monitoring mercury emissions from industrial sources. The probe extracts a flue gas sample at a flow rate of approximately 10 to 12 acfm through a ¾-inch diameter sample probe. The extracted gas then passes axially along the length of a ½-inch ID cylindrical porous filter element. A slipstream of sample gas is pulled radially through the filter element at a flow rate of a few liters per minute and directed to the sample collection and measurement system. Due to the high axial velocities in the sample probe and core of the cylindrical filter element, particles entrained in the gas stream are prevented from depositing on the inner walls of the filter. However, due to the pore size of the porous frit, (2 or 5 micron, depending on filter element), fine particles are capable of being trapped in the filter element over time. As a result, the filter element must be periodically removed for cleaning by backwashing. (Routine experiments have shown that significant pressure drop develops across the filter elements after sampling flue gas streams for several weeks of continuous operation.) As in the original SETS design, flow through the Apogee system is driven by an eductor, with the analyzer extracting about 2 slpm of hot sample gas upstream of the eductor. The excess gas not used for the actual measurement is returned to the host duct. A schematic diagram of the QSIS probe as adapted for $SO_3$ measurements is shown in Figure 6.

Prior to proceeding with the purchase and modification of a QSIS probe for use with the monitor, a brief series of tests was performed to check for any obvious problems with the use of the probe for $SO_3$ sampling. These tests were carried out in SRI's Coal Combustion Facility (CRF) in conjunction with a series of an ongoing mercury measurement program which utilized two such probes, one sampling at a point in the CRF at which the gas temperature was about 550 F and the second down stream of the first, following two heat exchangers, at which the gas temperature was about 325 F. A heated hose like that to be used between the probe and condensor for the $SO_3$ monitor was used at each location to convey a sample stream to a conventional controlled-condensation condensor setup. Data obtained with this setup was then taken for comparison with data obtained with conventional controlled condensation setups that were being operated to obtain information for the mercury emissions program. The results of these tests are shown in

Figure 7. The agreement was excellent at the 550 F location and was reasonably good at the 325 F location although the results with the QSIS probe were slightly higher than those from the conventional probe at the 325 F location. (The differences in concentrations between the two locations results from losses in the heat exchangers.) These results were deemed satisfactory enough to proceed with the purchase and modification of a QSIS probe for use with the $SO_3$ monitoring system. The completed QSIS probe after modification for use in the $SO_3$ system is shown in photographs in Figure 8.

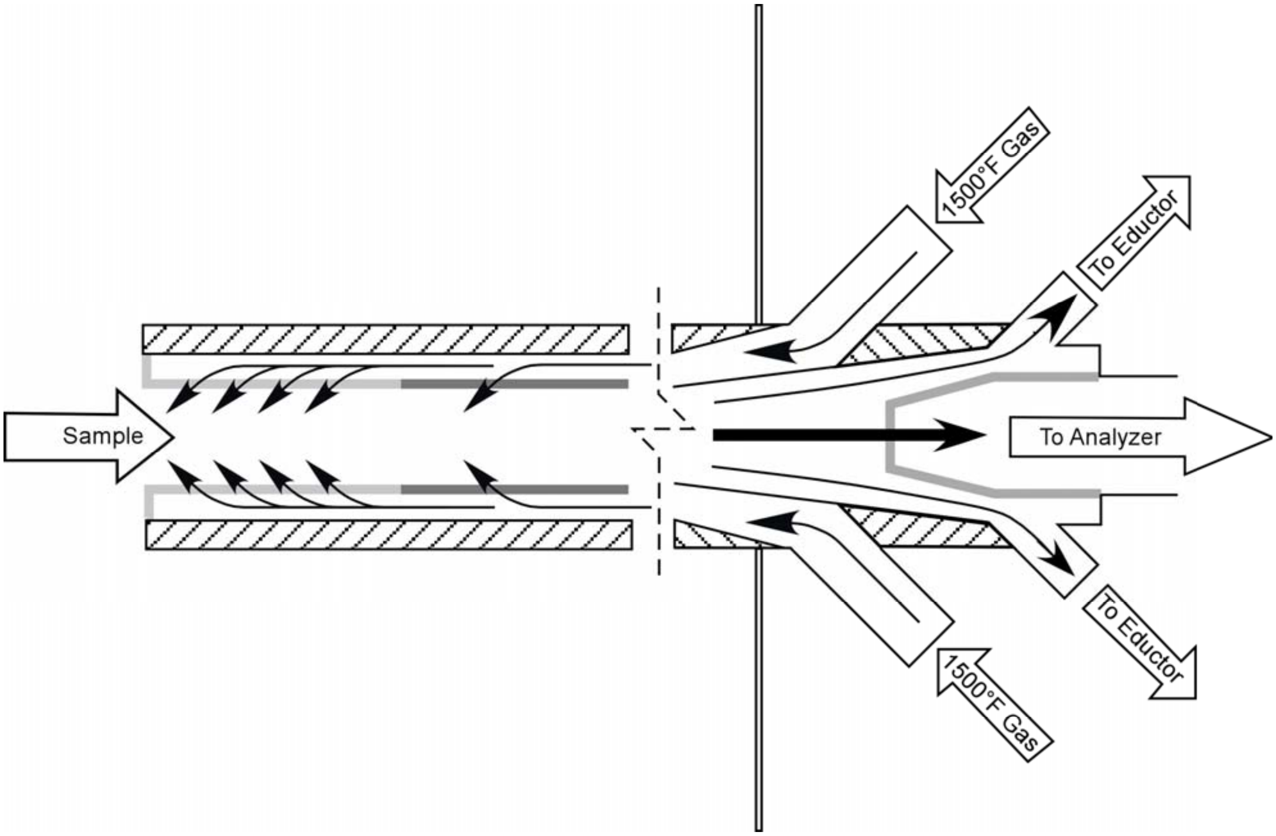


**Figure 5. Original Conceptual SETS probe design.**

The exhausts of some wet FGD scrubbers contain significant quantities of droplets that are too large (10s of microns) to evaporate quickly which would lead to their being lost on internal surfaces of the sampling nozzle and transport line. Over time, such droplets deposited on surfaces would dry, leaving a residue that would accumulate and interfere with normal operation of the system. Therefore, for monitoring downstream of wet FGD scrubbers the SETS will incorporate an inertial collector at the probe inlet (not shown in Figures 6 and 8) specifically designed to remove these droplets. In the past this approach has been found necessary for sample extraction in wet streams. In particular, SRI developed a series of such procedures for the California Air Resources Board for making particle size measurements in wet process streams that have been successfully utilized for over 10 years. Fortunately, the condensed acid tends to reside in droplets smaller having diameters of a few micrometers and smaller.

