



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
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5151662-10

*AN AUTOMATED SYSTEM FOR
CONTINUOUS MONITORING OF
CO₂, CO AND O₂ IN BOILER FLUE GAS*

R. K. JEFFREY AND G. K. LEE

FUELS RESEARCH CENTRE

SEPTEMBER 1969

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The Queen's Printer
Ottawa, Canada
1969

Mines Branch Technical Bulletin TB 115

AN AUTOMATED SYSTEM FOR CONTINUOUS MONITORING OF
CO₂, CO AND O₂ IN BOILER FLUE GAS

by

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

ABSTRACT

The report describes an automated system for sampling, analyzing and recording constituents of boiler flue gases. The system employs non-dispersive infrared spectrophotometers for analyzing CO₂ and CO and a thermomagnetic sensor for analyzing O₂. Each analyzer is supplied with a clean, dry stream of flue gas to ensure a high degree of analytical sensitivity, selectivity and accuracy. Response time between sample inlet and readout is less than 40 sec because the three analyzers require only about 2 per cent of the total sample flow.

The system has been in operation for over three years and during this time it has been proved reliable, rugged and trouble-free.

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Direction des mines

Bulletin technique TB 115

UN SYSTÈME AUTOMATISÉ DE CONTRÔLE CONTINU DE CO₂,
CO ET O₂ DANS LES GAZ DES CARNEAUX DE CHAUDIÈRE

par

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

RÉSUMÉ

Le rapport décrit un système automatisé d'échantillonnage, d'analyse et d'enregistrement des composants des gaz des carneaux de chaudière. On emploie des spectrophotomètres à infrarouge sans dispersion pour déterminer le teneur en CO₂ et en CO, et un détecteur thermomagnétique pour déterminer la teneur en O₂. Chaque analyseur est alimenté d'un jet pur et sec de gaz de carneau afin d'assurer un haut degré de sensibilité, de sélectivité et d'exactitude analytiques. Il ne faut que 40 secondes pour obtenir les résultats de l'analyse après l'introduction de l'échantillon dans l'appareil puisque les trois analyseurs n'utilisent qu'environ 2 p. 100 du débit total de l'échantillon.

L'appareil est en usage depuis plus de trois ans et s'est avéré fidèle, résistant et sûr.

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AN AUTOMATED SYSTEM FOR CONTINUOUS MONITORING OF
CO₂, CO AND O₂ IN BOILER FLUE GAS

by

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

INTRODUCTION

Ordinarily the flue gas from combustion processes is analyzed by means of either an Orsat apparatus or a gas chromatograph, which is set up to measure the gas components of greatest interest: carbon dioxide, carbon monoxide, and oxygen. However acceptable the results may be, the utilization of intermittent sampling techniques for gas streams with fluctuating compositions is not always satisfactory, because a batch sample can represent the composition of the gas at only a particular instant or place. Batch or thief sampling is only applicable where the material is of relatively homogeneous composition; it is not suitable where the gas sample is physically or chemically heterogeneous, i.e., where composition is variable. Somewhat related to the above, and perhaps a more serious drawback in the application of either the Orsat or chromatograph, is the fact that during the 10 to 15 min time interval required for the sampling and consequent analysis of a batch sample, conditions of combustion, however well-controlled, may have varied significantly without record. Continuous measurements of fluctuations in combustion gas composition are required for correlating other simultaneous and dependent parameters, particularly during transient state conditions in flames.

To alleviate the most pronounced sources of error in the traditional batch method of flue gas analysis, it is necessary to employ one or more analyzers that are designed to monitor continuously, rapidly and accurately for selected components in a complex mixture of gases.

Several analyzers utilizing chemical absorption, coulometry, colorimetry, electrical conductivity and polarography were evaluated, but none of these was considered to have the necessary degree of sensitivity, selectivity, reliability and response time for continuous flue-gas monitoring. Subsequent investigations revealed that these requirements could be met by incorporating two non-dispersive infrared analyzers^{1/}, one each for CO₂ and CO, and a thermomagnetic analyzer^{2/} for O₂ with a specially designed gas

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^{1/} M-S-A Lira Infrared Analyzer, Model 300, Mine Safety Appliances Company.

^{2/} Thermomagnetic Oxygen Analyzer, Model 7803-G, Leeds and Northrup Company.

sampling and preparation system that supplies a clean, liquid-free gas sample to each analyzer. Accordingly, a successful flue-gas monitoring system was built and has been in continuous use for the past two years. The purpose of this report is to describe it for others who may wish to employ a similar system. The particular models of instruments used in the system were selected from several which met the specifications and were competitive in price.

PART I

THE INFRARED ANALYZERS FOR CARBON DIOXIDE AND CARBON MONOXIDE

Theory

Every gaseous compound absorbs infrared radiation at unique wavelengths that are related to its molecular structure. Thus, any gaseous compound can be positively identified from its infrared absorption spectrum, which is in effect a 'fingerprint' for the compound.

In general, the spectrum of a mixture of compound gases such as boiler flue gas is the sum of the spectra of the component compounds. Figure 1 shows the infrared absorption spectrum for a typical boiler flue gas. It is evident that for each component a distinctive spectrum exists, and that there are certain wavelengths where no interference or superposition of infrared radiation occurs. The latter spectral characteristic can be used to identify most compounds in flue gas by means of non-dispersive infrared analyzers that are sensitized to absorb only wavelengths specific to the compound of interest. The amount of infrared energy absorbed at the selected wavelength is proportional to the percentage of the compound of interest in the flue gas in accordance with the Lambert-Beer law of light transmission. Elemental gases including N₂ and O₂ do not absorb infrared radiation and do not act as interferences.

