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AN AUTOMATED SYSTEM FOR CONTINUOUS MONITORING OF SO_2, NO_2 AND NO_x IN BOILER FLUE GAS

R. K. JEFFREY AND G. K. LEE

FUELS RESEARCH CENTRE

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AN AUTOMATED SYSTEM FOR CONTINUOUS MONITORING OF SO_2, NO_2 AND NO_x IN BOILER FLUE GAS

by

R.K. Jeffrey* and G.K. Lee**

ABSTRACT

This report describes an automated system for continuously sampling, analyzing and recording SO_2, NO_2 and NO_x levels in combustion products such as boiler flue gas. The system employs three parallel-connected, automated wet-chemical analyzers for monitoring each pollutant simultaneously and selectively. Each analyzer is supplied with a clean, moisture-free stream of flue gas which has been accurately diluted and blended with nitrogen to suit the concentration range of the selected methodologies. Response time between sample inlet and readout is 20 min for SO_2 and 7 min for both NO_2 and NO_x.

During the past two years, the system has been used to minitor a wide range of combustion research experiments with a high degree of reliability, precision and accuracy.

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*Technologist and **Research Scientist, Canadian Combustion Research Laboratory, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Bulletin technique TB 131

UN SYSTÈME AUTOMATISÉ POUR LE CONTRÔLE CONTINU DES NIVEAUX DE SO_2, NO_2 ET NO_x DANS LE GAZ D'ÉVACUATION DE CUAUDIÈRES

par

R. K. Jeffrey* et G. K. Lee**

RÉSUMÉ

Les auteurs décrivent au système automatisé d'échantillonnage, d'analyse et d'enregistrement continus des niveaux de SO_2, NO_2 et NO_x dans les produits de combustion comme le gaz d'évacuation des chaudières. Ce système utilise trois analyseurs par voie humide automatisés et reliés en parallèle pour contrôler chaque substance polluante simultanément et sélectivement. Chaque analyseur reçoit un courant de gaz d'évacuation propre et sec qui a été dilué avec précision et mélangé à de l'azote afin de le rendre compatible avec la gamme de concentrations propre à la méthode choisie. Le temps écoulé entre l'admission de l'échantillon et la lecture du résultat est de 20 minutes pour SO_2 et de 7 minutes pour NO_2 et NO_x.

Au cours des deux dernières années, le système a été utilisé pour le contrôle d'un large éventail d'expériences sur la combustion avec un haut niveau de fidélité, de précision et d'exactitude.

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*Technologue et **chercheur scientifique, Laboratoire canadien de recherches sur la combustion, Centre de recherche sur les combustibles, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

One of the prime considerations in monitoring effluents from combustion processes is the need for a large volume of reliable, definitive data to characterize the formation, evolution and emission of SO_2, NO_2 and NO_x[1] and to evaluate their effects on environmental air quality.

In the past, manual wet-chemical methods have been used exclusively to analyze sequential batch samples of combustion gas. However, the usefulness of these samples is considerably reduced because both the composition of the sample components and the combustion conditions may change significantly during the time required for sampling and analyses. Thus, continuous measurement of specific pollutants in flue gas is an essential adjunct to research on control of emissions from heat processes. Emissions of particular interest are those that can be controlled by flame aerodynamics, thermal loading, or chemical neutralization.

A survey of available instruments for continuous measurement of SO_2, NO_2 and NO_x revealed that all of the present analytical methodologies were either non-specific or only suitable for ambient air analysis. Subsequently, one instrument, utilizing micro wet-chemical procedures for ambient air analyses, was found to have the necessary reliability, flexibility and sensitivity for adaptation to monitoring corrosive, dust-laden combustion gases, where pollutant concentrations are about 2000 times higher than in ambient air. This instrument, known as an Autoanalyzer[2], consists of a train of interconnected modules which automatically perform the selected analytical functions in a continuously-flowing, segmented stream of absorbent containing the pollutant of interest. The Autoanalyzer yields accurate, reproducible measurements of SO_3, NO_2 and NO_x, when incorporated with a

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[1] NO_x = total toxic nitrogen oxides = $NO + NO_2$

[2] Technicon Corporation.

specially-designed sampling and preparation module, that cleans, heats and dilutes a sample stream of combustion gas prior to analysis. This report describes the components, functions and operation of both the sampling and preparation module and the Autoanalyzer train. It furthermore indicates the emission levels of SO_2, NO_2 and NO_x from actual combustion research experiments.

ANALYTICAL METHODOLOGIES

General

SO_2, NO_2 and NO_x are three of the most extensively investigated of all air pollutants, because of their known harmful effects to the environment. However, many methodologies for analyses of minor constituents in combustion gases are susceptible to significant errors, including unknown effects of interferences, normal daily variations in analytical technique, and contamination from glassware. These problems have been successfully overcome by the use of automated wet-chemical procedures in which absolute measurements are replaced by ratio comparisons.

The Autoanalyzer is essentially a continuous flow system that is designed to monitor automatically minor constituents in gaseous mixtures by micro-wet-chemical methods. In this flow system, the gaseous constituent of interest is removed selectively by an absorbent, contacted with additional reagents if necessary, and complexed with a colour indicator. The liquid stream containing the absorbed gas is then blended and conditioned until the colour indicator reacts with the absorbed gas to produce a reaction product having a distinctive colour. The colour intensity of the stream, which is measured in a continuous flow cell, is recorded on a calibrated chart that provides a direct reading of the concentration of the absorbed constituent. The analyzer system is standardized periodically by means of an automatic programmer against known standards to ensure accuracy. The methodologies adapted for use with the A utoanalyzer are internationally accepted as being specific for the component of interest and are described in the following sections.

Sulfur Dioxide

The West-Gaeke method (1) as modified by Welch and Terry (2) is used for analyzing sulfur dioxide. In this method, SO_2, after being absorbed in a solution of sodium tetrachloromercurate, is reacted with dilute formaldehyde and complexed with bleached pararosaniline hydrochloride to produce a magenta-coloured dye. Sulfamic acid is added to the analyte stream (absorbent plus pollutant) to eliminate interference in colour development due to nitrogen dioxide. The final solution first passes through a 10-min time-delay coil at 37°C, where colour development proceeds to completion, and then through a colorimeter for specific quantitative analysis. The light transmittance of the coloured solution is proportional to the SO_2 present in accordance with the Lambert-Beer law when measured at a wavelength of 560 mμ. SO_2 concentrations up to 2.0 ppm v/v can be accurately determined by this technique.

Nitrogen Dioxide

Nitrogen dioxide (NO_2) is determined by a procedure developed by Yunghans and Monroe (3). In this procedure a modified Saltzman reagent, comprising a combined solution of glacial acetic acid, sulfanilic acid and N-1-naphthylethylenediamine dihydrochloride, is used to absorb NO_2 selectively. The modified Saltzman reagent, after reaction with NO_2, produces a distinctive violet colour, which can be quantitatively monitored by a colorimeter. The light transmittance of the coloured solution when measured at 555 mμ is proportional to the NO_2 present in accordance with the Lambert-Beer law. The method is valid for NO_2 concentrations up to 0.4 ppm v/v.

Total Nitrogen Oxides

In the determination of total nitrogen oxides (NO_x), chromium trioxide paper is used as an oxidant to convert any nitric oxide (NO) to nitrogen dioxide (NO_2). The total oxides of nitrogen ($NO + NO_2 = NO_x$) are then determined by the procedure of Yunghans and Monroe (3). It follows that the level of NO in the gas sample is the difference between the NO_x and the NO_2 levels.

POLLUTANT MONITORING SYSTEM

Gas Sampling and Preparation

The sampling and preparation module developed for the continuous monitoring of SO_2, NO_2 and NO_x in boiler flue gas is shown schematically in Figure 1. It consists of a 24 in. x 16 in. x 16 in. constant-temperature oven which houses the following items:

(a) a 3/8-in.-O.D. x 6-in.-long stainless-steel gas-sampling probe, attached to a 14-in. stainless-steel flexible metal hose connector with quick-connect fittings;

(b) a high-efficiency stainless-steel cyclone dust collector (4), 1-1/2 in. O.D. x 6 in. long, for removing all +10 micron particulate matter, Figure 2;

(c) a 1-in.-O.D. x 4-in.-long stainless-steel filter charged with quartz wool to remove fine particulate matter, Figure 2;

(d) a diaphragm pump having a minimum capacity of 4 scfm at 3 in. Hg;

(e) a 500-cc glass expansion flask fitted with a fritted tube to minimize pulsations in the flue-gas flow;

(f) two parallel-mounted micrometer valves and flowmeters to regulate flow of flue gas to two entrainment-type gas blenders;

(g) two parallel-mounted entrainment-type blenders for mixing flue gas with diluent gas;

(h) a by-pass throttle valve to control pressure and flow of flue-gas sample to the flowmeters (f);

(i) a dial thermometer;

(j) located at the front of the oven are a thermoregulator for controlling oven temperature, and a power switch for the diaphragm pump.

The following components are mounted externally on the right side of the oven behind a protective screen:

(k) the diaphragm pump motor;

(l) two needle valves and flowmeters to regulate flow of diluent gases;

(m) two 300-cc, parallel-connected glass accumulator flasks. One flask supplies the SO_2 absorption column, while the other supplies both the NO_2 and NO_x absorption columns;

(n) remote control knobs for the micrometer valves (f) and the throttle valve (h).

The flue-gas sampling and preparation module serves three important functions. First, by maintaining the flue-gas-sample lines at a minimum temperature of 165°F, large systematic errors due to absorption of SO_2, NO_2 and NO_x by condensed moisture are eliminated. Second, by ensuring a supply of dust-free flue gas to each of the entrainment-type blenders, optimum conditions are provided for accurate metering and mixing of the flue gas with diluent gas. Third, by diluting the pollutant concentration of the flue gas to less than 1.0 ppm, methodologies developed for selective analyses of ambient air can be used. The diluted flue gas leaving each blender flows under pressure at about 2 in.W.G., via the two parallel-connected accumulator flasks, to the three gas-absorption columns described below. Total lag time between the sample probe and the inlet to the gas absorption columns is kept to less than 15 sec by selecting small internal diameter transport lines of minimal length.

The Autoanalyzer Train

General

The essential benefits of using the analyzer system for monitoring selected pollutants are:

(a) Continuous automated sampling and analysis increases the precision, for monitoring accuracy, of a given microchemical methodology.

(b) Sample and reagent introduction, reaction and mixing time, temperature control, measurement of ultimate end products, and automatic standardization to reagent base line are all accurately programmed. With such a system, exact flow conditions are automatically maintained and reproduced from sample to sample.

(c) The system, being continuous and automatic, increases productivity and provides quantitative data on any fluctuations in stream composition. Thus, remedial control measures can be taken during a test.

(d) The cost of automated sampling and analysis is much less than with comparable manual methods.

(e) The system is adaptable to nearly all types of manual wet-chemical analyses and can be converted from monitoring one chemical component to another is less than one hour.

Details of the Autoanalyzer system for analyzing SO_2, NO_2 and NO_x are described below.

Gas Absorption Trains

The three gas-absorption trains for SO_2, NO_2 and NO_x are mounted vertically on a perforated steel panel. Each gas-absorption train (Figure 3) consists of a "T" manifold, a helical absorption column packed with glass beads, a gas-liquid separator, a moisture trap, a needle valve, and a flowmeter. Diluted flue gas from the sampling and preparation module is pumped continuously to the manifold at the top of each column, where a portion of the gas is drawn into the column and contacted with absorbing solution; the excess gas is vented to atmosphere and maintains the column inlet at room pressure. Both the gas sample and the absorbing solution cascade concurrently down the column, where the pollutant of interest is scrubbed from the gas. At the base of the column, the pollutant-free gas is separated from the analyte solution (absorbent plus pollutant) and aliquots of the analyte solution are continuously withdrawn by the proportioning pump for microchemical analysis. The scrubbed gas is split into two streams, a very minute portion being utilized for air segmentation of the analyte solution during analysis, with the balance passing through the moisture trap before being exhausted to atmosphere. The gas-flow rate through the gas absorption columns is regulated by the needle-valve-and-flowmeter combination at the outlet of the moisture trap.

In general, column absorption efficiencies for any chemical pollutant may range from 95% to 100%, depending on coil length, coil tube diameter, bead diameter, ratio of flue gas to liquid absorbent flow rates, and concentration of the liquid absorbent.

Proportioning Pump and Manifold Assembly

The proportioning pump and manifold assemblies are the heart of the analyzing system. Each pump-manifold assembly introduces, meters and mixes both absorbing solution and reagents, segments the analyte stream with analyte-free gas, and moves the segmented stream through the other modules in the system.

A. Proportioning Pumps

The drive mechanism on each of the peristaltic proportioning pumps consists of two parallel stainless-steel roller chains that are bridged by five stainless-steel rollers. The chain-and-roller assembly moves in an elliptical path so that the rollers contact and move along a spring-loaded bakelite platen. When the chain-and-roller assembly is locked into position, continuous pressure is exerted on the platen, and the constant-speed gear motor is electrically activated. A manifold, which can hold up to fourteen plastic metering tubes, each having a constant wall thickness, is located between the platen and the roller. As the roller moves over the metering tubes, pressure occludes the tubes at the moving point of contact as shown in Figure 4. This pushes fluids forward through the tubes and draws more fluids into the tubes from behind. The volume of fluid aspirated and moved into the system by this process ranges from 0.015 cc/min to 3.9 cc/min and is proportional to the inside diameters of the pump tubes.