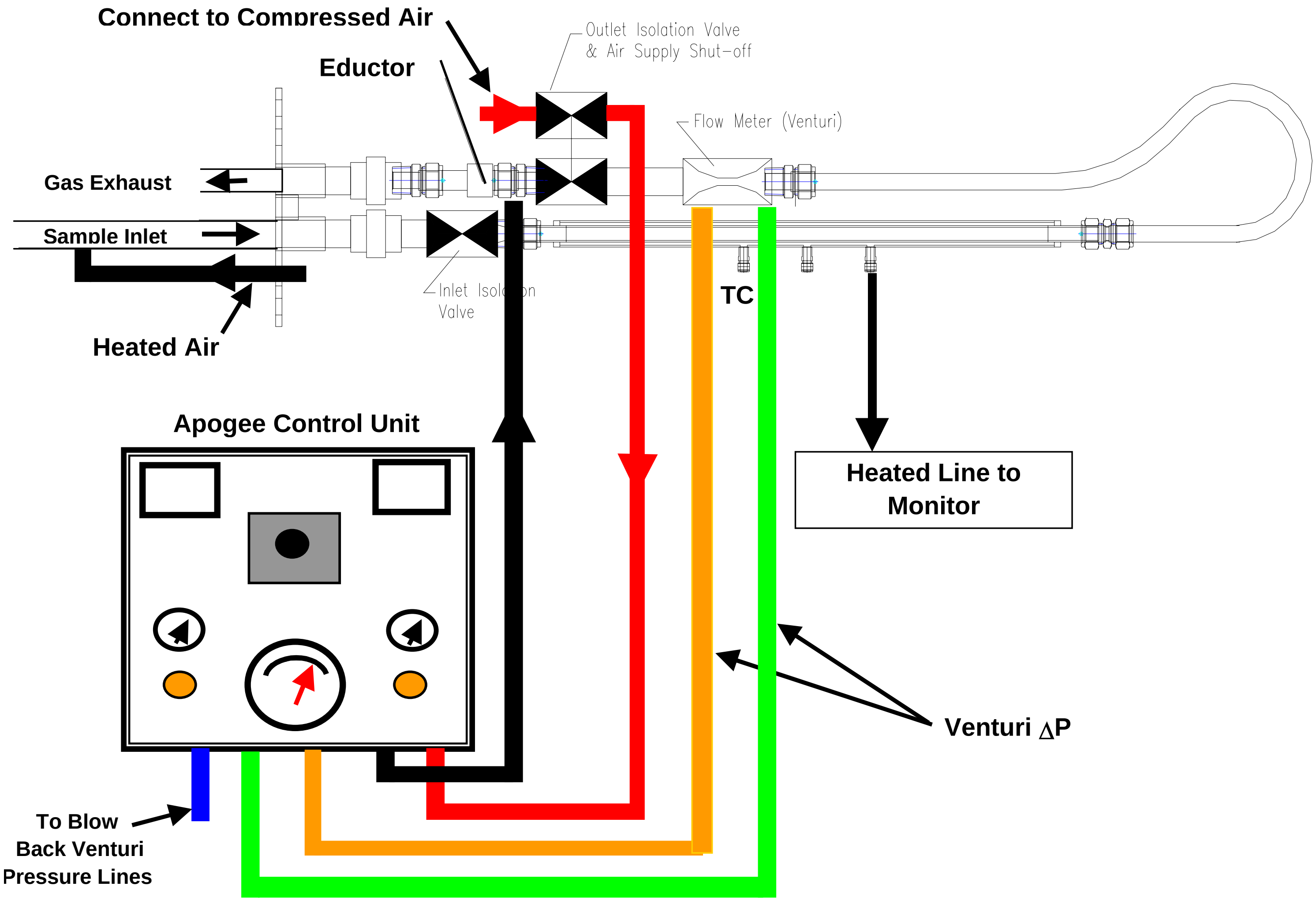


Figure 6. Schematic diagram of the Apogee QSIS probe modified for use with the $SO_3$ monitor.

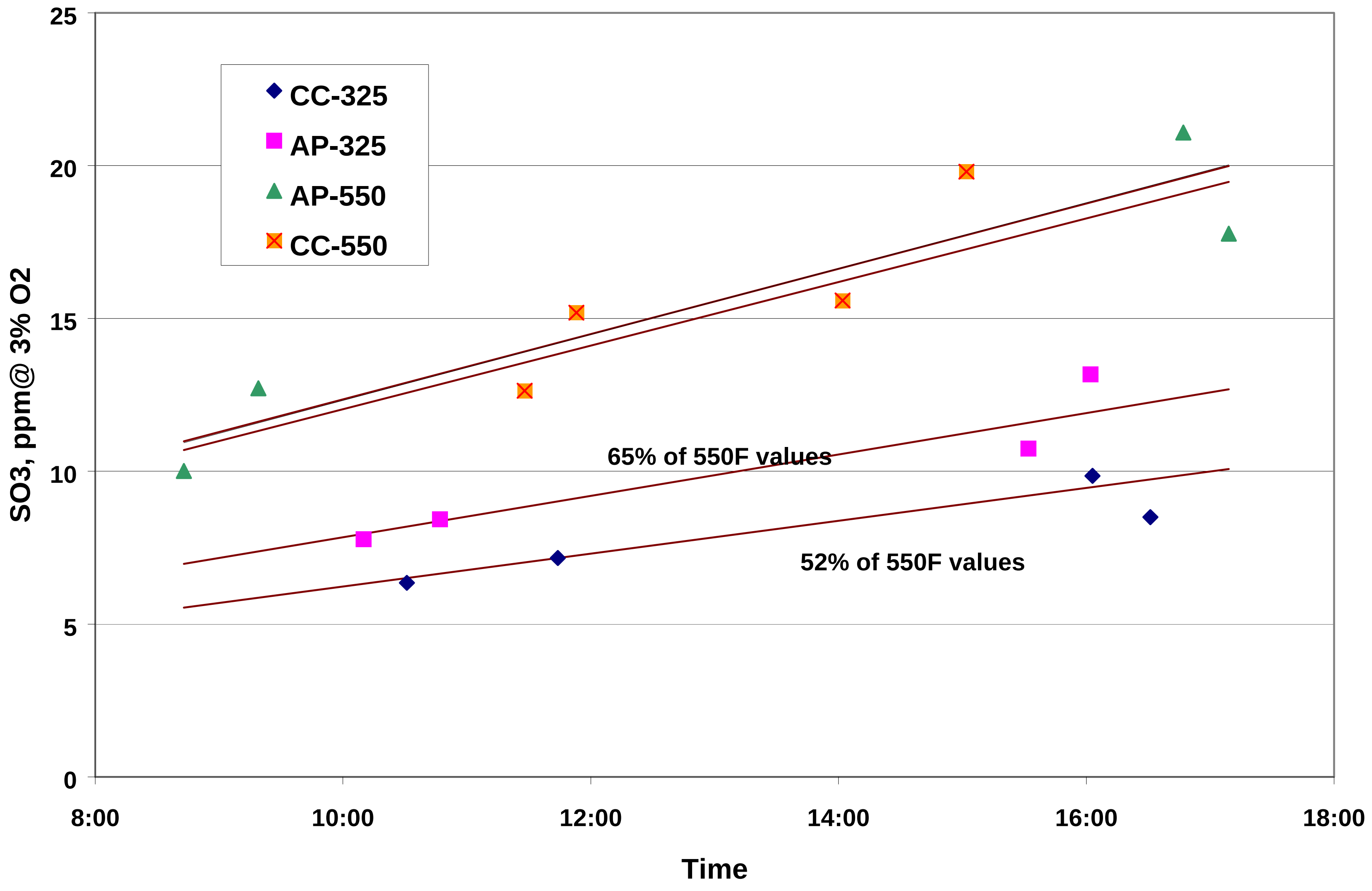


**Figure 7. Comparisons of $SO_3$ concentrations measured by conventional controlled-condensation methods (CC) with those measured using QSIS probes and a heated hose to deliver samples to a controlled-condensation condensor (AP).**