Description

Figure 2(a) shows a schematic illustration of the infrared analyzer for monitoring either CO₂ or CO. In the analyzer, two identical infrared beams are directed through two parallel gold-plated gas cells mounted in a solid aluminum block. One cell contains a known reference gas, while the other contains the unknown sample gas. After the infrared beams pass through the gas cells they are directed into a single detector unit that contains a sealed-in gas. As the gas in the detector absorbs infrared radiation its temperature rises and causes a volume increase which, in turn, moves a sensitive membrane in the detector unit. The movement of this membrane is converted to an electronic output signal that is proportional to the concentration of the compound to be analyzed.

Between the two infrared sources and the gas cells, a half-circle beam chopper, Figure 2(b), rotates at two cycles per second and alternately blocks the infrared radiation beam from each source. Thus, the detector unit alternately responds to the infrared energy transmitted by the gas in each cell. With no sample flowing or a flow of 'zero gas' in the sample cell, both

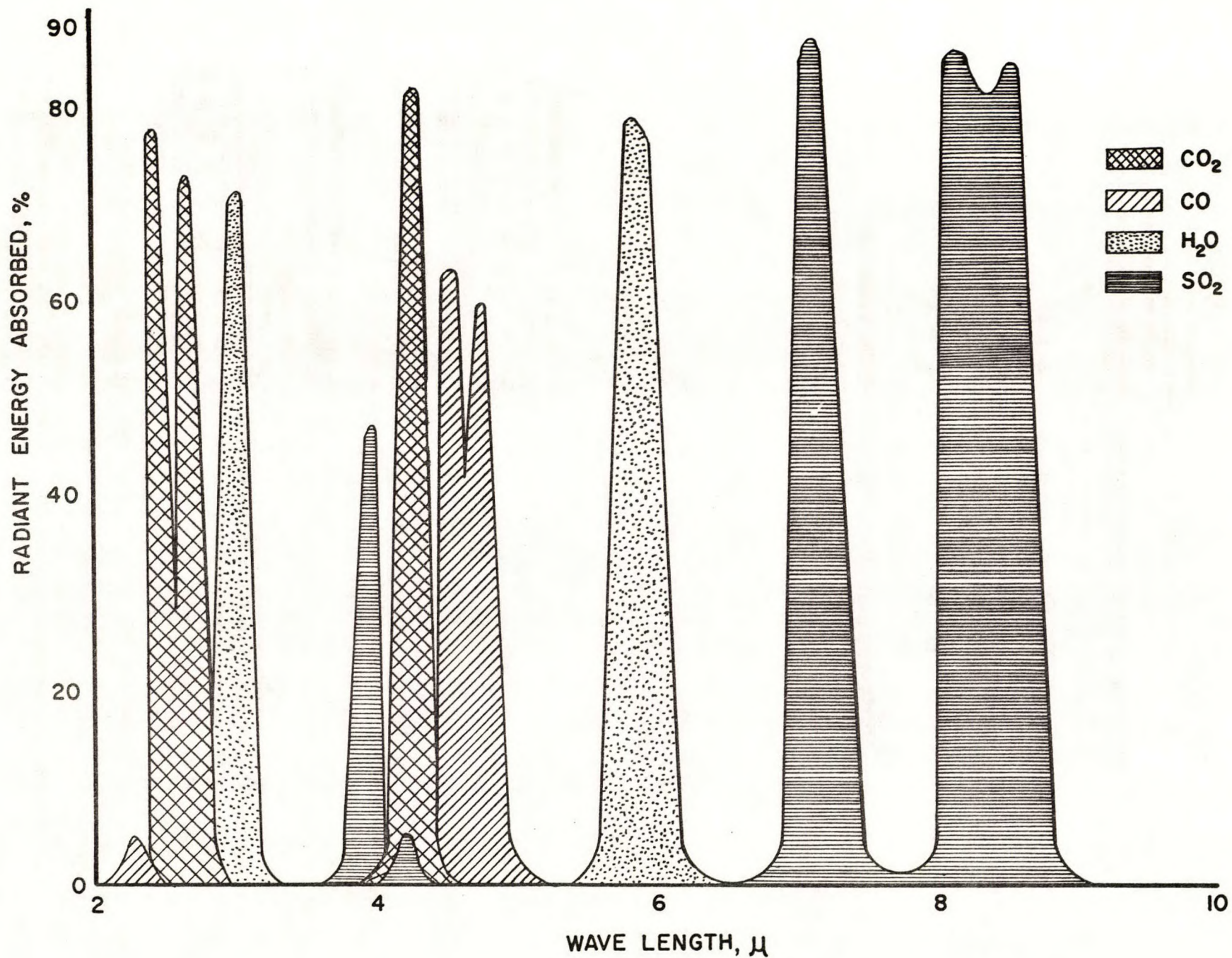
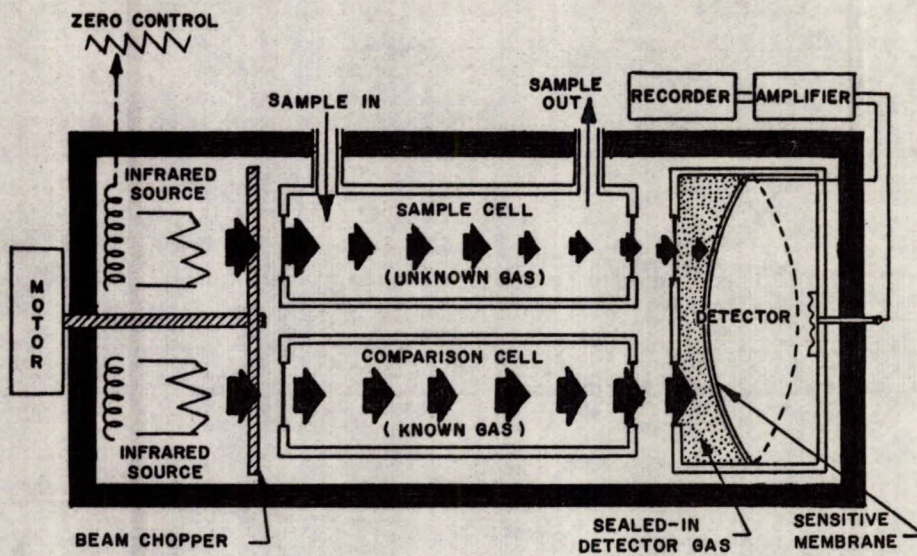
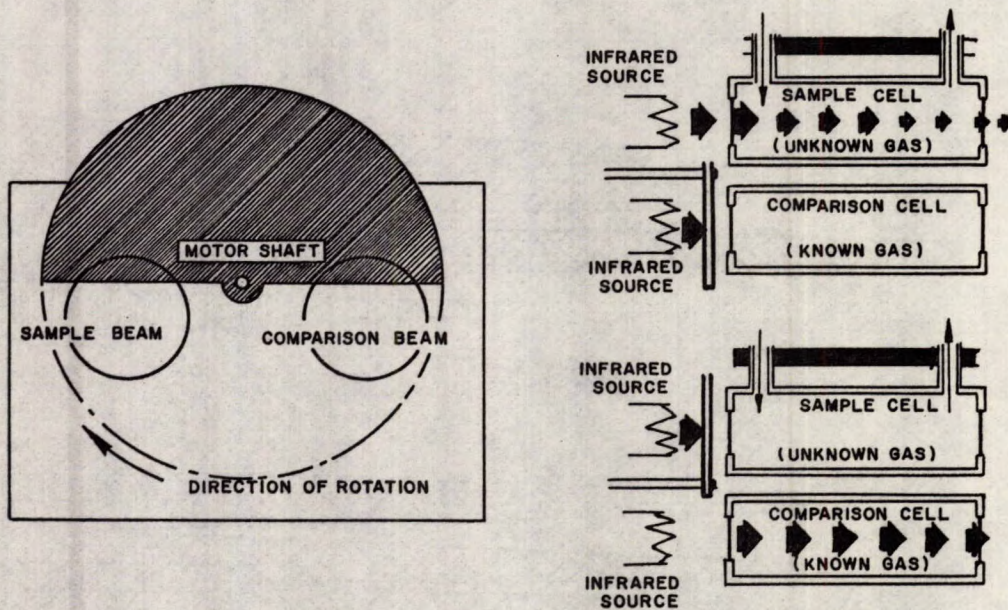