By selecting specific pump-tube diameters, fixed proportions of the absorbent, analyte, analyte-free gas and reagents are uniformly and simultaneously pumped through the system. This technique assures precise, reproducible and accurate determinations.

Separation of the analyte stream into aliquots by analyte-free gas segmentation is a unique procedure for efficient mixing of liquids and effective cleaning of reaction coils. The "gas bubble" also prevents any contamination by back diffusion into subsequent aliquots of the analyte stream, and acts as a receptacle for released gas that may be analyzed if desired.

B. Manifolds

Each manifold, complete with metering, segmenting, reacting and mixing components, is mounted on a plastic platter to facilitate storage, to reduce breakage, to protect the pump from spillage, and to provide for easy access to all components. All manifold assemblies, Figure 4, consist of the following basic parts:

(a) Pump tubes, glass fittings and polythylene nipples for interconnecting manifold pump tubes and coils (The fittings also permit confluence or separation of reagents and air segmentation or debubbling of the analyte stream.)

(b) Mixing coils.

(c) Time delay coils.

(d) End blocks which hold and control the tension of the metering tubes on the pump platen.

(e) A platter which holds the above parts in an optimum layout.

(f) A reagent coupler.

Figures 5 and 6 are flow diagrams showing how the methodologies selected for analyses of SO_2, NO_2 and NO_x are incorporated into each manifold.

Sulfur Dioxide Heating Bath

The sulfur dioxide heating bath, Figure 7, ensures optimum time-temperature conditions for colour development of the SO_2—indicating reagents. This module, which is kept at a constant temperature of 37 ± 0.08°C by a thermoregulator-heater element, contains a 2.6-mm-O.D. x 1.6-mm-I.D. x 40-ft-long glass coil that provides a residence time of 10 min for the analyte stream. A motorized stirrer continuously circulates the liquid to maintain a uniform bath temperature.

Colorimeter-Recorder System

Each of the three colorimeters, Figure 7, continuously monitors the concentration level of an analyte stream (or standard) which passes through a tubular flowcell, Figure 8. Any increase in the concentration of the pollutant of interest causes a corresponding increase in the colour intensity of the liquid sample stream, which in turn results in a proportional decrease of light transmitted through the flowcell. Each flowcell has a light path of 50 mm and a volume of about 0.3 ml; thus, high sensitivity and rapid response times are assured. The colorimeter employs a single prefocus lamp which provides twin light beams. One beam passes through the sample flowcell to a permanently stable photocell, while the other beam passes directly to an identical reference photocell. The ratio of the sample voltage to the reference voltage is continuously transmitted to a null-balance system of a recorder which plots a permanent record of analysis. Two variable-speed, 12 in. strip-chart recorders are employed in the system: a single-pen unit logs the SO_2 concentrations, while a dual-pen, twin-channel unit logs NO_2 and NO_x concentrations simultaneously. Each of the three null-balance ratio recording systems is equipped with an automatic baseline compensation circuit to eliminate both chemical and instrumental drift. Liquid standards are automatically introduced into the analytical train at predetermined times and the compensation mechanism automatically restores the stylus to the initial predetermined setting (i.e. zero, baseline, or a standard value of known concentration). The three compensation circuits can be automatically or manually energized by a programmer unit, described below.

Range Expander

The function of the three range expanders, Figure 7, is to improve the readibility of limited-range tests on the recorder. To permit interpolation within scale divisions on the recorder strip-chart, each range expander is used to electronically magnify the stylus deflection in its own circuit by interposing appropriate resistive networks in the recorder slidewire circuit. Three magnification factors, 2X, 4X and 10X, permit the magnification to full scale of any 50%, 25% or 10% portions of the recorder scale respectively. Electrically, the range expander is positioned between its particular colorimeter and recorder circuit.

Programmer Unit

The programmer unit, Figure 7, permits each of the three analyzing trains to monitor either the analyte stream or the baseline solution (unreacted absorbing reagent) in any preselected sequence and time interval. It can be energized manually or set automatically to supply any selected solution to an analyzer by means of two-way teflon solenoid valves. Essentially, the programmer consists of a synchronous motor driving a series of cam-operated microswitches. The microswitches control the closure time of the two-way solenoid valves and are programmed to provide any desired time cycle through an adjustable split-cam mechanism. The time for one complete revolution of the timer can be controlled by installing the correct gear rack and timer motor. Lamps indicate whether the analyzing systems are on SAMPLE stream or STANDARD solution.

Voltage Stabilizers

Three stabilizer transformers individually supply each colorimeter with a constant 115-volt AC power source for operating the photometer lamp. A stabilizer lamp voltage of 6.0 volts AC is maintained despite line fluctuations ranging from 100 to 140 volts. The colorimeter is the only module that operates from the transformer.

Ancillary Equipment

Vacuum Pumps

Two radiant-cooled, direct-drive vacuum pumps continuously draw the diluted flue gas down through the gas absorption columns. One pump supplies the two absorption columns for NO_2 and NO_x respectively. Each pump is rated at 0.3 scfm at 10 in. Hg vacuum.

Leak detectors continuously monitor the condition of the metering tubes on each manifold. Should leakage from the pump tubes form a bridge between two platinum strips located across each pump platen, the affected pump will automatically be shut down and an alarm will be triggered simultaneously. Starting and stopping of each proportioning pump is controlled by the power switch on its corresponding leak detector.

Circulating Fan

A 400-scfm squirrel-cage fan, mounted on the top of the analyzer cabinet, serves two functions. The first is to pressurize the analyzer cabinet with filtered air at 0.05 in. W.G. to prevent dust and corrosive fumes from contacting the analyzer modules, while the second is to maintain the analyzer cabinet at constant ambient temperature to minimize instrument drift.

All Autoanalyzer equipment modules are mounted in a movable cabinet which is equipped with a power circuit to supply the electrical components of the system. The wiring diagram for the cabinet is shown in Figure 9, and a schematic layout of the SO_2, NO_2 and NO_x monitoring system is shown in Figure 10. Figure 11 is a photograph of the cabinet-mounted Autoanalyzer equipment, together with the flue gas sampling and preparation module.

SO_2, NO_2 AND NO_x MEASUREMENTS

To illustrate some of the major advantages of continuously monitoring SO_2, NO_2 and NO_x in flue gas, four Autoanalyzer charts from actual combustion research experiments are reproduced in Figures 12, 13, 14 and 15.

Figure 12 shows that instantaneous SO_2 levels fluctuated from 768 to 448 ppm over a 73-min period while burning a solid fuel at constant excess air; by comparison, a 20-min batch sample yielded an average SO_2 reading of 595 ppm. Figure 13 shows the time at which a large increase in excess combustion air caused a corresponding decrease through dilution in the SO_2 level emitted by an oil flame.

In Figure 14, it is evident that both NO_2 and NO_x levels increased significantly when the fuel to the burners was switched from residual oil to pulverized coal with constant excess air. Figure 15 shows clearly the effect of flame luminosity on emissions of NO_2 and NO_x. With the blue, non-luminous oil flame, NO_2 and NO_x levels were both about 9 ppm, while with the yellow, luminous oil flame NO_2 and NO_x levels stabilized at 2.5 and 32.5 ppm respectively.

CONCLUSIONS

By continuously monitoring SO_2, NO_2 and NO_x in flue gas, using automated wet-chemical methodologies, it is possible to eliminate virtually all interferences and schematic errors that are inherent in batch sampling and analyses. Furthermore, the capability for detecting and recording momentary changes in emission rates of these pollutants has provided new information on the effects of both combustion conditions and fuel quality on pollutant fixation processes.

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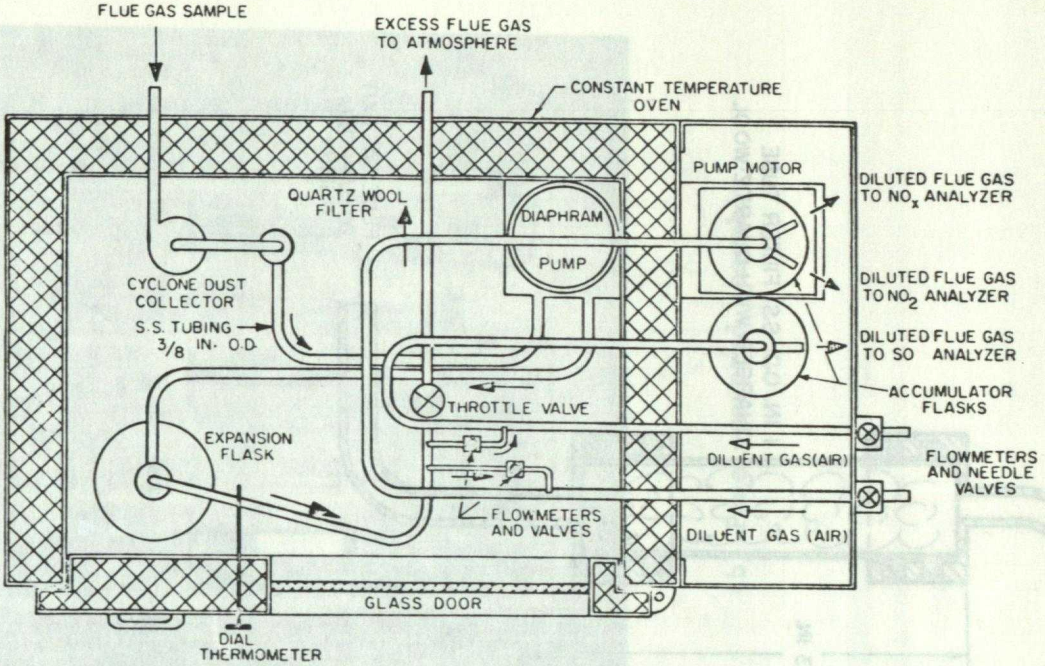
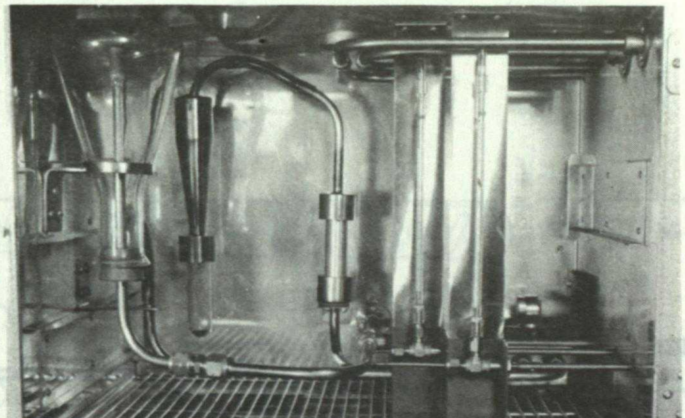


(a) Schematic top view.



(b) Front view

Figure 1. Flue-gas sampling and preparation module.