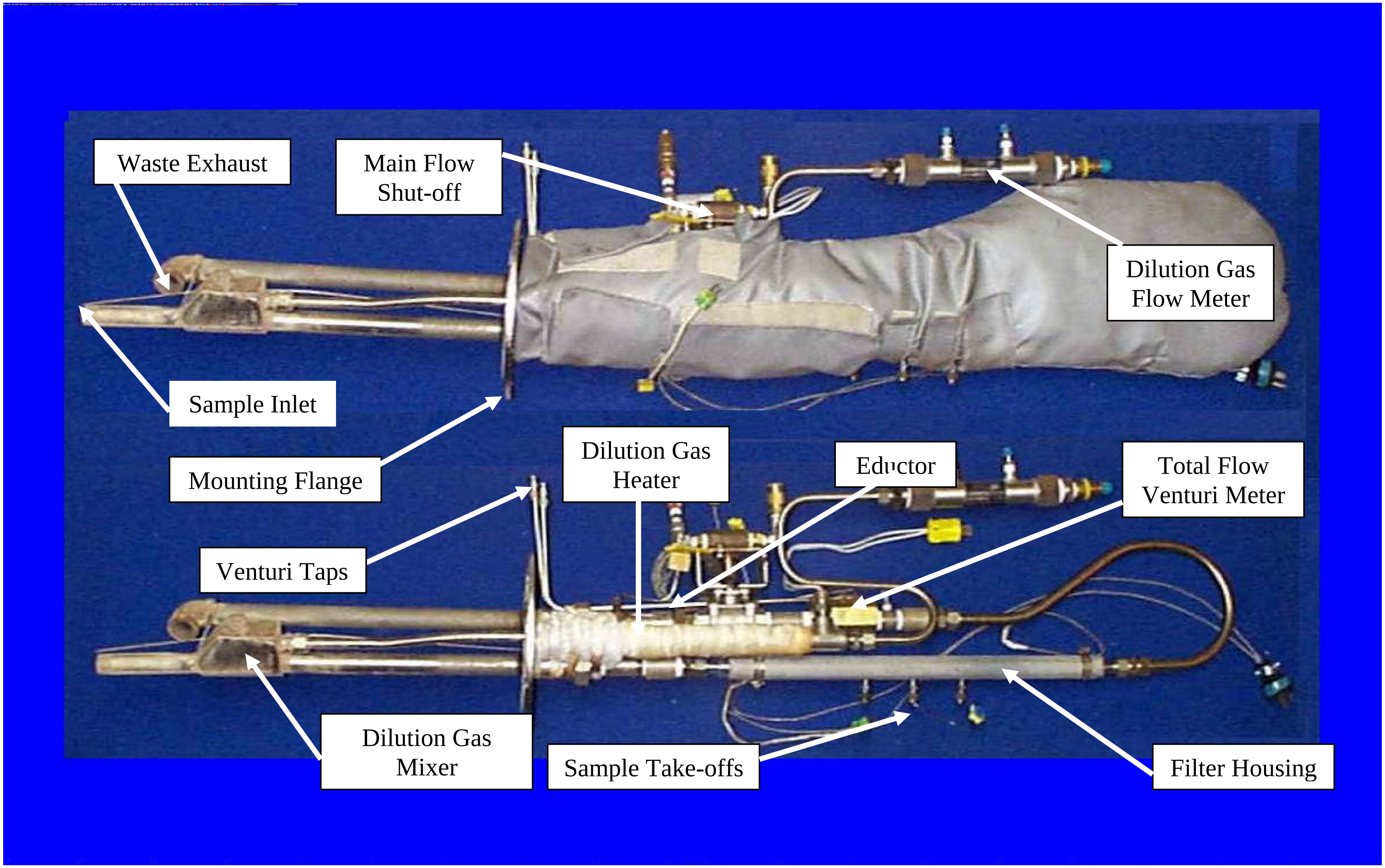


**Figure 8. Modified Apogee QSIS Sampling Probe. Upper: probe with insulating jacket in place. Lower: Probe with jacket removed to show principal components.**

## TESTING AND INSTRUMENT MODIFICATION.

The repackaged prototype system suitable for field trials was delivered to Southern for final assembly and testing on September 8, 2004. Here the prototype was automated with a PLC controller, and tested in both manual and automated run modes using a proven laboratory $SO_3$ generator in Southern's laboratories. Final design of the base sample extraction and transport system (SETS) was completed and the remaining needed components were purchased, received and assembled.

Upon delivery of the prototype monitor it was installed on two caster-equipped frames and set up on SRI's Ash Resistivity Laboratory where a well-proven continuous simulated flue gas stream was available which includes a controllable and reproducible $SO_3$ source. Preliminary calibrations were carried out on the unit, after which a series of tests were made using an $SO_3$ laden stream produced by the resistivity apparatus. Concentrations of $SO_3$ were confirmed by conventional manual controlled-condensation measurements. A PLC controller was also installed and programmed to allow automated operation of the monitor.

A summary of the results of the laboratory tests are provided in Table 1. During the initial testing of the device the results from the monitor were erratic and systematically low, as can be seen in the data from 9/23 and 9/24. At that time the condensor in use was a glass-wool-packed, vertical tube in a water jacket as illustrated in Figure 9. Observation of the flow of water through the condensor revealed that the walls of the condensor were not being uniformly and fully contacted by the wash water. Consequently, when the original condensor broke on 9/24, a helical, coiled-tube condensor was substituted for the straight-tube condensor as shown in Figure 10. Tests of this condensor arrangement on 9/25 resulted in much more reproducible values being obtained. However, the results were still systematically low. It was also noted that the timing sequences suggested by AMETEK did not seem to allow enough time for the wash liquid to completely drain to the measurement cell. The timing was then altered to allow more drainage time and the wash was changed from a single, large-volume wash to two smaller-volume washes in succession. At this point the results shown for 9/26 were obtained. The latter were deemed to be satisfactory and the system was moved from the resistivity lab to the pilot-scale Combustion Research Facility (CRF) for the Task 3 short-term tests of the complete unit, including the modified QSIS probe on an actual flue gas stream. These tests were conducted in the pilot-scale combustor facility on September 28-29, 2004.

It was intended that the tests with flue gas be be carried out on a coal-combustion gas stream in conjunction with another CRF test program. However, hurricane Ivan led to a delay of that test and scheduling conflicts with other programs caused an indefinite postponement of the coal burn. Consequently, in order to complete the short-term $SO_3$ flue gas test in a timely manner, it was decided that the the monitor be tested with the CRF fired by natural gas with SO3 being injectected from two catalytic generators. Two days of testing with the SO3 generators were conducted, beginning with cold start on the first day of testing. Layouts of injection and measurement planes are shown in Figure 11. The results of the CRF tests are shown in Figures 12 and 13. The agreement between the monitor and the CCRM results in these tests was generally good and encouraging.