Figure 1. Infrared absorption spectrum for a typical boiler flue gas.



(a) Optical bench



(b) Beam chopper showing infrared absorption technique

Figure 2. Schematic diagram of infrared analyzer for either CO₂ or CO.

beams radiate equal energy to the detector and an instrument with properly aligned optics will read zero.

After the gas to be analyzed is introduced into the sample cell, infrared energy is absorbed by the compound of interest and the infrared radiation that reaches the detector unit from the sample cell is correspondingly reduced. As a result the two beams become unequal, because the detector receives a bright pulse of radiation from the reference cell followed by a dim pulse of radiation from the sample cell during each revolution of the beam chopper. The detector gas thus expands and contracts in proportion to the energy difference between the two beams.

The electronic circuit for the infrared analyzer, shown in Figure 3, is tuned so that only variations in capacitance created by the energy difference between the two beams entering the detector unit produce an output voltage. When the compound of interest (CO_2 or CO) is present in the sample cell, an output signal is transmitted to an indicator and an auxiliary recorder. The infrared analyzer has a response time of 90% of final reading in 5 seconds and its components are designed so that absorption of infrared energy is in good agreement with the Lambert-Beer law.

PART II

THE THERMOMAGNETIC ANALYZER FOR OXYGEN

Theory

Oxygen is one of the few gases that are strongly attracted by a magnetic field. This property, known as paramagnetism, can be used for the selective measurement of oxygen in complex gas mixtures, including boiler flue gas, where other gas components are either slightly or non-paramagnetic. The magnetic susceptibility or the degree of magnetization produced in a gas sample by a magnetic field is inversely proportional to its absolute temperature. Thus, an oxygen-bearing gas sample that is exposed to the combined effects of a magnetic and a thermal gradient in a confined space will be forced to flow by thermomagnetic convection in the direction of the magnetic field. The magnitude of the gas flow thus produced, other factors being constant, is dependent upon the concentration of oxygen in the flue-gas sample. In the thermomagnetic method, the magnetically and thermally induced gas flow changes the resistance of a hot wire which is calibrated as a function of oxygen concentration.