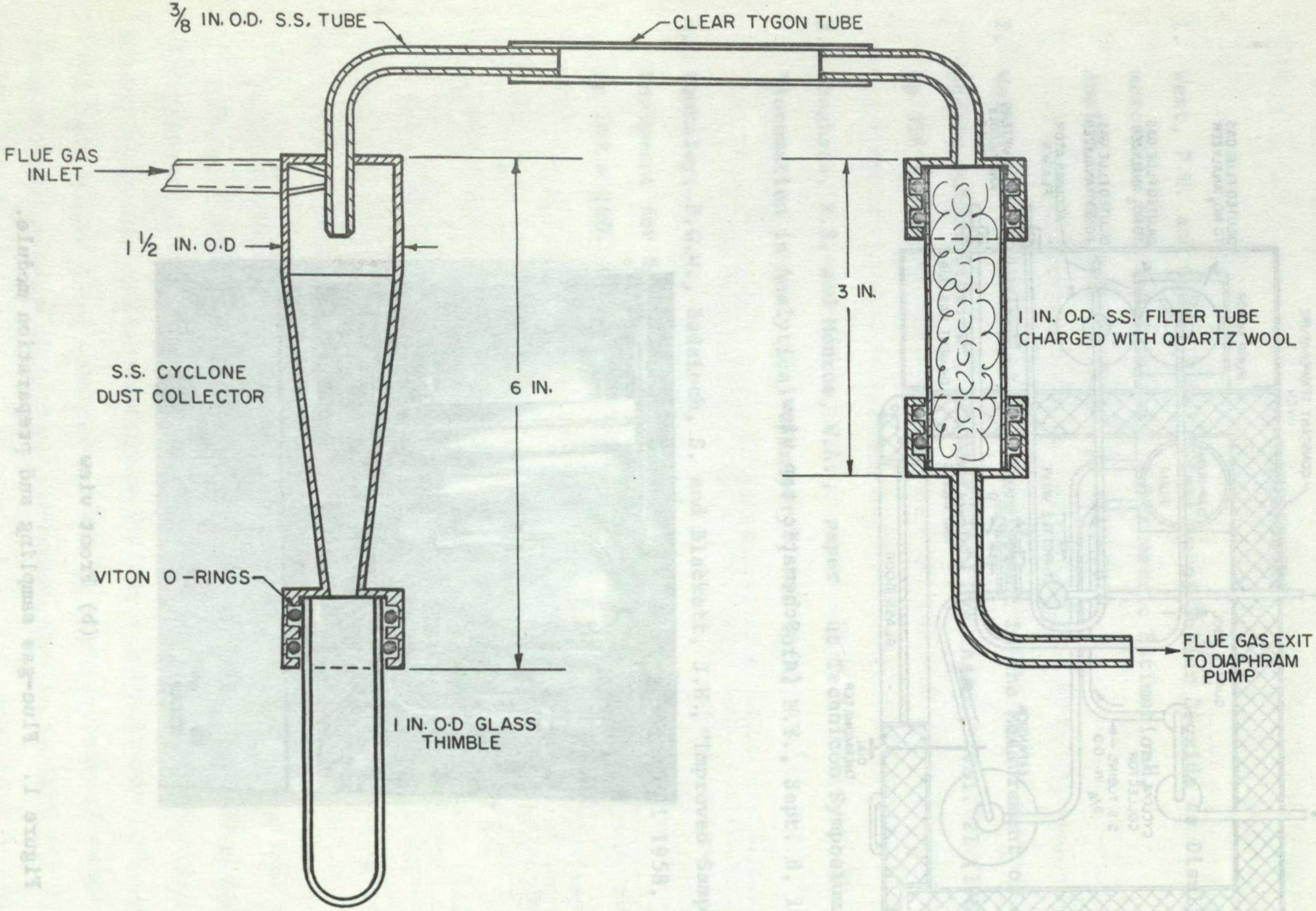
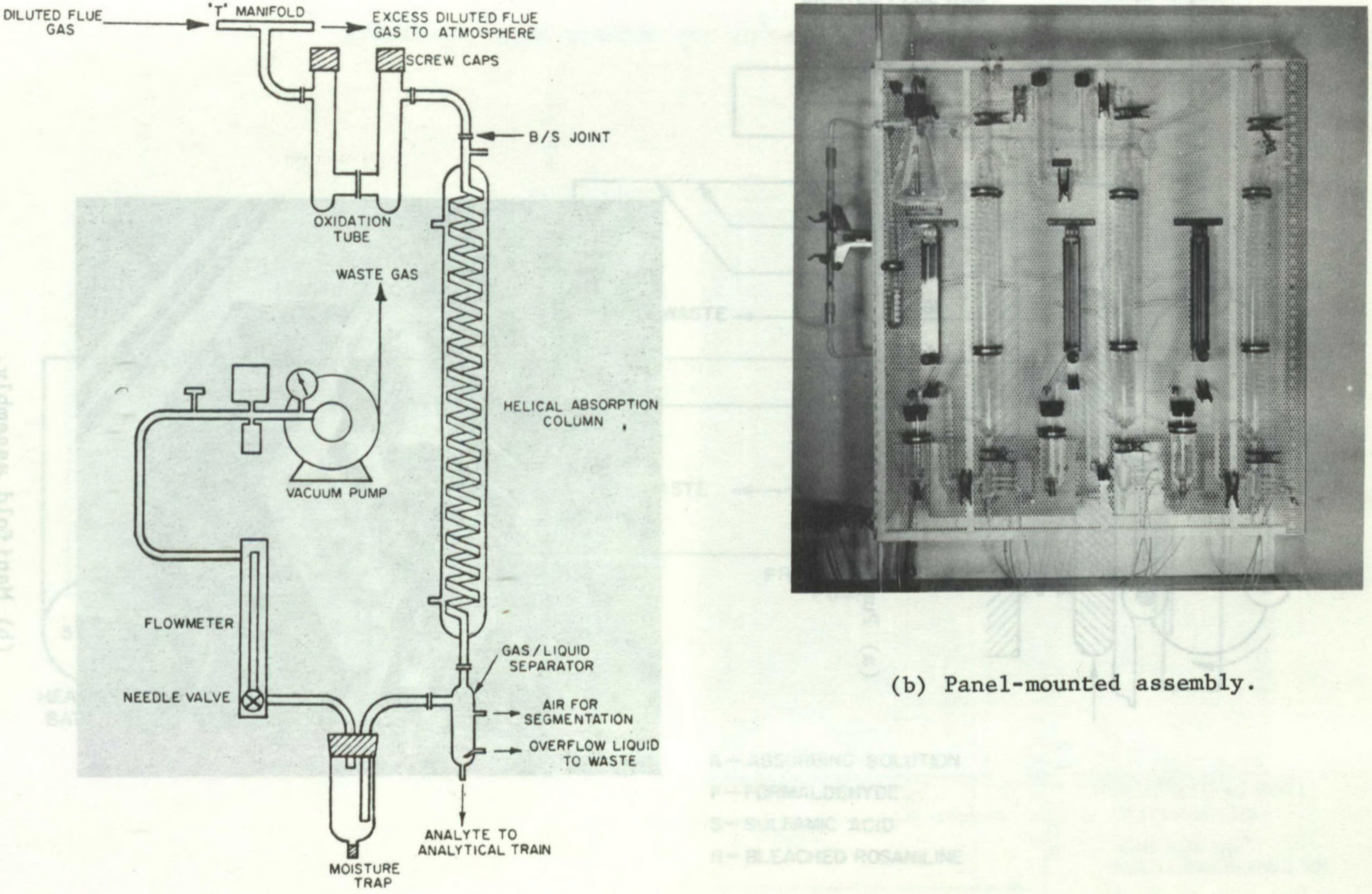


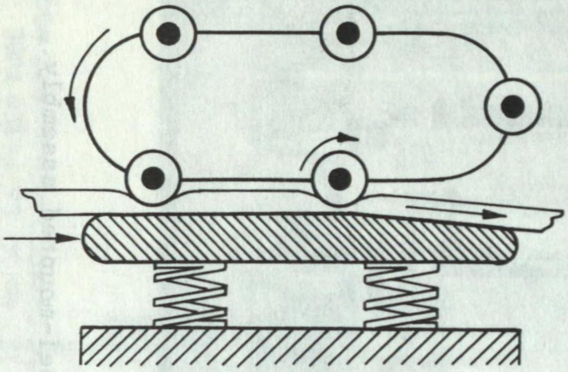
Figure 2. High-efficiency dust collector system.



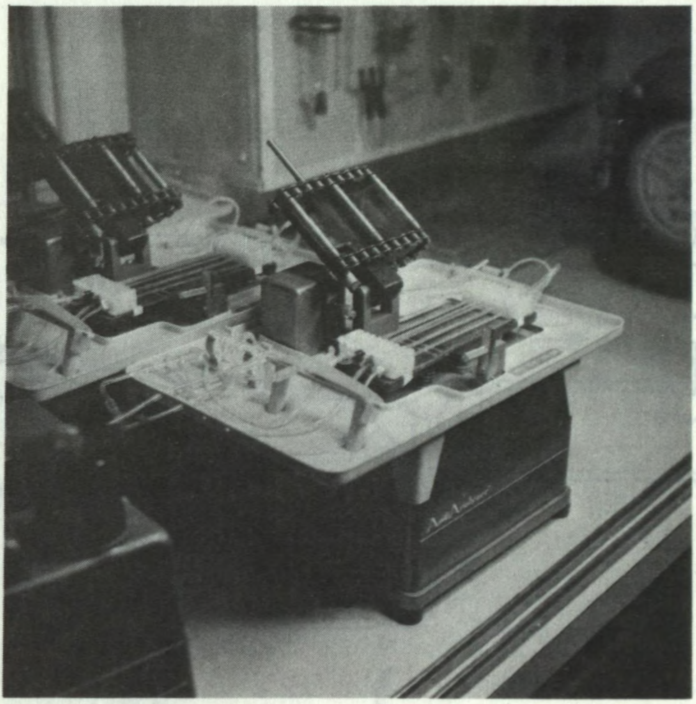
(a) Schematic illustration.

(b) Panel-mounted assembly.

Figure 3. Gas absorption train.



(a) Pump drive mechanism.



(b) Manifold assembly.

Figure 4. Proportioning pump.