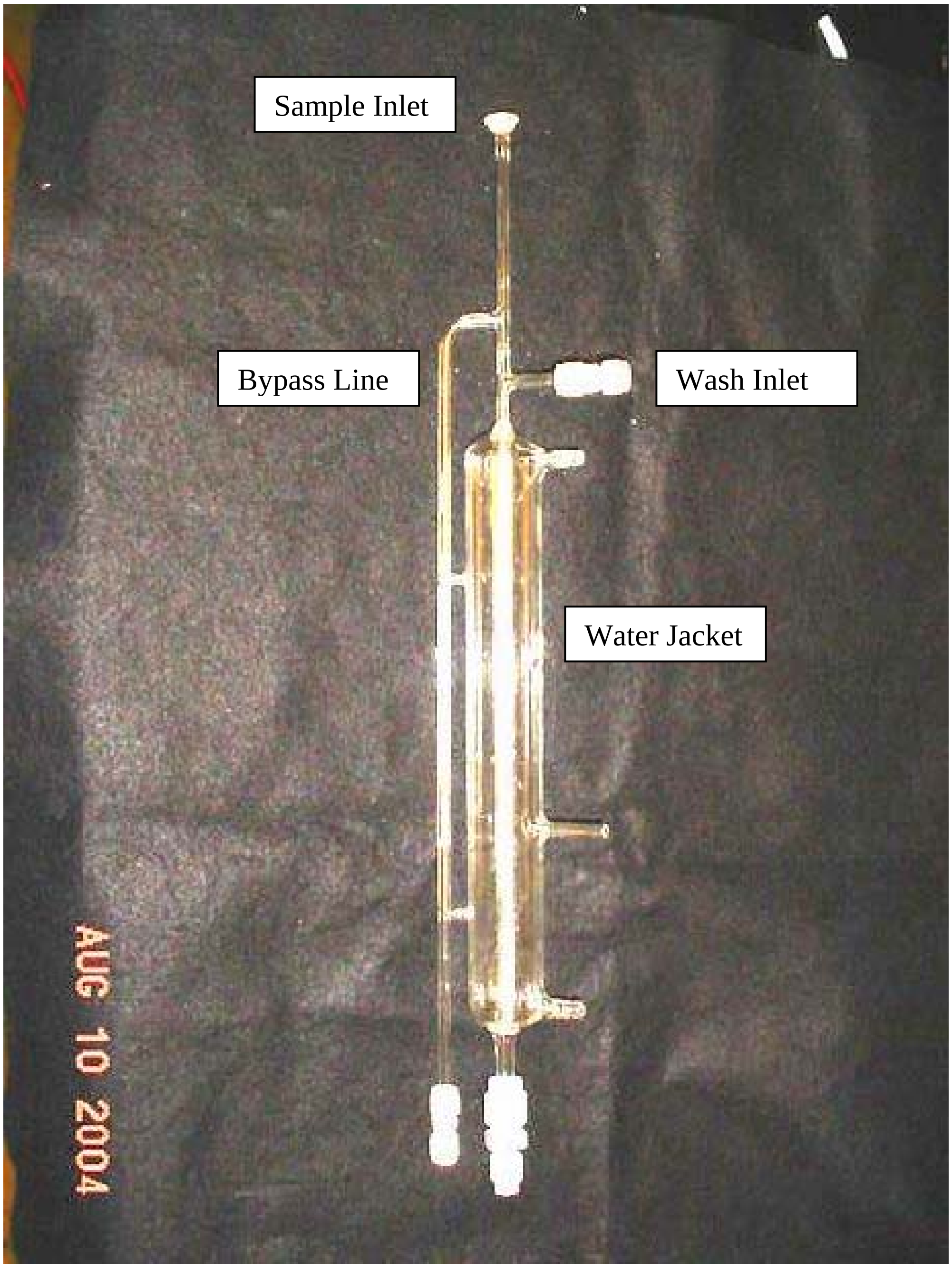


**Figure 9. Original AMETEK condensor assembly for $SO_3$ monitor.**

**Table 1. Tests Using Lab Resistivity System as SO3 Source**

| Date | Time | Monitor $SO_3$, ppm | Controlled Condensation $SO_3$, ppm | Percent Recovery | Comments |
|---|---|---|---|---|---|
| | | | | | |
| 21-Sep | 1442 | | 6.06 | | |
| | | | | | |
| 22-Sep | | | 18.82 | | Increase $SO_3$ concentration |
| | | | | | |
| 23-Sep | 1422 | 10.7 | | 74.6 | insufficient reheat time? Poor wash? |
| | 1435 | 7.7 | | 53.7 | |
| | 1501 | 5.5 | 14.25 | 38.3 | |
| | | | Average: | 55.5 | |
| | | | | | |
| 24-Sep | 920 | 6 | | 41.8 | Significant amount of wash water went to bypass leg. Top end of original condensor assembly broke when wash began for next sample. |
| | 1424 | | 14.44 | | |
| | 1601 | | 14.29 | | |
| | | | | | |
| 25-Sep | 1459 | 9.1 | | 63.9 | Substituted VOST helical coil condensor for straight-tube controlled condensation type. |
| | 1520 | 10.8 | | 75.9 | |
| | 1612 | 10.6 | | 74.5 | |
| | 1657 | 10.1 | | 71.0 | |
| | | | Average: | 71.3 | |
| | | | | | |
| 26-Sep | | 13 | | 91.4 | Automated operation after adding second condensor wash and altering timings to allow complete drainage to cell. Also added post analysis final wash to rinse cell and add idle time at end of measurement cycle to allow reheat before taking next sample. |
| | | 14.7 | | 103.3 | |
| | | 13.8 | | 97.0 | |
| | | 13.8 | | 97.0 | |
| | | | Average: | 97.2 | |
| | | | | | |
| 27-Sep | | | 13.96 | | |
| 24th & 27th Average: | | | 14.23 | | |

Although the results of the tests at the CRF showed reasonable agreement between the monitor and the reference method values, it was noted that the response at low $SO_3$ concentrations was low and very slow to develop. Insofar as the operation of the monitor is concerned, this problem might be ameliorated by increasing the sampling time; however, this reduces the measurement frequency. Assuming that $SO_3/BaCl_2$ reaction is a first-order reaction, it seemed that the reaction rate might be increased by either injecting more of the $BaCl_2$ solution or by increasing the concentration of $BaCl_2$ in the injected reagent or both. Several trials were made, first using multiple injections of the originally recommended 4% $BaCl_2$ solution. These were found to result in marked increases in the rate of development of turbidity for all $SO_3$ concentrations, with the effect being especially evident at low $SO_3$ concentrations as illustrated in Figure 14. Based on these results, the use of a 16% $BaCl_2$ solution is recommended rather than the original 4% solution. With this higher concentration reagent, the monitor can be expected to perform well for SO3 concentrations at the condensor inlet down to 2.5 ppm at with a measurement frequency of two samples per hour. The calibration curve for the unit, based on use of the 16% reagent with a gas sample volume of 20 liters at dry standard conditions is shown in Figure 15. Lower concentrations can be measured effectively by increasing the sampling time although this will reduce the measurement frequency.

Figures 16 through 18 show photographs of the probe and detector systems in use at Southern's Coal Combustion Facility.

In view of the project delays and task budget impacts significant modifications to the initial project scope were necessary. The actual expenditures for Tasks 1 and 2 significantly exceeded original budgets, and the added technical redesign required much of the Task 4 evaluation and design refinement to be conducted on the prototype system before Task 3. Accordingly, inadequate funds remained for the Task 5 long term field component originally planned for the project.

## RECOMMENDATIONS FOR FURTHER DEVELOPMENT.

1. Perform tests utilizing the hot gas dilution system to check for artifact SO3 formation by oxidation of SO2.

2. Perform tests downstream of a scrubber to verify performance when the predominant form of SO3 is condensed-phase H2SO4.