Description

In the oxygen analyzer, a thermomagnetic cell is utilized in which an electrically heated, temperature-sensitive element provides both the thermal gradient in the gas sample and the means for measuring the magnitude of induced gas flow.

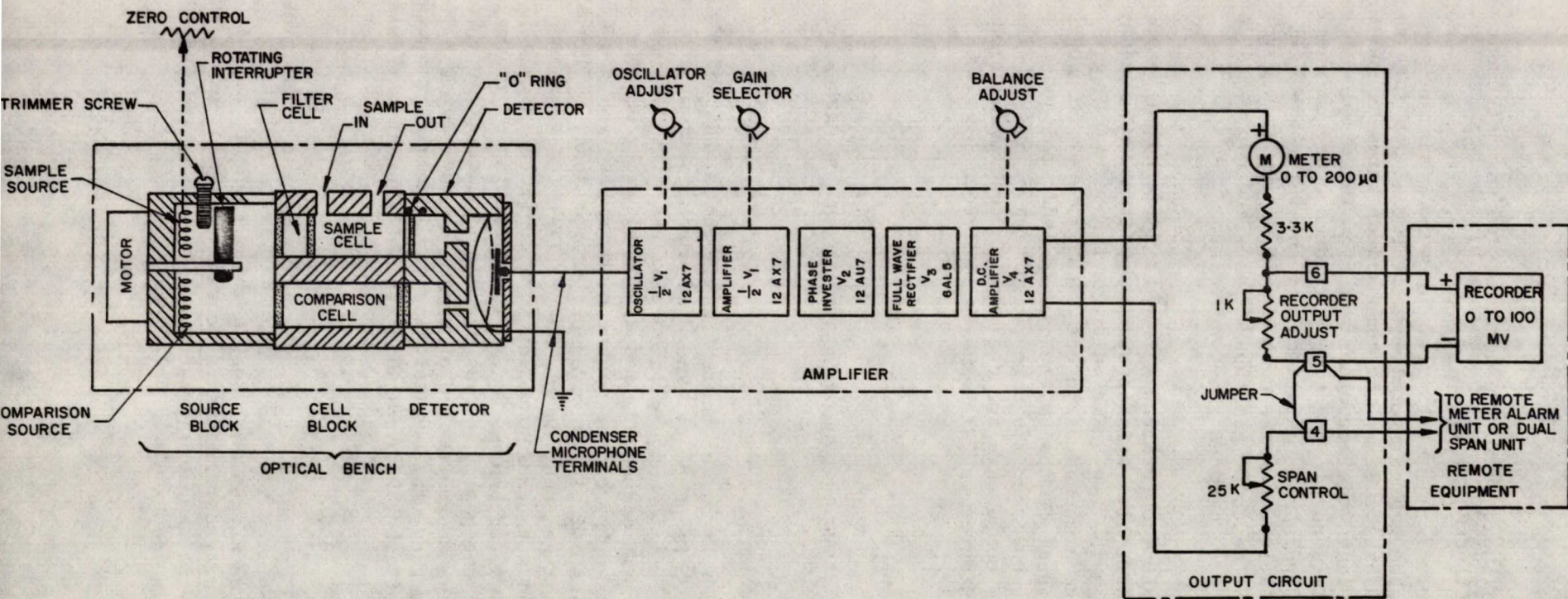


Figure 3. Electronic diagram of infrared analyzer.

Figure 4 shows a simplified schematic diagram of the thermomagnetic analyzer. The analyzing system consists of a self-compensating cell-block assembly containing four cells designated 1, 2, 3 and 4. Centred in each cell are sensitive, constant-temperature, hot-wire resistance elements that are connected in a single Wheatstone bridge circuit. Cell 1, which has a strong magnetic field directed across the resistance element, is for sample measuring; cell 2 is for sample referencing, and cells 3 and 4 are for atmospheric-pressure compensation.

The gas to be analyzed is pumped continuously past the inlet to cells 1 and 2, where a portion of the passing gas stream diffuses simultaneously into each cell before exiting to atmosphere. With no oxygen in the gas stream, the diffused gas sample causes equal cooling of the resistance elements in both cells 1 and 2 by thermal convection and the resistance of the bridge remains balanced. However, with oxygen present in the gas stream, the resistance element in cell 1 experiences additional cooling due to the combined effect of both thermal and magnetic convection, and the net result is an imbalance in the resistance of the Wheatstone bridge. This produces a millivolt output proportional to the oxygen concentration in cells 1 and 2.

To compensate for errors in oxygen concentration due to changes in atmospheric pressure, cells 3 and 4 are continuously exposed to clean, stagnant atmospheric air. Cell 3, which contains a larger cell volume than cell 4, is designed to compensate for the influence of pressure changes on the combined thermomagnetic convection rate in cell 1 (sample measuring), while cell 4 is designed to offset only the thermal convection rate in cell 2 (sample referencing).

Flue-Gas Flow System

The flue-gas flow system is schematically shown in Figure 5, with the components shown in the same relative position as they are in the analyzer. The gas to be monitored is pumped under positive pressure to the analyzer sample inlet at 1 to 45 SCFH*, although 30 SCFH is preferable. Downstream from the sample inlet, the gas stream enters the connection block where any condensate is removed and collected in the seal pipe. The sample then passes through tube S to the valve assembly on the front panel. With the sample valve opened (air valve closed), sample gas is directed consecutively through tube F, the filter block, tube I, the sample-measuring and -referencing cells, tube O, cell flowmeter, tube E, to the connection block, and finally exits through the exhaust outlet. The flow of sample gas that enters the cell block assembly is regulated at about 0.5 SCFH by adjusting the sample valve. Any excess of sample gas is diverted to the bypass outlet on the connection block. The pressure relief valve, connected to this outlet, maintains a constant flow of sample gas through the measuring cells regardless of sample-gas pressure variations.