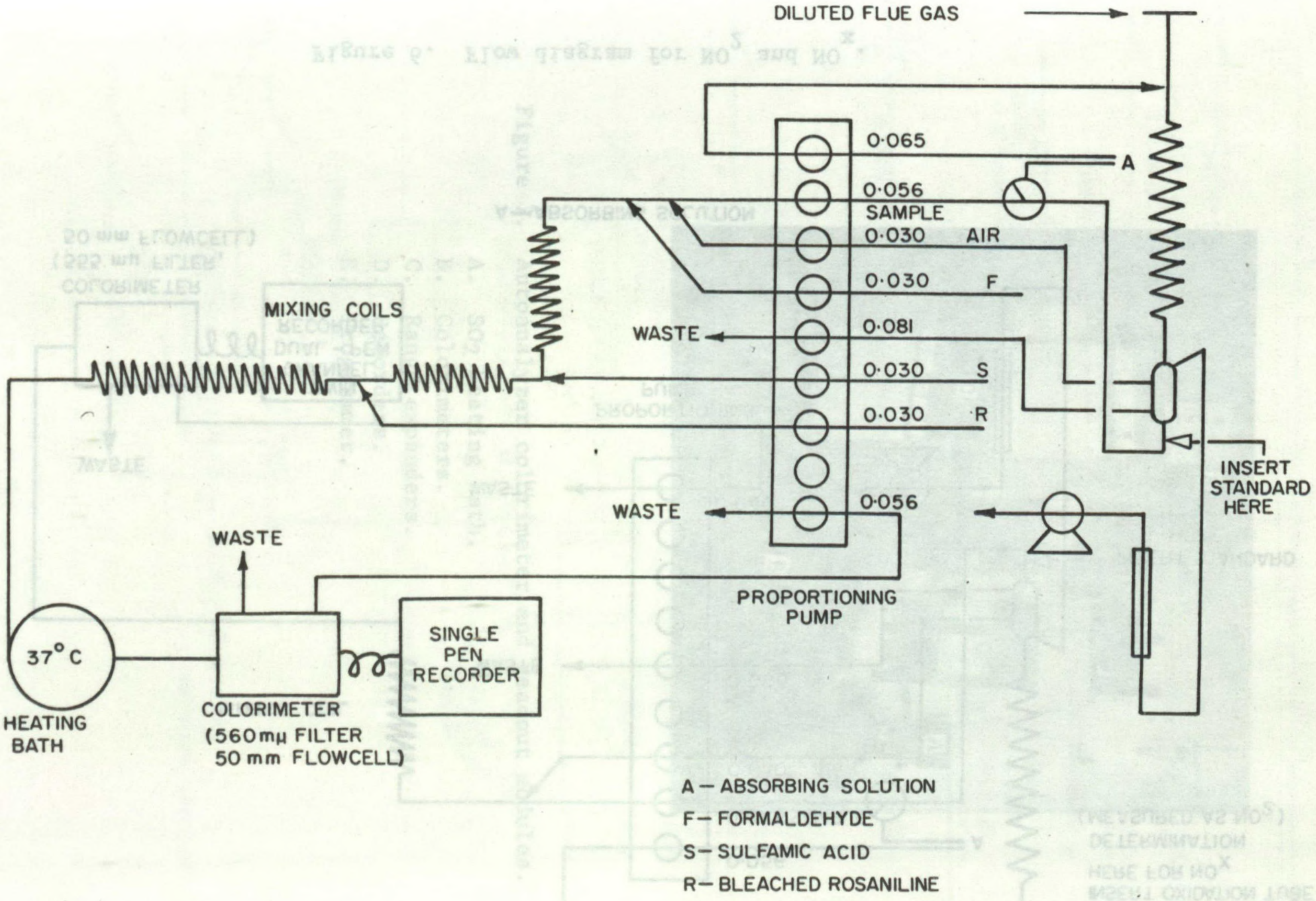


Figure 5. Flow diagram for SO_2.
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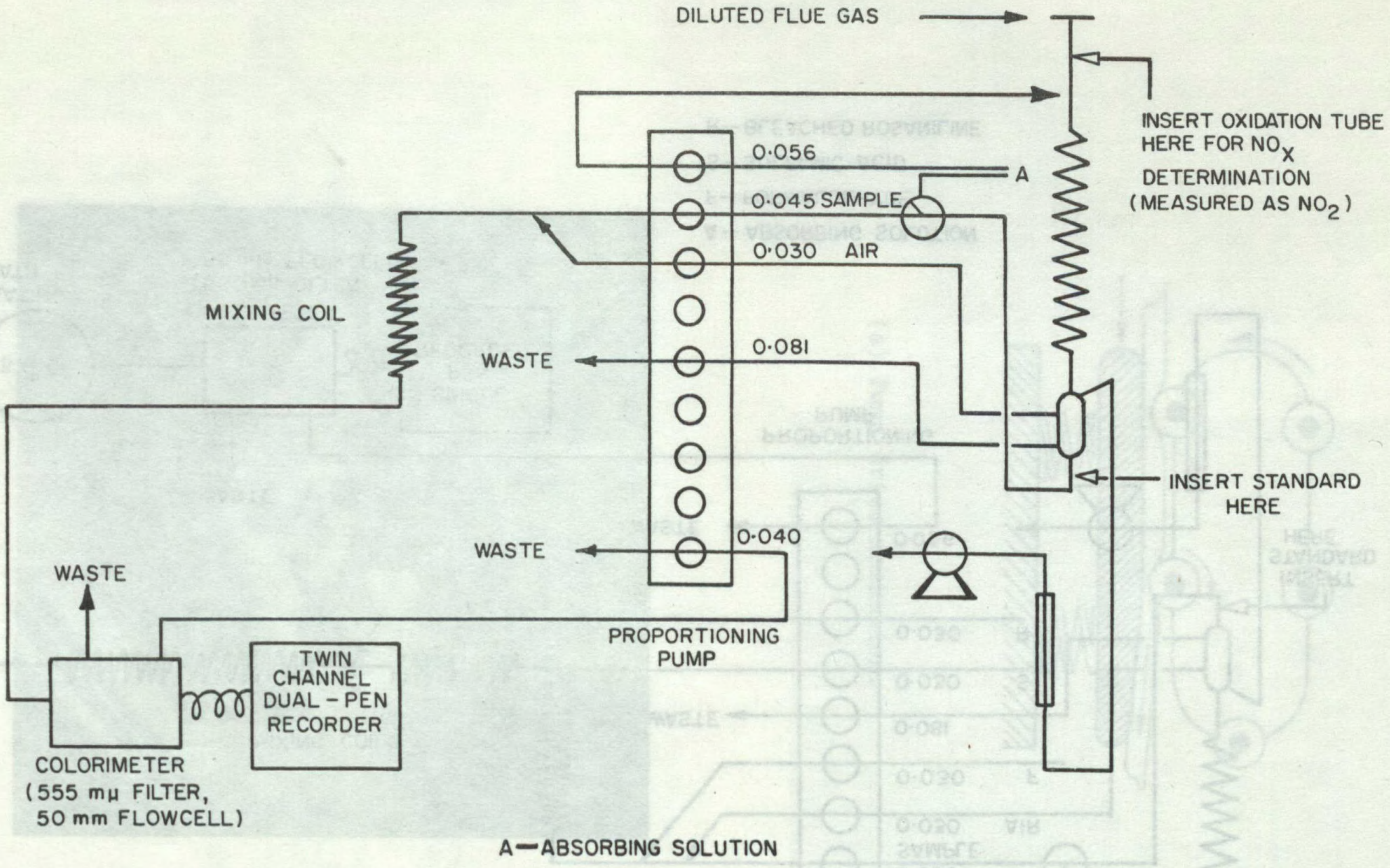


Figure 6. Flow diagram for NO_2 and NO_x.

Figure 7. Autoanalyzer colorimeter and readout modules.

A. SO_2 heating bath.
B. Colorimeters.
C. Range expanders.
D. Recorders.
E. Programmer.

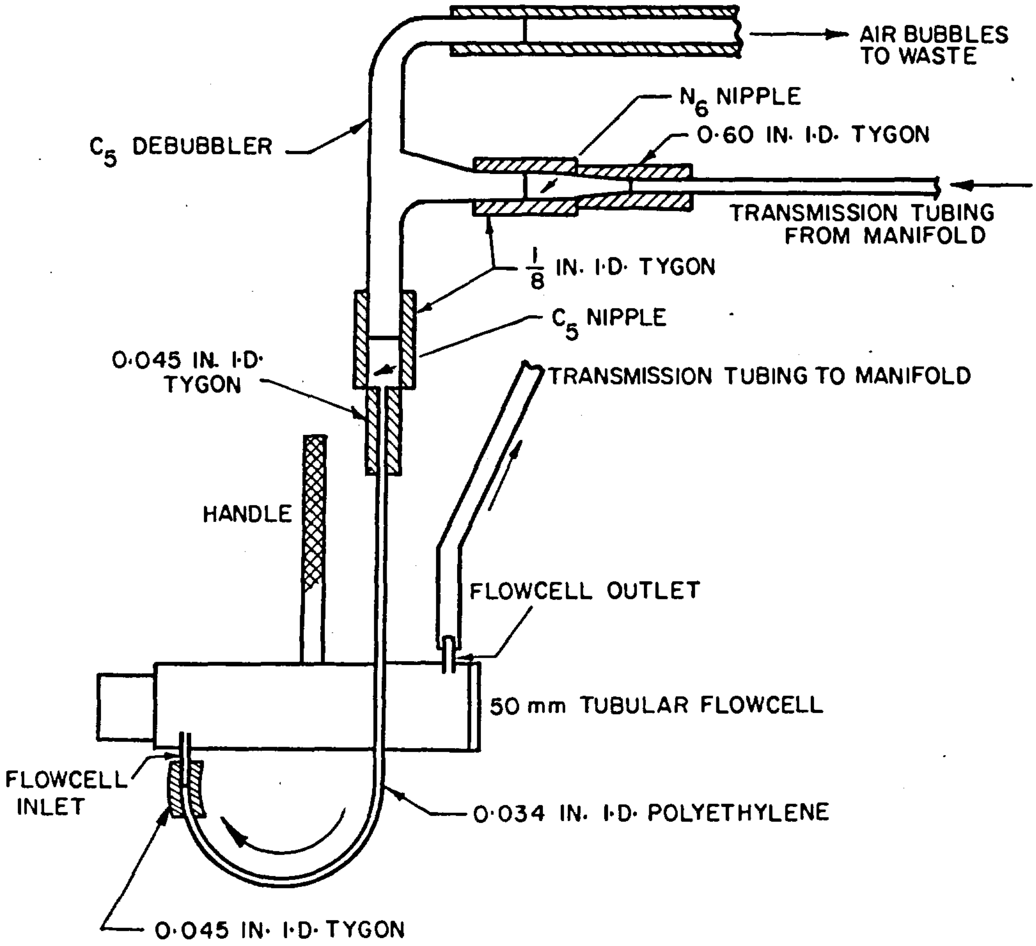
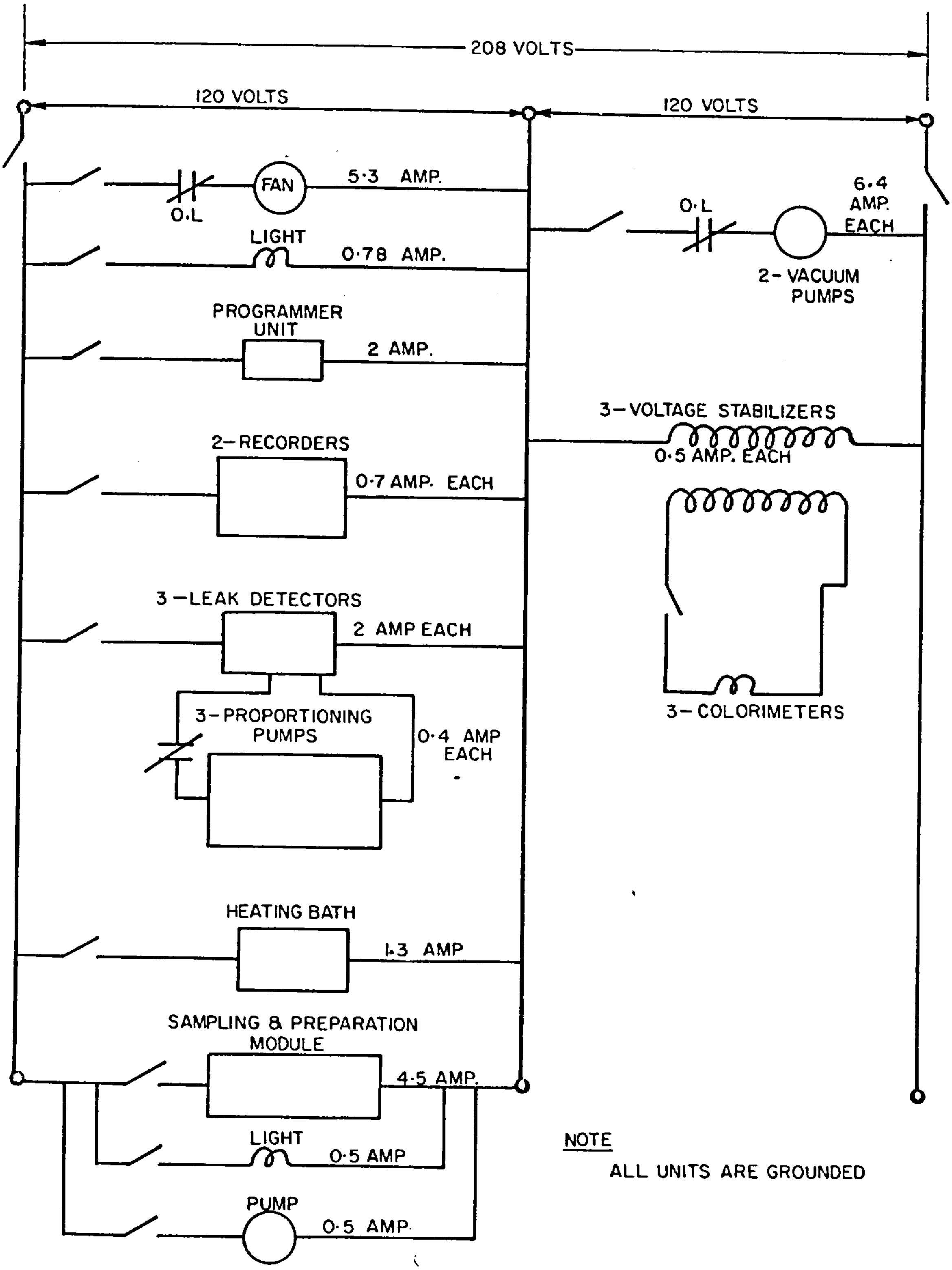


Figure 8. Tubular flowcell assembly.



NOTE

ALL UNITS ARE GROUNDED

Figure 9. Wiring diagram for Autoanalyzer cabinet.

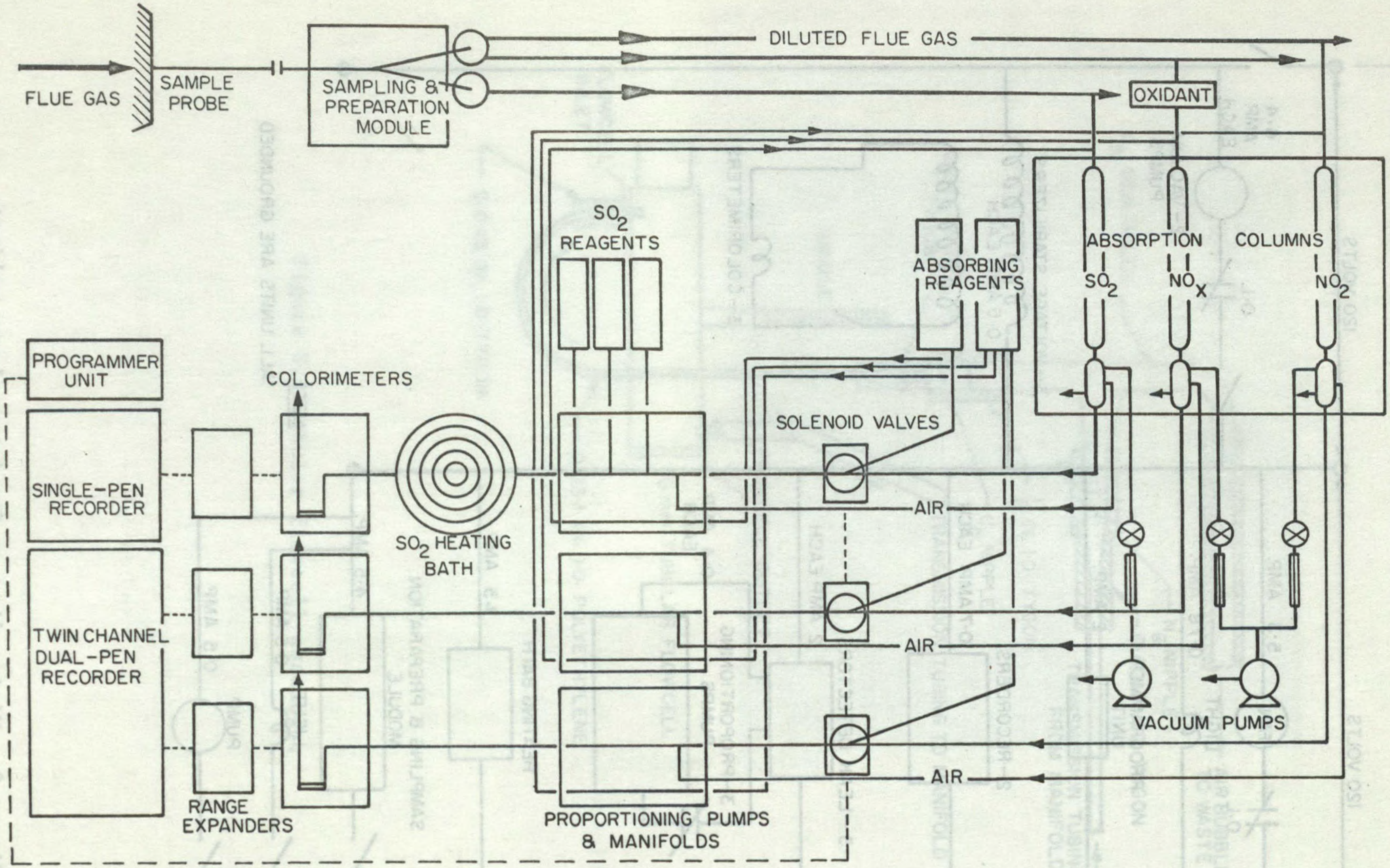


Figure 10. Schematic layout of SO_2, NO_2 and NO_x monitoring system.