3. Repackage the system in more compact and field usable form.

4. Perform long-term tests of the system in the field.

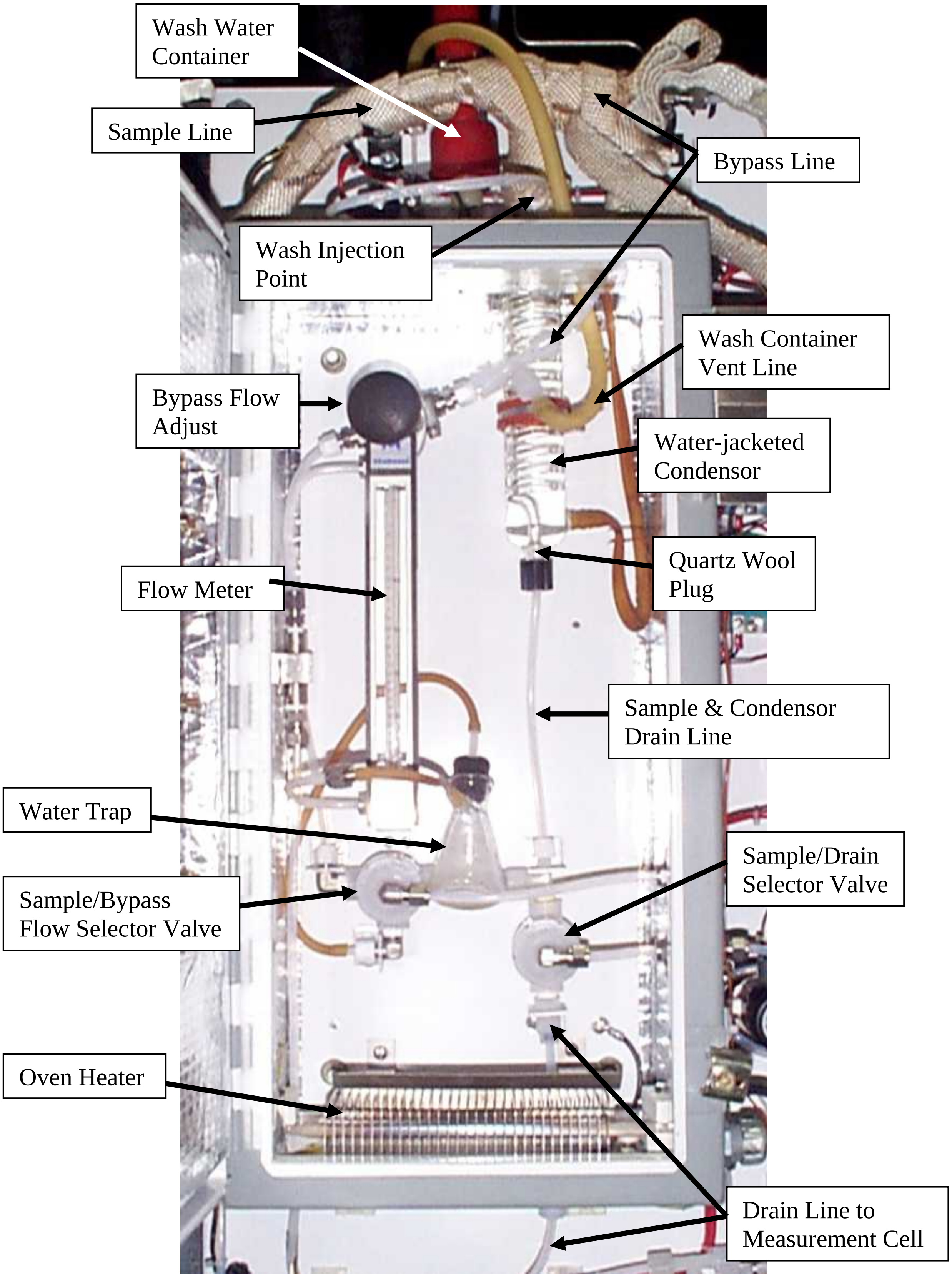
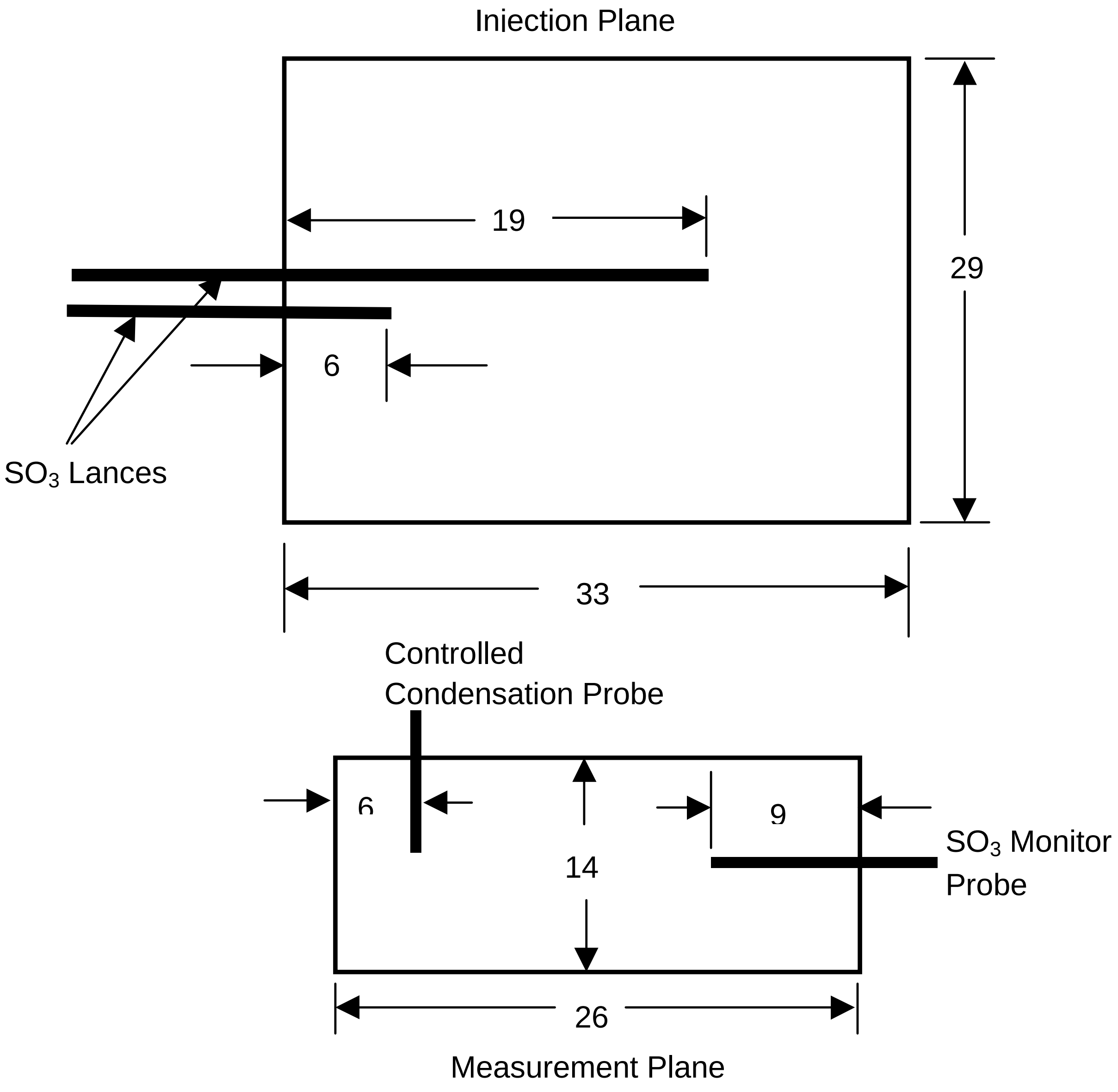


**Figure 10. Condensor assembly in temperature-controlled oven.**



184 inches from injection plane to measurement plane through two shell & tube heat exchangers.

Figure 11. Layout of the CRF $SO_3$ injection and sampling points.