*SCFH = Standard cubic feet per hour.

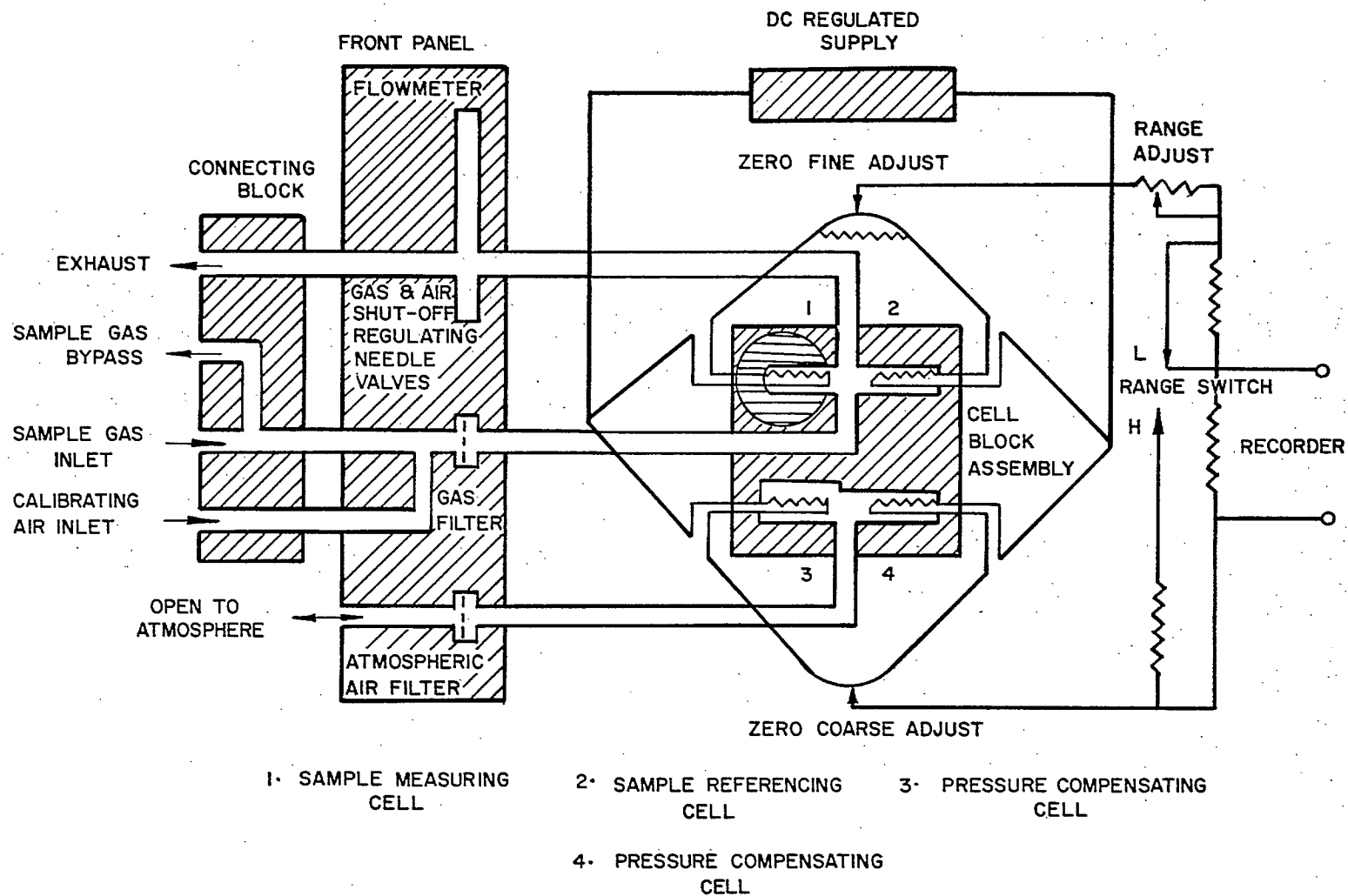


Figure 4. Schematic illustration of thermomagnetic analyzer.