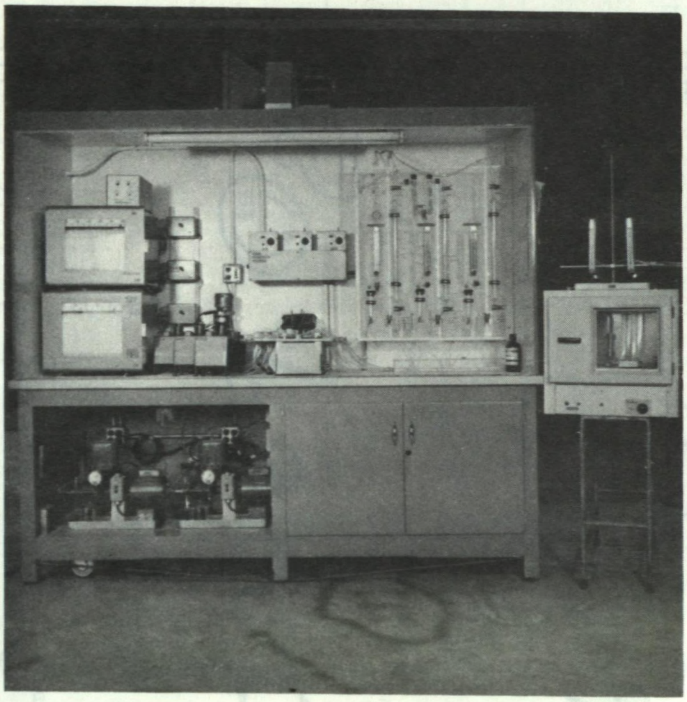


Figure 11. Cabinet-mounted SO_2, NO_2 and NO_x monitoring system.

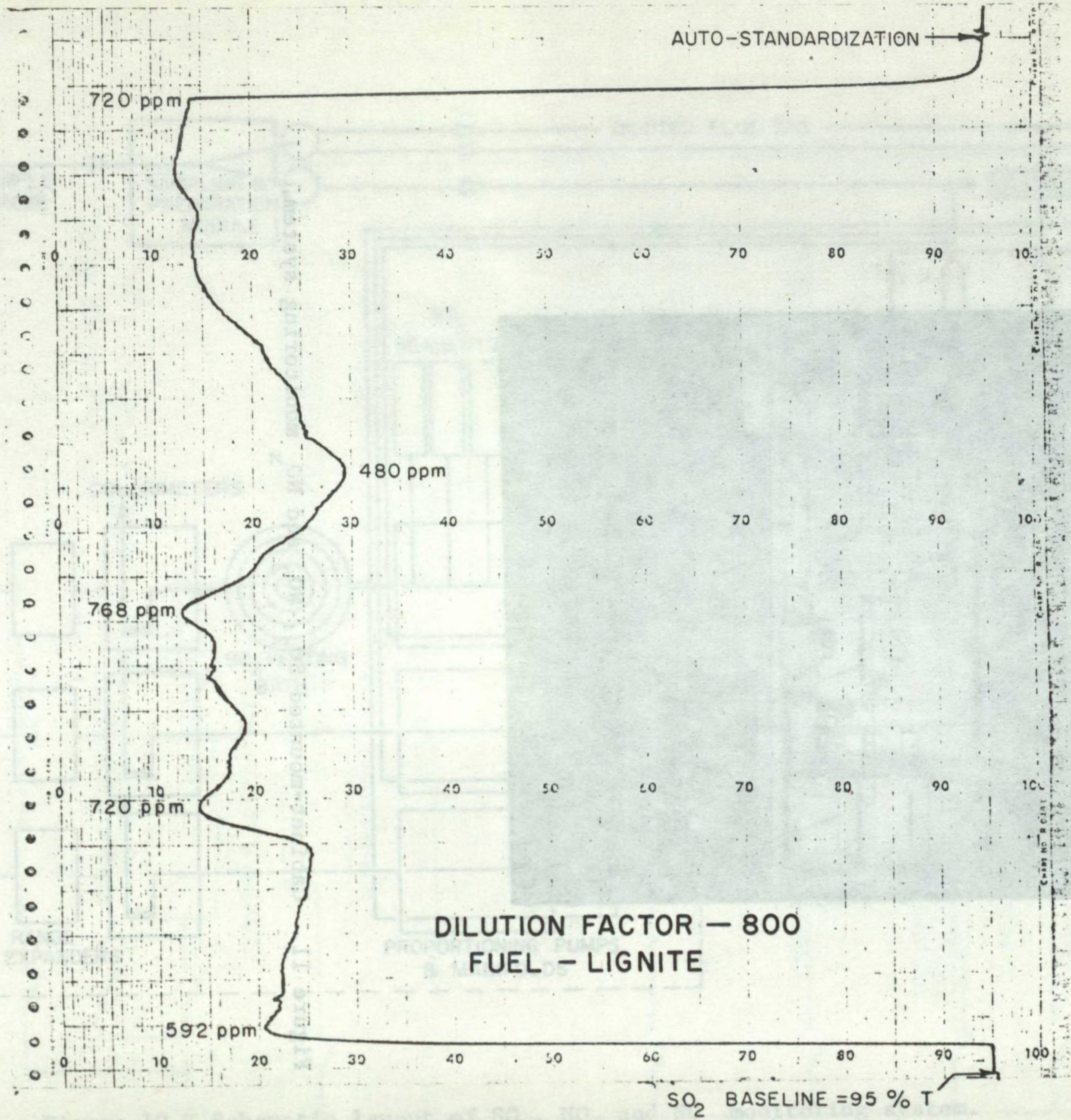


Figure 12. SO_2 levels at constant excess air; pulverized coal.

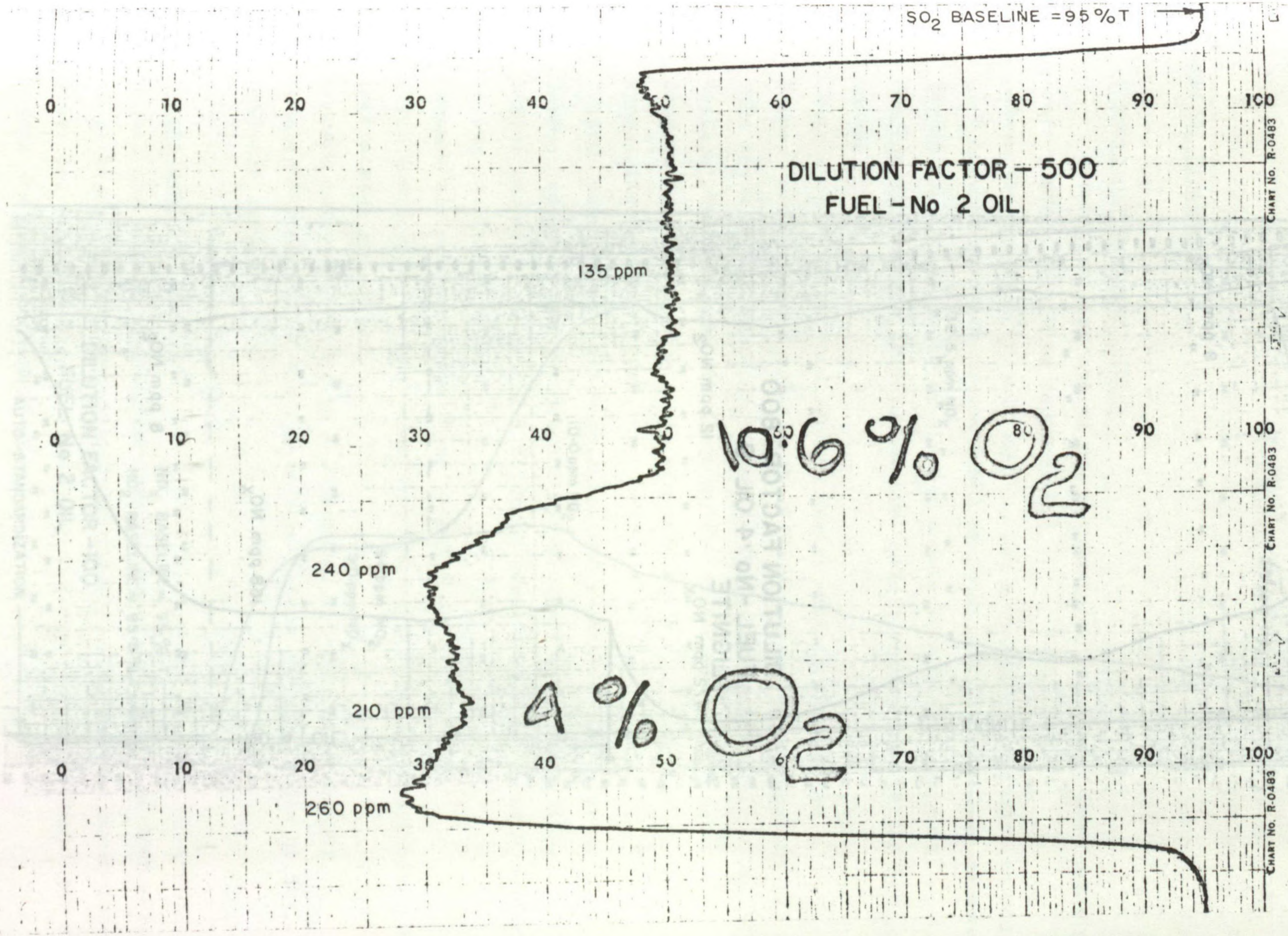


Figure 13. SO$_2$ levels in flue gas at two levels of excess combustion air; fuel, No. 2 oil.

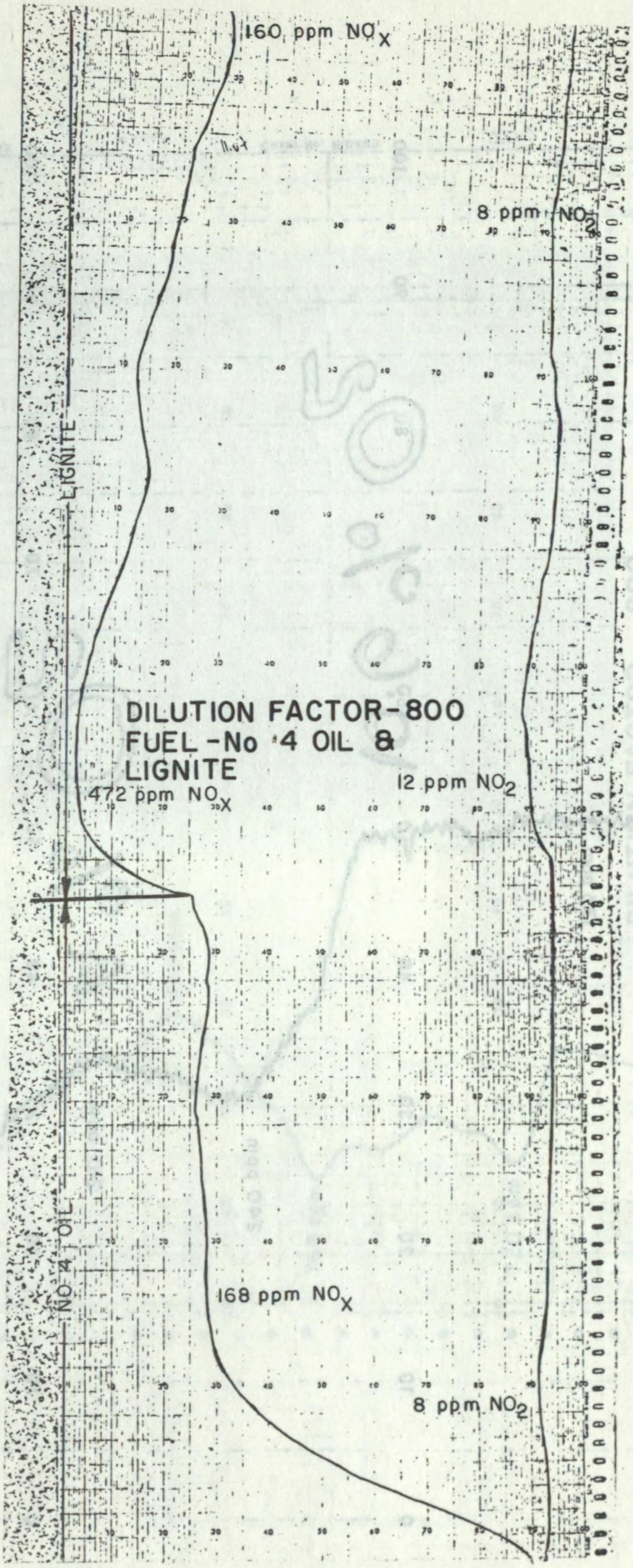


Figure 14. NO_2 and NO_x levels at constant excess air; No. 4 oil and pulverized coal.