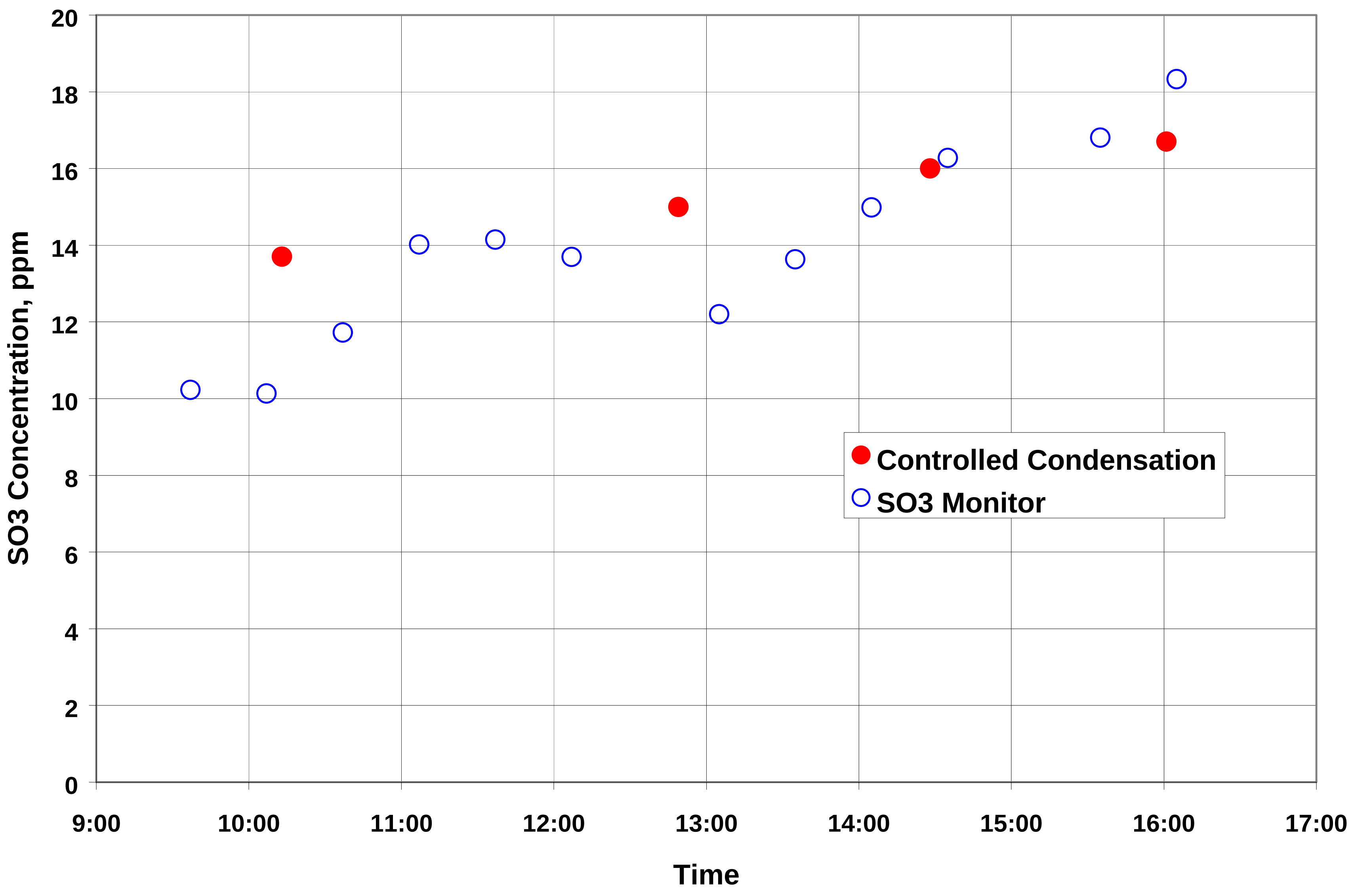


**Figure 12. Concentration *versus* time from the $SO_3$ monitor and controlled-ccondensation measurements on 9/29/2004.**

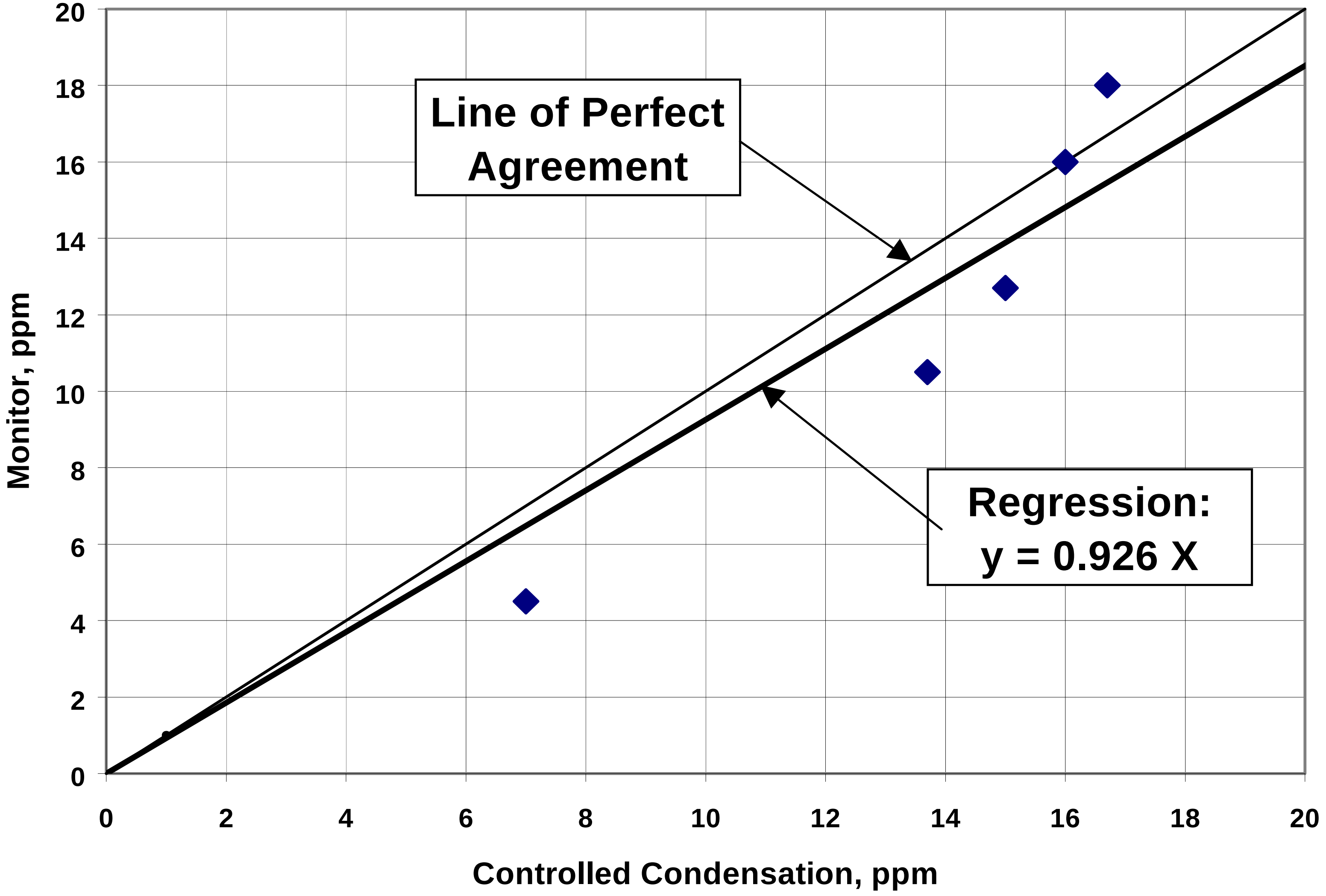


**Figure 13. Comparison of results from contolled condensation and monitor measurements during the natural gas fired combustor tests with $SO_3$ injection.**