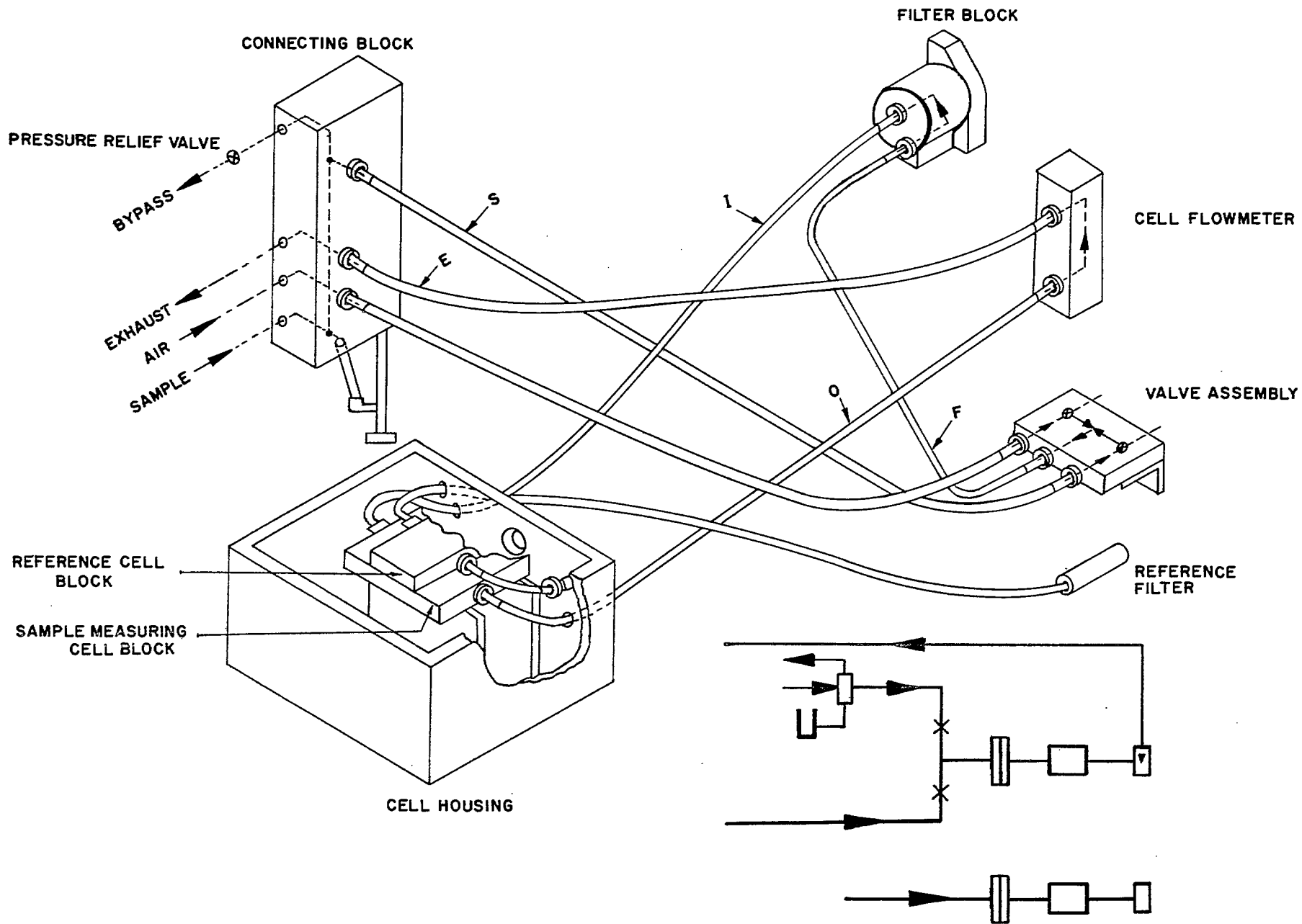


Figure 5. Gas flow path of thermomagnetic analyzer.

PART III

FLUE-GAS SAMPLING SYSTEM

Description

The sampling system developed for continuous monitoring of CO₂, CO and O₂ in boiler flue gas is shown schematically in Figure 6. Basically it consists of:

- (A) a 0.375-in.-O.D., stainless-steel, gas-sampling tube;
- (B) two parallel-connected 2-in.-O.D. x 17-in., glass, filtering columns charged with pyrex-glass wool to remove coarse solid and liquid particulate matter;
- (C) a diaphragm pump and motor having a minimum capacity of 4 SCFM at 3 in. Hg;
- (D) an automatic pressure relief valve;
- (E) a manually operated micrometer valve to control pressure in the sample system at 2 psig;
- (F) a cyclonic dust filter and liquid separator for removing all plus-10-micron particulate matter;
- (G) a manifold containing three toggle valves for supplying either sample gas, zero gas or span gas to each analyzer;
- (H) a 1.25-in.-O.D. x 14-in. drying column filled with minus 8-mesh, indicating Drierite;
- (I) a dial thermometer to measure temperature of sample gas;
- (J) a pressure gauge to indicate sample pressure at the inlet to the ultra-fine filter (K);
- (K) an ultra-fine, convoluted, fibreglass filter to remove all plus-0.3-micron particles from the gas stream to the CO₂ and CO analyzers;
- (L) a pressure gauge to indicate sample pressure at the outlet of the ultra-fine filter (K);
- (M) a needle valve to control gas flow to the CO₂ and CO analyzers;
- (N) a flowmeter to ensure that both the CO₂ and CO analyzers are provided with 2 SCFH of sample gas at essentially atmospheric pressure;