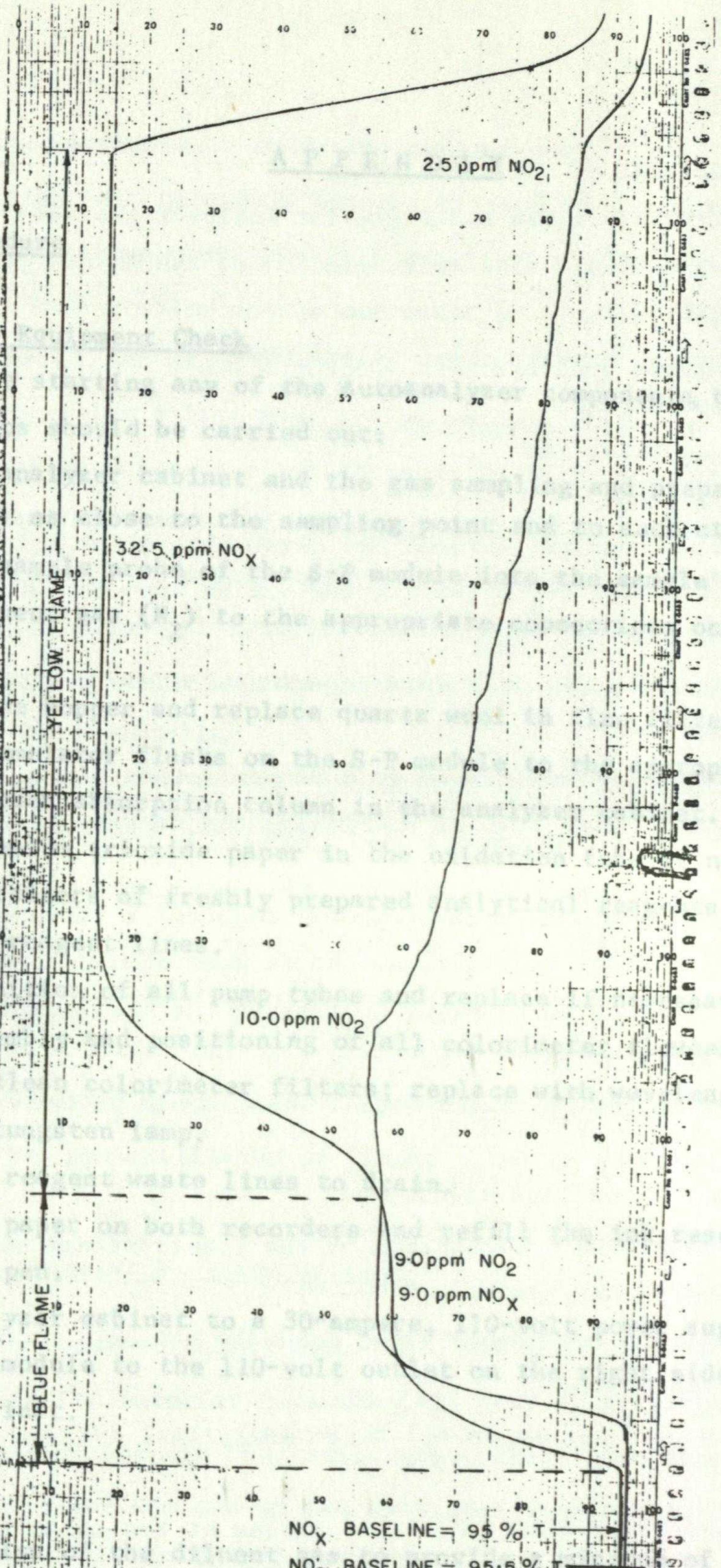


Figure 15. NO_2 and NO_x levels from non-luminous and luminous oil flames.

APPENDIX

Operating Procedure

Preparatory Equipment Check

Before starting any of the Autoanalyzer components, the following preparatory steps should be carried out:

1. Locate the analyzer cabinet and the gas sampling and preparation module (S-P module) as close to the sampling point and to each other as possible.
2. Insert the sample probe of the S-P module into the sample port.
3. Connect diluent gas (N_2) to the appropriate connections on the S-P module.
4. Clean cyclone hopper and replace quartz wool in fine filter.
5. Connect accumulator flasks on the S-P module to the appropriate 'T' tube above each absorption column in the analyzer cabinet.
6. Replace chromium trioxide paper in the oxidation tube if necessary.
7. Connect containers of freshly prepared analytical reagents to the appropriate reagent lines.
8. Inspect condition of all pump tubes and replace if necessary.
9. Inspect assembly and positioning of all colorimeter flowcells.
10. Remove and clean colorimeter filters; replace with wavelength notation facing the tungsten lamp.
11. Connect all reagent waste lines to drain.
12. Check chart paper on both recorders and refill the ink reservoirs for each stylus pen.
13. Connect analyzer cabinet to a 30-ampere, 110-volt power supply.
14. Connect S-P module to the 110-volt outlet on the right side of the analyzer cabinet.

Operational

1. Adjust the flow of the diluent gas to provide a minimum of 2000 cc/min of nitrogen to both the accumulator flask for SO_2 and the accumulator flask for NO_2 and NO_x. The calibration curves for the diluent gas flowmeters are shown in Figure 16.
2. Start the following components in sequence:

(a) heating element on the S-P module;
(b) forced circulation fan and light for analyzer cabinet;
(c) programmer unit with the mode selector on MANUAL and stream selector on STANDARD;
(d) two recorders, leaving chart drives OFF;
(e) three colorimeters;
(f) SO_2 heating bath; and
(g) two vacuum pumps.

3. Adjust flow of diluent gas through the three absorption columns, i.e., settings of 9.0 on the SO_2 flowmeter and 4.1 on both the NO_2 and NO_x flowmeters.
4. Secure the end blocks for each metering-tube manifold on the platen positioning pins.
5. Clamp roller-driver assemblies on each proportioning pump.
6. Start each proportioning pump by energizing the corresponding leak detector.
7. At this point, a 30-min warm-up period is required to ensure adequate chemical and electrical equilibrium. Adjustment should be made during this period to the thermoregulator control on the S-P module, to provide an oven temperature of 165 ± 5°F.
8. During the warm-up period, continuous checks should be made to ensure that:
   (a) diluent gas flows have stabilized,
   (b) uniform air-bubble segmentation of the liquid stream exists throughout the analytical train,
   (c) all connections are properly and securely butted,
   (d) no leaks are present,
   (e) aspiration of reagents to all three analytical systems is adequate, and
   (f) air is de-bubbled from the liquid stream at the inlet to the colorimeter flowcell.

9. The following are important operating precautions:
   (a) On start-up, air generally becomes trapped in the flowcell and the corresponding recorder pen will oscillate rapidly up and down the chart. This problem can be corrected by pinching the outlet line of the flowcell for about 5 sec and then suddenly releasing the pressure.
   (b) The colorimeter filter <u>must not be removed</u> while the tungsten lamp is operating unless a blank aperture is first inserted between the filter and the lamp. If unfiltered white light from the lamp strikes the photocell, temporary insensitivity or permanent damage can result. It is also essential that the covers over the reference and sample sides of each colorimeter be properly seated so that no outside light can strike the photocells.
   (c) The amplifier gain on the recorder should be checked after (i) servicing the amplifier, (ii) replacing a tungsten lamp, and (iii) changing reagents. Optimal gain occurs when the recorder pen returns to within 0.1% of its original setting when the large bull gear, located just behind the roller in the recorder, is displaced to the left or right of its null position. If the pen does not return quickly to the proper value,the gain is too low; and if the pen oscillates or 'hunts', the gain is too high.

Recorder-Colorimeter Baseline Setting

Turn the recorder chart drive ON. Set the large balancing motor pot located inside the recorder near the bull gear at midrange, i.e. at 1.5. With reagents running through the train, check the transmittance value (% T) on the recorder. Place any one of the apertures in position (numbers up) on the reference side. DO NOT INSERT ANY APERTURE ON THE SAMPLE SIDE. Turn the 100% T control dial on the colorimeter until the pen on the recorder chart reads the desired baseline setting for the particular test,

i.e. 95% T for SO_2,
95% T for NO_x,
95.5% T for NO_2.

The proper aperture for the particular test will be the one that gives a reading of between 1 and 9 major units on the 100% T colorimeter control dial. The proper aperture must be determined for each test before setting its zero adjustment.

NOTE: If the desired baseline setting cannot be reached for a particular test with a No. 1 aperture, recheck the flowcell alignment, as described in the Autoanalyzer manual under "General Operating Instructions". If this does not permit the baseline setting to be reached, use a No. 1 aperture with a 0.2 or 0.6 neutral density filter over the aperture opening on the reference side.

When the desired baseline setting for a particular test has been satisfactorily obtained on the recorder chart, the automatic standardization pot must be balanced with the 100% T control dial on the colorimeter. To accomplish this, the small standardization pot located inside the recorder is set at or near the same reading as the 100% T control dial on the colorimeter. The balancing motor is then energized by manually engaging (downwards) the balancing motor switch located under the standardization pot. If the recorder-colorimeter system is balanced, the recorder-pen will either not move or will displace an equal distance to either side of the baseline tracing, quickly returning to the original % T setting.

Should the systems be unbalanced, the pen will trace an unequal displacement to either side of the original baseline setting. The balancing motor pot must then be reset at midrange, the desired baseline setting readjusted by the 100% T control dial on the colorimeter, and a new setting chosen for the standardization pot. The balancing motor is again energized and the pen displacement observed. This procedure is repeated until the recorder-colorimeter system is balanced, whereupon the balancing motor switch is engaged upwards to lock in the auto-standardization function of the system. Both the 100% T control dial and the standardization pot are then locked at their balanced setting.

Recorder-Colorimeter Zero Setting

Put the blank or No. 0 aperture in the appropriate slot on the sample side of the optical bench. The pen on the recorder should now move toward the zero end of the scale. Turn the zero adjustment on the colorimeter to bring the pen exactly to zero on the paper. Once the zero is set, remove the zero aperture from the sample side and replace the cover. If necessary, readjust the pen for the desired baseline % T on the recorder by turning the 100% T control dial on the colorimeter. Recheck the torque on the large bull gear and reset the gain control if necessary.

Standard Calibration

Upon satisfactory completion of zero and baseline settings, the three analytical trains are ready for calibration using liquid standards (see Section entitled Analytical Reagents). To calibrate each analytical train, the vacuum pumps are shut off, the sample lines are disconnected at the gas-liquid separator, and a beaker is placed under each tube to collect absorbing reagent. The SO_2 sample line is then immersed in the 0.2-ppm v/v sodium metabisulphite standard and both the NO_x and NO_2 sample lines are immersed in the 0.027 ppm v/v sodium nitrite standard.

The stream selector on the programmer unit is switched to STREAM and a 10 min period allowed for standard sampling. The stream selector is then returned to STANDARD and 10 min allowed for recorder pens to return to baseline. While the stream selector is on STANDARD, absorbent flows through the system and the sample lines are immersed in the next higher standard.

The above procedure is repeated to cover the full range of standards. When the last SO_2 and NO_2 standard has been sampled, the stream selector is returned to STANDARD, the sample lines are re-connected to the appropriate gas-liquid separators, and the vacuum pumps are turned ON.

The resulting standard curves are plotted on two-cycle, semi-log graph paper showing transmittance (as %) vs concentration (as ppm v/v). Standard calibration must always be carried out whenever a fresh reagent is used in the system.

Sampling and Monitoring Procedure

Sampling

Before proceeding with continuous monitoring of pollutants, it is necessary to either calculate from combustion theory or estimate from experience the maximum concentrations of the three pollutants to be analyzed. The flue gas sample can then be blended with diluent gas to provide a gas for the three pollutants ,

i.e. 0 to 1.0 ppm for the SO_2 analyzer (at 1.0X amplification), and

0 to 0.4 ppm for the NO_2 and NO_x analyzers (at 1.0X amplification)

Both diluent flowmeters are equipped with F-P No. 448-324 tubes and 1/4-in. black cadmium glass floats, and are capable of delivering 2000 to 10,000 cc of diluent gas per minute. In the event that a higher volume is desired (10,000 to 20,000 cc/min), a 1/4-in. stainless-steel float may be used. Figure 16 shows the flowmeter calibration for both floats.

Each of the two flowmeters located inside the S-P module delivers 2 to 20 cc of flue gas per minute to the dilution trains and is equipped with a F-P No. 448-035 tube and a 1/16-in. sapphire float. Figure 17 is a calibration curve for these flowmeters, which has been corrected to provide known volumes of 165°F flue gas at standard temperature (70°F).

Monitoring

For continuous monitoring the procedure is as follows:

(a) With stream selector of programmer unit on STANDARD and mode selector on MANUAL, turn ON the pump in the S-P module and adjust the flue-gas and diluent gas flowmeters to provide the desired flow rates. It is important that the flow of diluent gas always exceed 2000 cc/min, to prevent leakage of ambient air into the absorption columns.