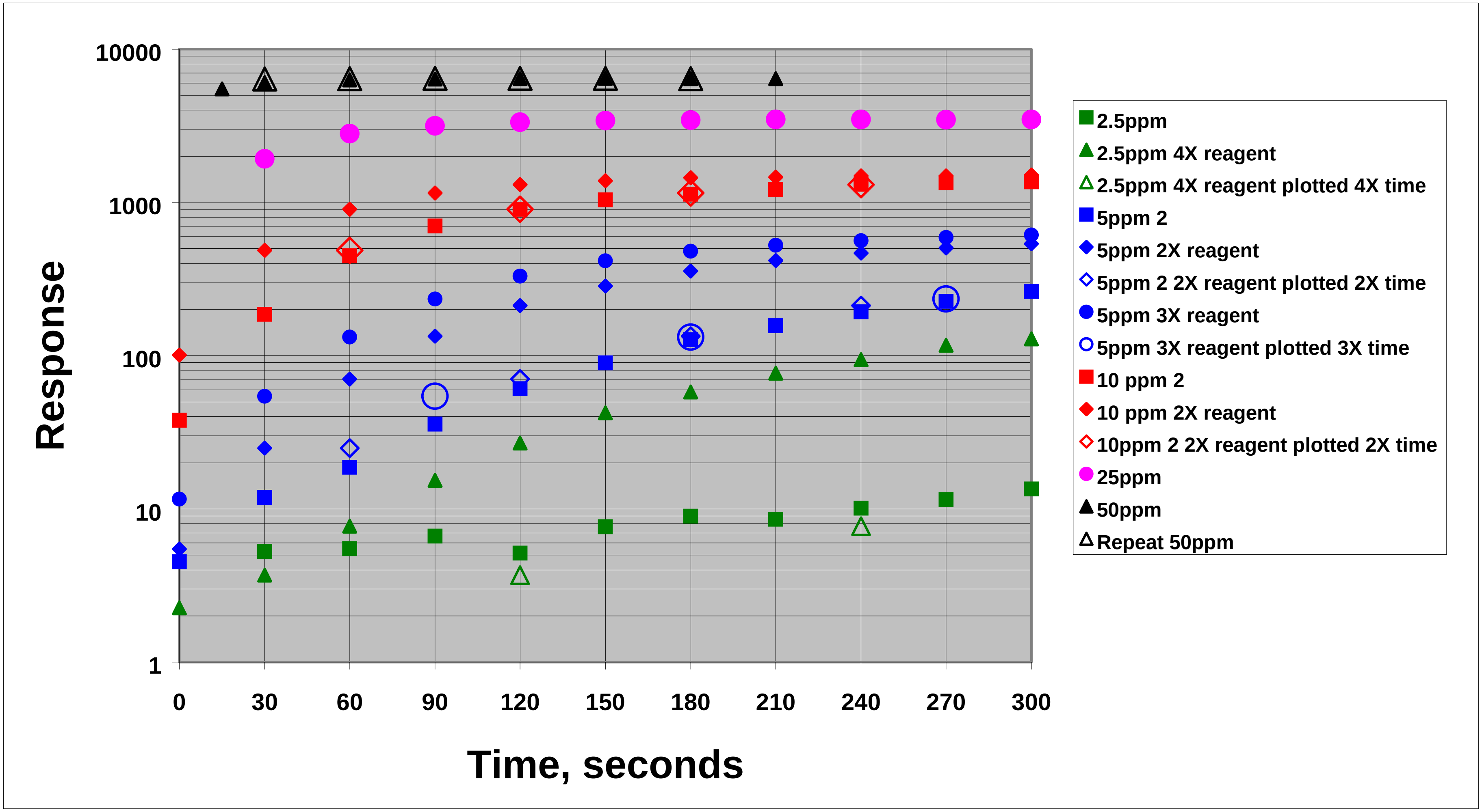


**Figure 14. Monitor response in arbitrary units *versus* time in seconds for several SO3 concentrations and reagent injection quantities. (1 to 4 ml of 4% $BaCl_2$ added)**

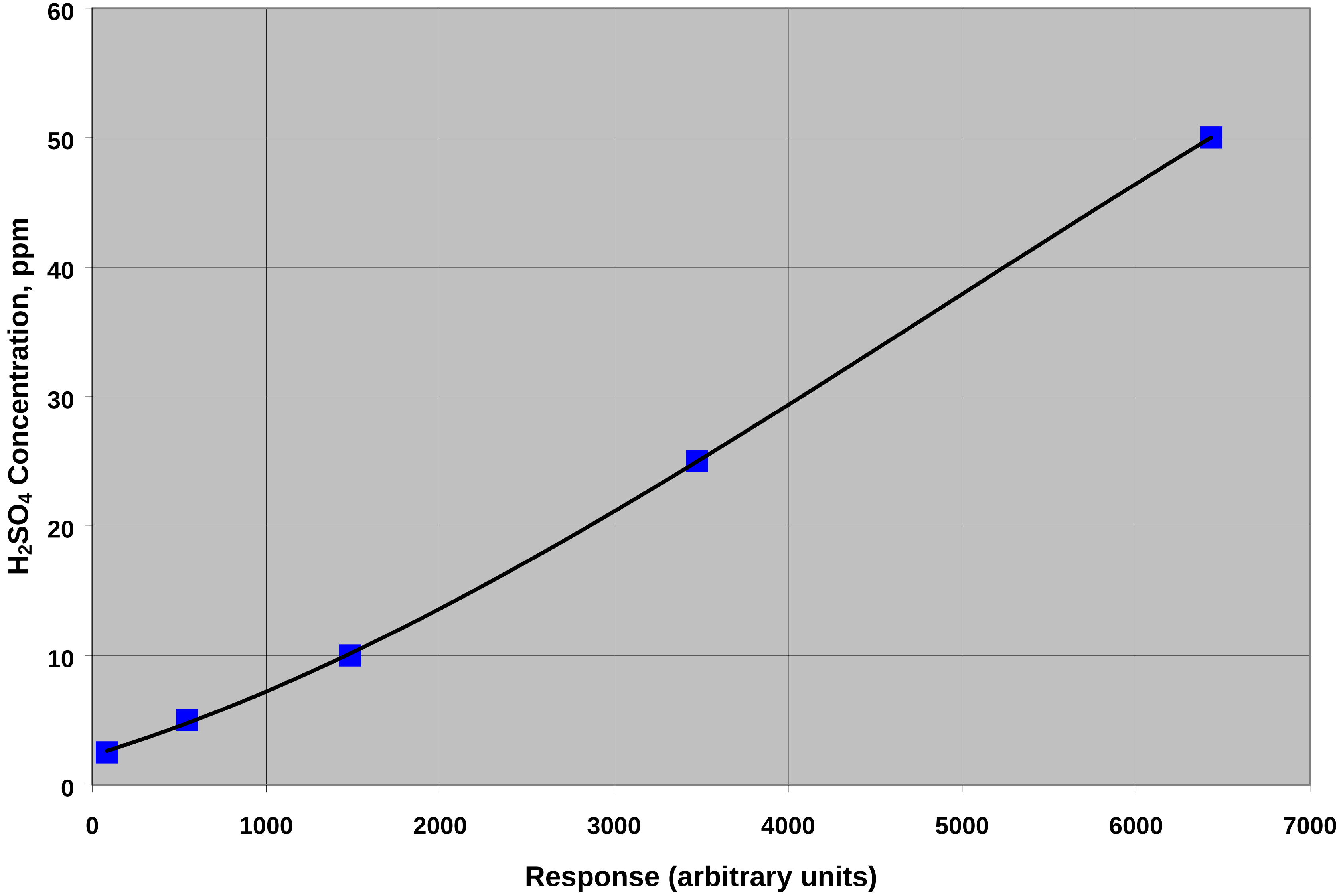


**Figure 15. Calibration curve based on monitor response at 150 seconds after reagent injection for a sampling time of five minutes at a flowrate of 2 dslpm using a 16% $BaCl_2$ reagent solution.**