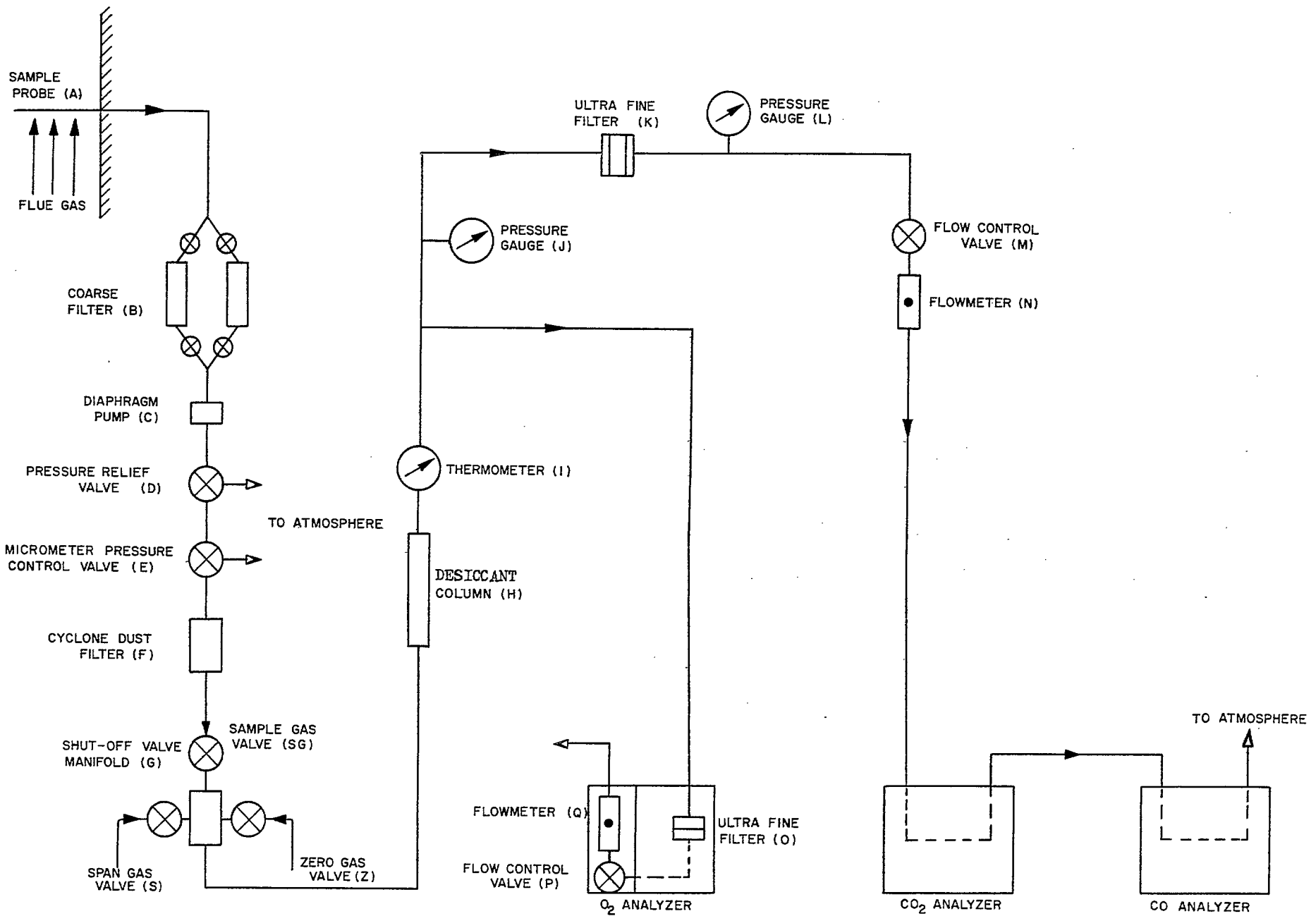


Figure 6. System flow diagram for continuous monitoring of CO_2 , CO and O_2 .

- (O) an ultra-fine filter to remove particulate matter from the gas stream to the O₂ analyzers;
- (P) a needle valve to control gas flow to the O₂ analyzer;
- (Q) a flowmeter which is integral with the O₂ analyzer to ensure that the sample cells in the instrument are provided with a sample flow of 30 SCFH at 0.5 to 2 psig.

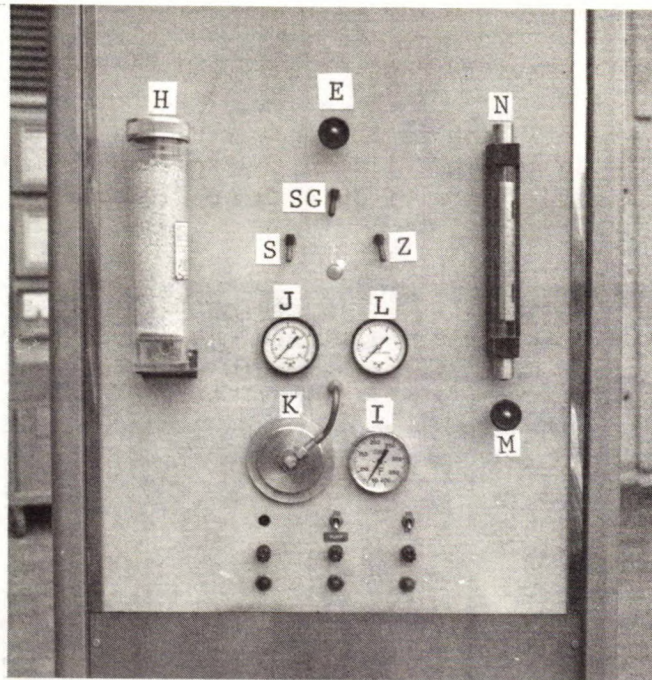
It is important that all materials that contact the gas sample be corrosion-proof because the sample gas normally contains corrosive droplets of dilute acid, particularly between the sample probe (A) and the desiccant column (H). Components (A) to (N) inclusive are connected with corrosion-proof 0.25-in.-O.D. tubing of either stainless steel, aluminum, or tygon.