(b) After approximately 10 min, switch stream selector on programmer unit to STREAM. The system is now operational for continuous monitoring in the manual mode of SO_2, NO_2 and NO_x in combustion gas.

For automatic programming of STANDARD and STREAM in the continuous monitoring cycle, (a) is repeated, followed by (c):

(c) After approximately 10 min, the timer dial located on the back plate of the programmer chassis is set at the beginning of the stream cycle. The mode selector is then switched to AUTO, resulting in an automatic energizing of the stream cycle. The Autoanalyzer system is now fully operational in the automatic mode for continuous monitoring on STANDARD and STREAM with automatic baseline correction for electrical and/or chemical drift.

During prolonged operation, occasional readjustments to sample gas flow will be required as a result of dust loading across the fine filter in the S-P module.

Shutdown

To shut down the analytical system, the following routine should be carried out.

(a) Switch mode selector on programmer unit to MANUAL. Switch the stream selector to STANDARD. Turn off both the pump and the heating element in the S-P module.

(b) After sampling baseline solutions for approximately 15 min, immerse all reagent lines in a one-litre bottle of distilled, deionized water. Wait approximately 15 min, then switch the stream selector on the programmer unit to STREAM.

(c) Turn off both recorders, recorder chart drives, the three colorimeters, and the SO_2 heating bath. Shut off the flow of diluent gases to the S-P module.

(d) After water-washing on STREAM for approximately 10 min, turn off the two vacuum pumps and the three proportioning pumps. WATER MUST ALWAYS BE LEFT IN THE SYSTEM OVERNIGHT.

(e) Raise the roller head assemblies off the platens. Check all pump tubing and replace any tubes showing signs of wear or internal build-up of chemicals. Lift the one end block of the pump tubes off the platen pins to relax tubes. Clean and dry surfaces of pump platen, rollers and tubes if necessary.

Analytical Reagents

SO_2 Absorbing and Complexing Reagents

A 0.01 M Sodium Tetrachloromercurate Absorbing Solution

5.44 g mercuric chloride plus
2.95 g sodium chloride dissolved in
2000 ml H_2O*

B 0.1% Formaldehyde

5 ml of 40% stock solution diluted to
2000 ml with H_2O

C 0.025% Sulfamic Acid

0.25 g dissolved in 1000 ml H_2O

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* All water used for reagent preparation must be distilled and deionized.

D Pararosaniline Hydrochloride Stock

2.00 g of pararosaniline hydrochloride dissolved in 1000 ml H_2O. Let stand for 3 days and filter. Store in pigmented glass bottle.

E Bleached Pararosaniline Hydrochloride Solution

To 10 ml of pararosaniline hydrochloride stock solution add 50 ml of concentrated HCl, wait for 10 minutes, filter, and dilute to 1000 ml.

SO_2 Standards

Gaseous standards are prepared according to the dynamic calibration method schematically illustrated in Figure 18. Liquid standards are prepared from sodium metabisulfite dissolved in the absorbing reagent.

A Standard Sulfite Stock Solution (prepared weekly)

385 mg sodium metabisulfite is dissolved in 1000 ml of 0.01 M sodium tetrachloromercurate absorbing solution.

B Working Standards (prepared daily)

10 ml of the standard sulfite stock solution is diluted to 250 ml with absorbing solution.

For working standards equivalent to 0.2, 0.4, 0.6, 0.8 and 1.0 ppm SO_2 v/v respectively, 5-, 10-, 15-, 20- and 25-ml aliquots of the diluted sulfite stock solution are further diluted to 100 ml with absorbing solution. A typical SO_2 calibration graph for liquid standards is shown in Figure 19.

SO_2 Operating Data

Vacuum Pump....	10 in. Hg
Diluted Gas Sample Flow Rate...	1500 cc/min corresponding to a setting of 9.0 on SO_2 flowmeter
Absorption Efficiency....	96%
Range Expander..........	1X = 0 to 1.0 ppm

Response Time........... 21 minutes.
Diluent Gas............. nitrogen
S-P Module Range........ 0 to 5000 ppm

NO_2 Absorbing and Complexing Reagents

10.0 g sulfanilic acid plus 0.2 g N - 1 - naphylethylene-diamine dihydrochloride dissolved in 100 ml concentrated glacial acetic acid and diluted to 2000 ml with H_2O.

NO_2 Standards

Gaseous standards are prepared in accordance with the instructions for dynamic calibration as shown schematically in Figure 18. Liquid standards are prepared from sodium nitrite as described below. Saltzman's conversion factor (i.e., 2.03μg sodium nitrite is equivalent to 1μg nitrogen dioxide) is used in the following directions.

A Standard Nitrite Stock Solution (prepared weekly)

81.2 mg $NaNO_2$ is dissolved in 1000 ml of H_2O.

B Working Standards (prepared daily)

10 ml of the stand nitrite stock solution is diluted to 250 ml with H_2O.

Working standards equivalent to 0.03, 0.08, 0.14, 0.27 and 0.41 ppm v/v respectively are prepared by diluting 1-, 3-, 5-, 10- and 15-ml aliquots of the diluted nitrite stock solution to 1000 ml with NO_2 absorbing reagent.

NO_2 Operating Data

Vacuum Pump................ 10 in. Hg

Gas Sample Flow Rate	710 cc/min, corresponding to a setting of 4.1 on the NO_2 flowmeter
Absorption Efficiency	97%
Range Expander	1X = 0 to 0.4 ppm
Response Time	7 minutes
Diluent Gas	nitrogen
S-P Module Range	0 to 500 ppm

NO_x Absorbing and Complexing Reagents and Standards

The absorbing and complexing reagents and standard solutions are identical to those used for the determination of NO_2. Chromium trioxide paper for oxidizing NO to NO_2 may be purchased from Scott Laboratories, Pittsburgh, Pa., or manufactured using the procedure described by Saltzman and Wartburg[1]. An NO_x calibration graph for 0.03, 0.08, 0.14, 0.27 and 0.41 ppm v/v is shown in Figure 20.

NO_x Operating Data

Operating data are identical to those given for NO_2.

Monthly Maintenance

(a) Clean out all flowmeter tubes with soap solution followed by an acetone rinse. Dry thoroughly.

(b) Examine the condition and connections of all reagent and sample lines.

(c) Apply lubricating oil to internal chain drive and sprocket of proportioning pump. Apply light oil to felt pads on chain guides and to oil hole in central area of chain support. BE SURE OIL DOES NOT DRIP ON ROLLER SURFACES.

(d) Oil top and bottom motor bearings on the SO_2 heating bath.

(e) Check condition of oil in the heating bath and replace if discoloured

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[1] Anal. Chem., May 1965, p 779

or rancid. Oil must be replaced every six months. If oil is excessively dirty, check glass coil for leaks and check the coil interior for dirt or hard chemical deposits. Remove any deposits or foreign matter inside the pot and scour thoroughly.

(f) Clean any spills inside the colorimeter. Remove flowcell and rinse. Clean windows of the flowcells. Clean filters and check flowcell alignment in light path. Realign flowcell if necessary.

Supply and Accessory Inventory

A stock of the following accessories and spare parts is recommended as minimum requirements for continuous Autoanalyzer operation:

Item	No. Required
No. 18 B/S Clamps	12 only
500- cc Erlenmeyer expansion flask fitted with fritted tube	6 only
Reagent bottles	6 only
Reagent line manifold	1 only
Quick-connect reagent line couplings	3 only
560-mμ filters for SO_2 colorimeter	1 only
555-mμ filters for NO_2 and NO_x colorimeters	2 only
Colorimeter apertures	3 sets
12-in. strip-chart recording paper	12 rolls
Red and green ink	2 bottles of each
1-in. Viton O-rings	4 only
Absorption column and separator tube	1 only
Glass fittings; C5, D1, H3	6 of each
Glass mixing coil; small and large	3 of each
Polyethylene nipples; N5, N6, N7, N8, N9	6 of each
Colorimeter flowcells	3 only

Tungsten colorimeter. lamps	3 only
Pump tube end blocks	6 only
Pump tubes: 0.030, 0.035, 0.040, 0.045, 0.051, 0.056 0.060, 0.065, 0.073, 0.081, 0.090, 0.100 in. I.D.	1 pkg of each
Tubing: 1/16, 1/8, 1/4 and 1/2 in. I.D. tygon 1/16 and 1/8 in. I.D. polyethylene 0.034 in. I.D. polyethylene	30 ft of each
Glass tubing: 1.6 mm I.D.	30 ft

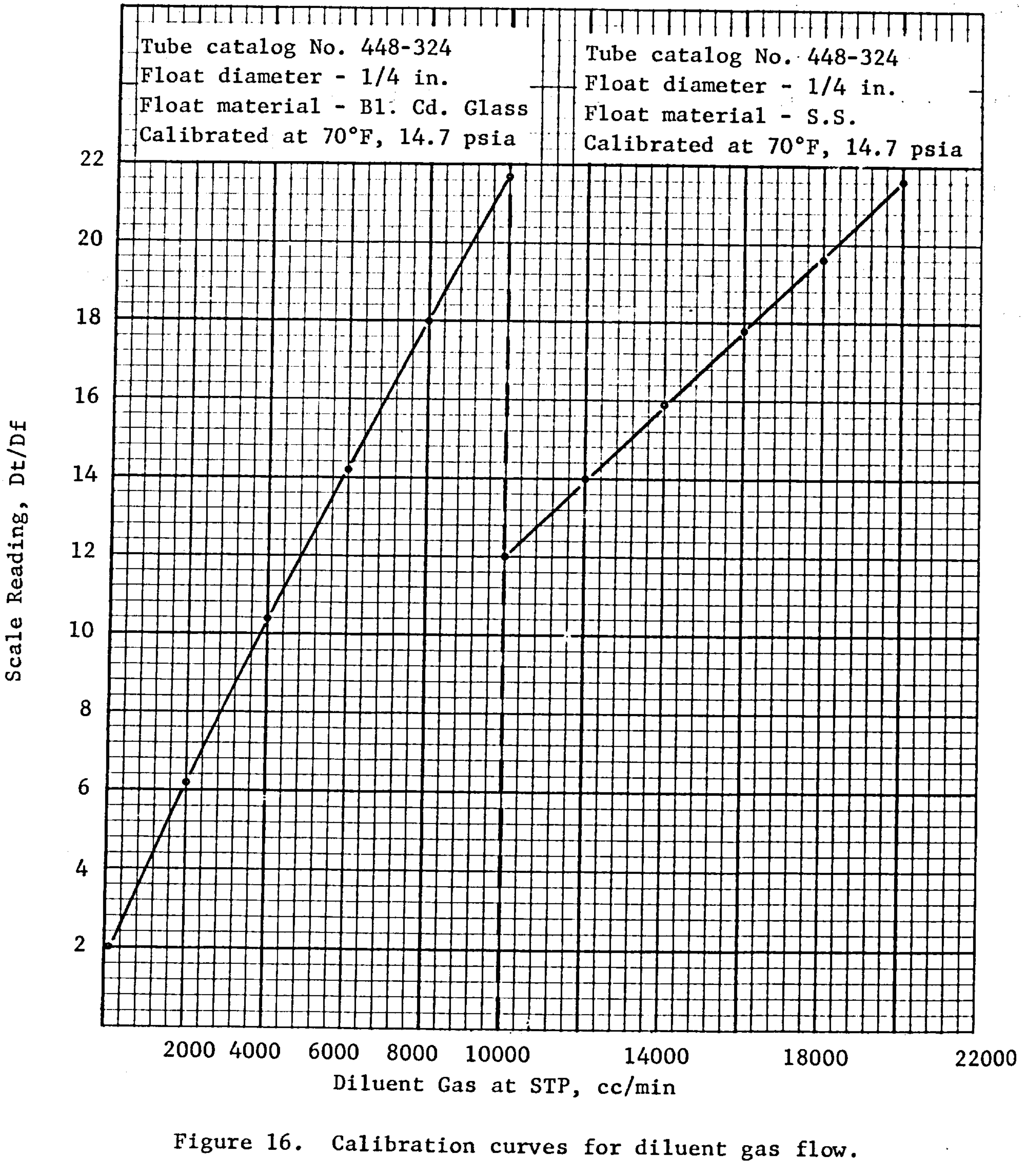

Figure 16. Calibration curves for diluent gas flow.