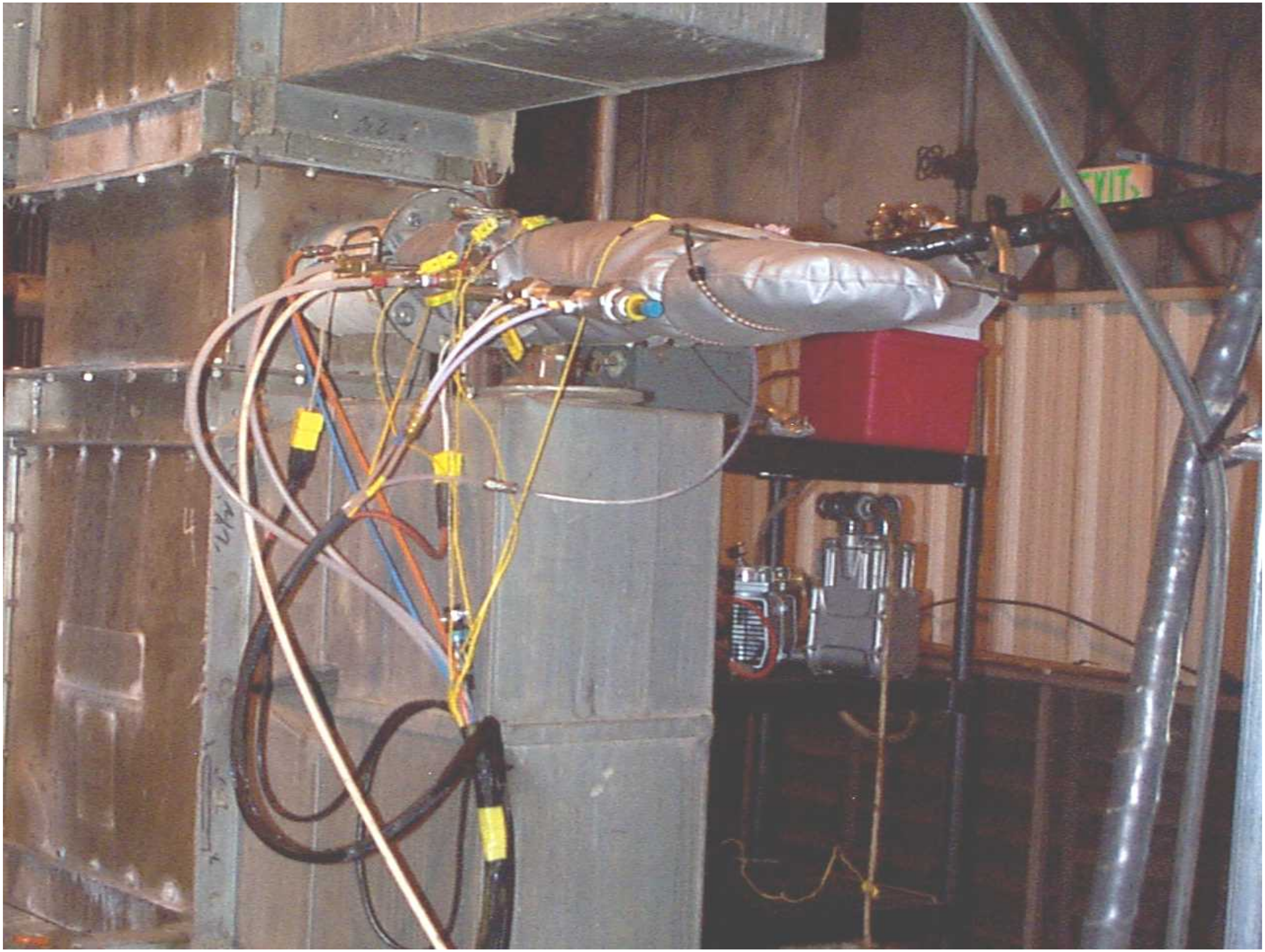


**Figure 16. Photograph of the modified Apogee QSIS probe installed at the nominal 550F sampling location of the combustor.**

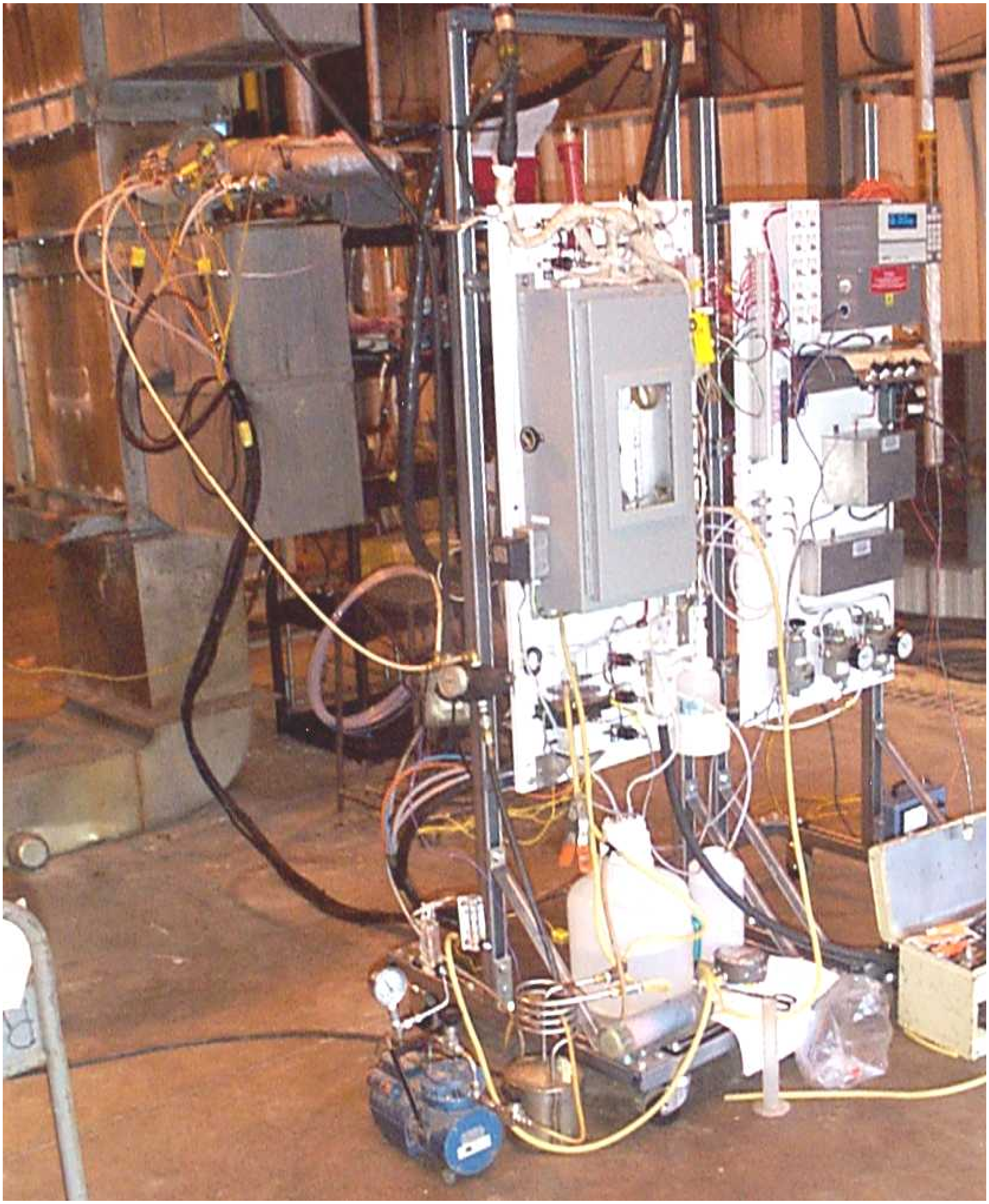


**Figure 17. Photograph of the probe and SO3 monitor. The control and readout electronics are on the right-hand panel. The condensor is in the grey oven on the left-hand panel with the measurement cell mounted under the oven at the lower left of the left-hand panel and the reagent reservoir and injector is mounted on the lower right of the left-hand panel.**

**Figure 18. Photograph of the back sides of the monitor panels. The PLC unit controlling the operation of the system can be seen on the panel to the left while the control system for the Apogee probe in on the panel to the right. The heated hose carrying the sample from the probe to the monitor can be seen near the top of the photo.**

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