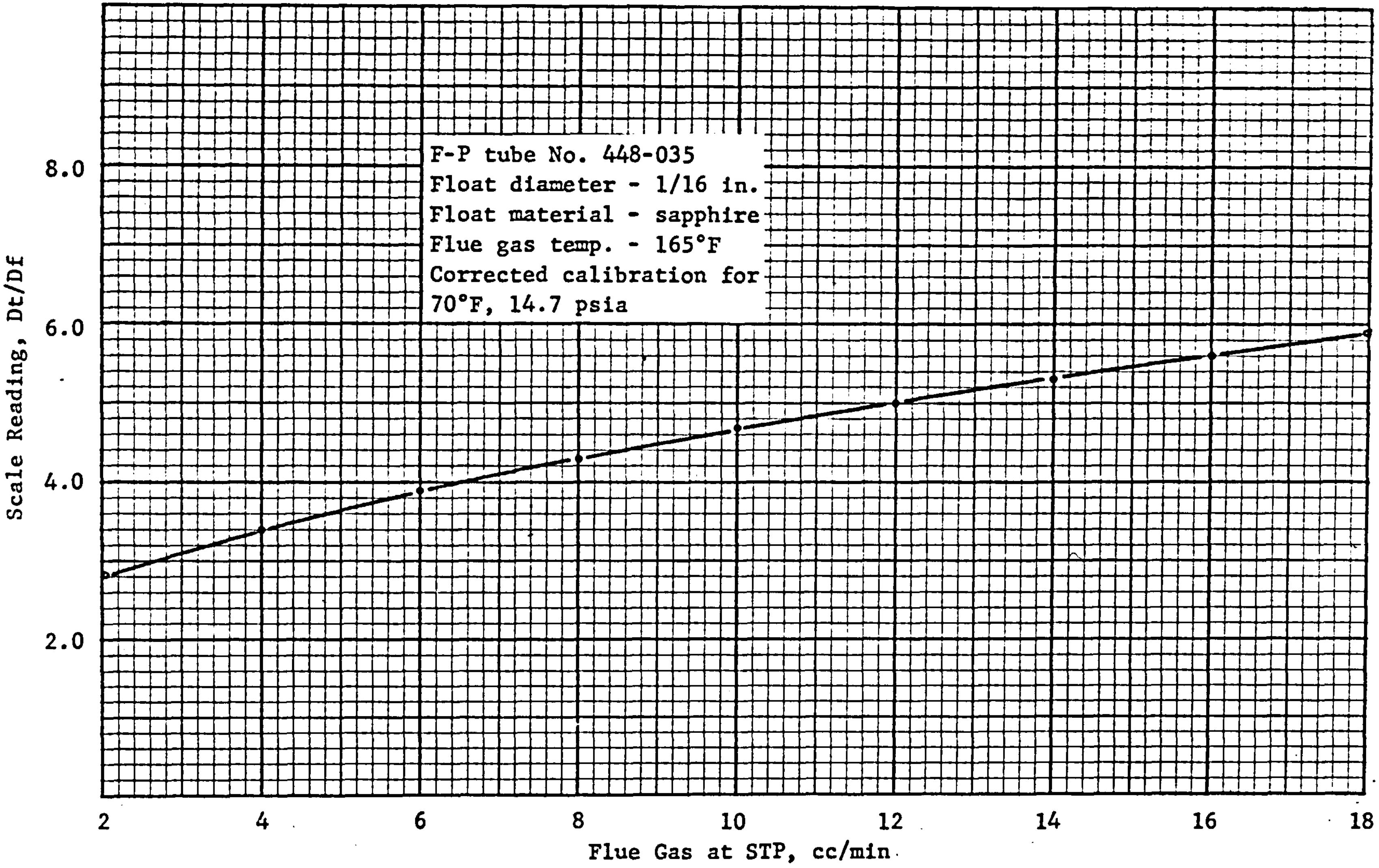

Figure 17. Calibration curves for flue gas flow.

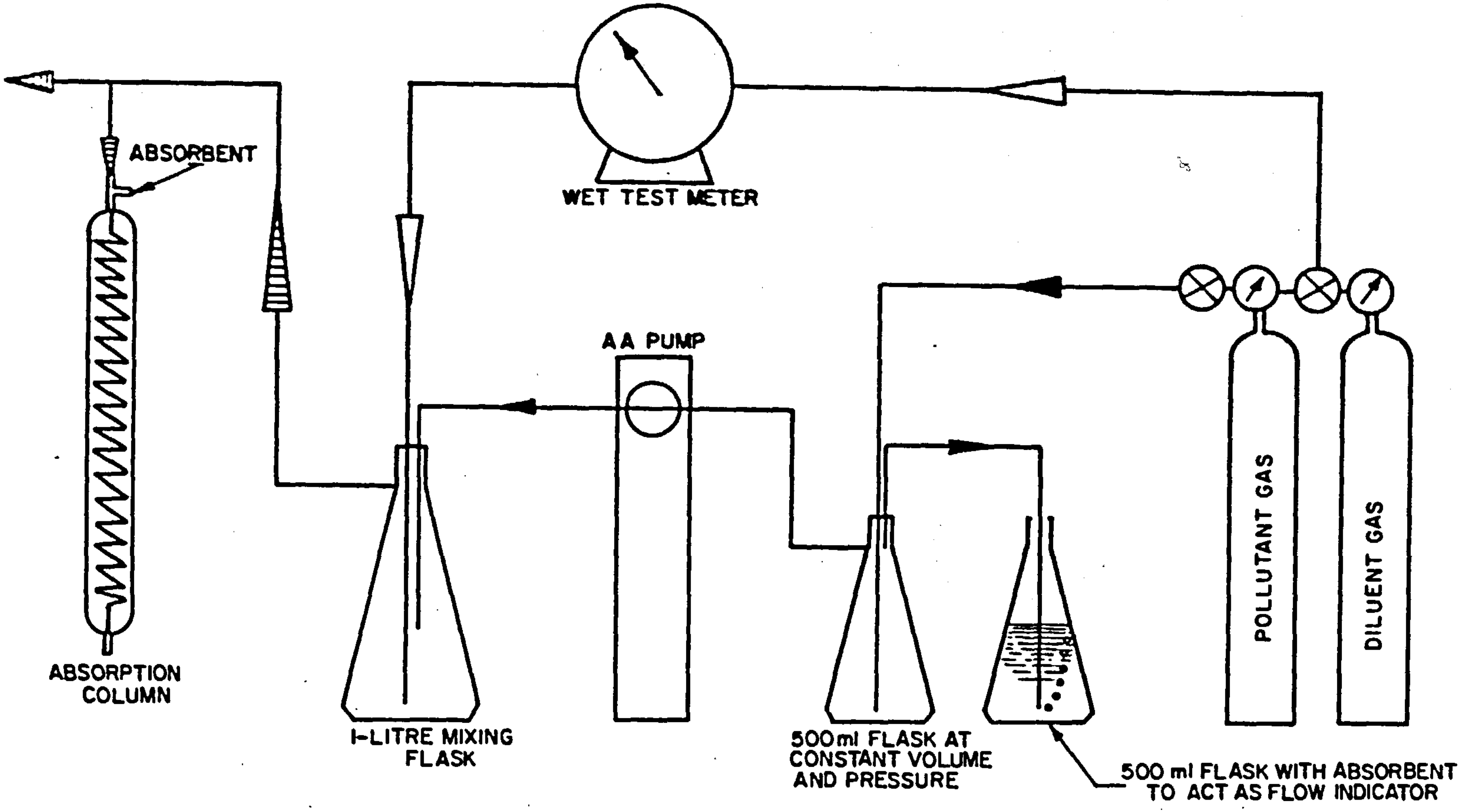

Figure 18. Flow system for dynamic gas calibration of pollutants using the Autoanalyzer.

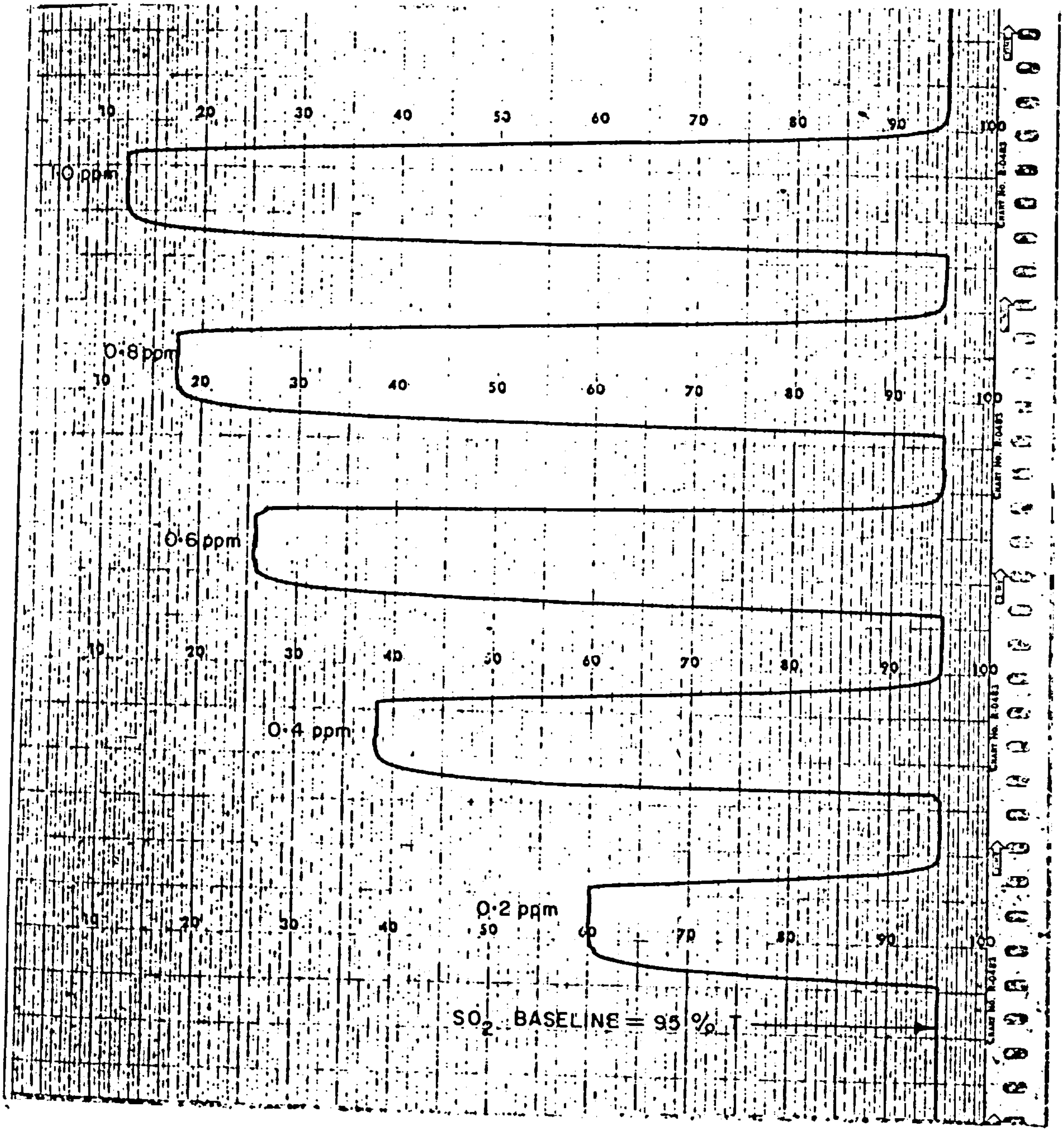

Figure 19. Calibration curves for SO_2 liquid standards.

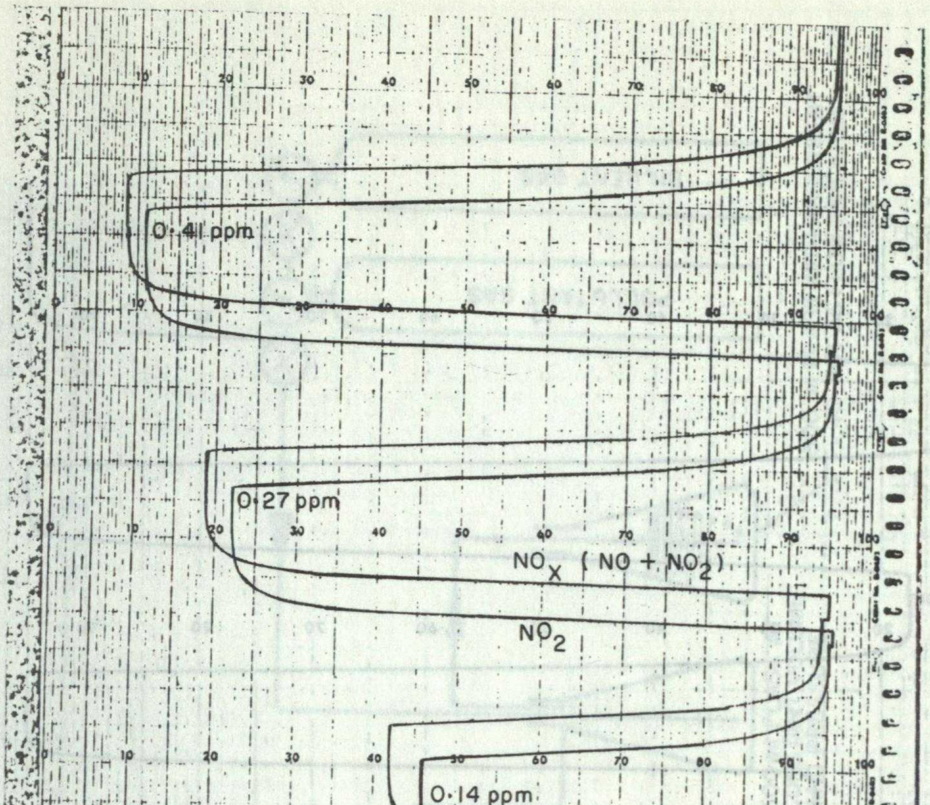

Figure 20. Calibration curves for NO_2 and NO_x liquid standards.