The assembled flue-gas sampling system, shown in Figure 7, continuously supplies a clean, liquid-free gas sample to each analyzer at the flow rates and pressures recommended by the instrument supplier. In addition, the lag time in the system is reduced to about 90 sec by pumping the sample gas stream at a rate of 4.0 SCFM* from the sample probe (A) to the system-pressure control valve (E), where about 90 per cent of the gas sample is exhausted to atmosphere. The remainder of the gas sample is then divided into two streams, one to the O₂ analyzer at 30 SCFH and one to the series-connected CO₂ and CO analyzers at 2 SCFH.

The entire sampling and analyzing systems, together with three strip-chart recorders**, are mounted in two portable metal cabinets as shown in Figure 8.

* SCFM = Standard cubic feet per minute.

** The infrared analyzers employ L & N Model S recorders, while the thermo-magnetic analyzer employs a L & N Model S recorder with a special measuring circuit.



(a) Front view



(b) Rear view

Figure 7. Flue-gas sampling system.

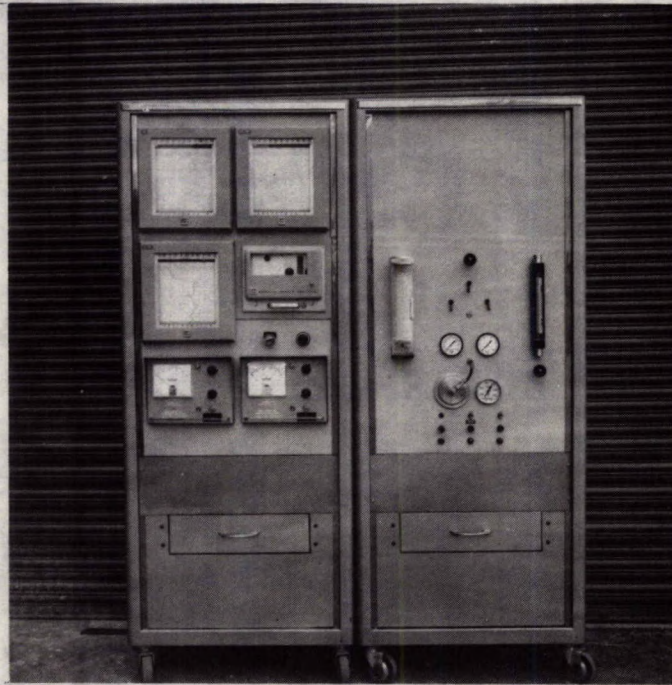


Figure 8. Panel-mounted flue-gas sampling and analyzer systems.

APPENDIX

DAILY OPERATING PROCEDURE

Preparation for Operation

The procedure used to prepare the system for sampling, analyzing and recording levels of CO₂, CO and O₂ during normal operation is described below.

1. Check silica-wool filter columns (B) for dust content and replace wool if necessary.
2. Check drying column (H) and replace Drierite if necessary.

Should the moisture content of the sample gas require several recharges of Drierite during a normal daily operation, the sample line from the probe to the system can be water-cooled and a suitable moisture trap positioned ahead of the filtering columns (B).

3. Although not required on a daily basis, the condition of the ultra-fine filter should be checked periodically.
4. A periodic leak test of the entire sampling system should be performed, particularly after any minor adjustments or changes have been made to the system plumbing. Standard routine is simply to block the sample probe inlet while the pumping system is operating and note the sample flow rate. Zero flow indicates a leak-proof system.
5. Turn the master switch on. Turn the three analyzer and three recorder amplifier switches to on and the recorder chart drives to off. Allow at least 3 hours for the electrical components to reach thermal equilibrium. This state has been reached when the recorders, with chart drives on, show no drift over a period of one-half hour. During warm-up and operation the analyzers should be opened only when necessary, because more time will be required to attain thermal equilibrium.

Zero Gas Calibration - CO₂, CO and O₂ Analyzers

1. Connect zero gas (clean, compressed air) to manifold (G).
2. Close sample-gas toggle valve (SG); close span-gas toggle valve (S); open zero-gas toggle valve (Z); close sample-gas valve (P) on O₂ analyzer (see Figure 9).
3. Gradually open regulator on bottle of compressed air to provide 2 psig to system.

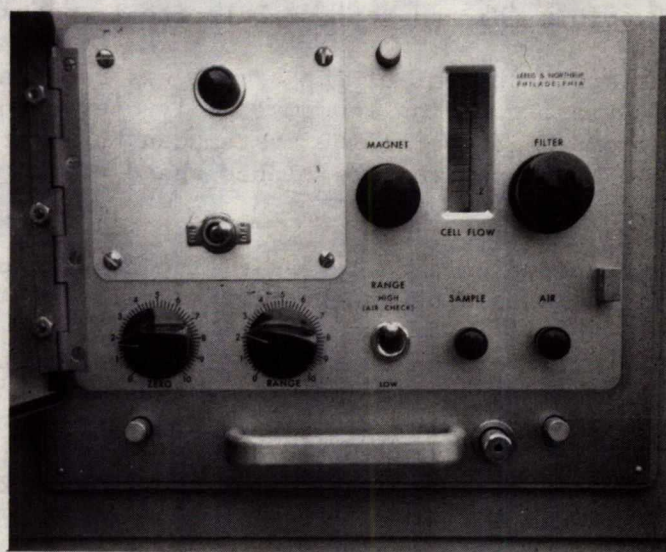


Figure 9. Thermomagnetic oxygen analyzer, front panel.

4. Open infrared-analyzer flow control valve (M) to obtain a flow of 2 SCFH on flowmeter (N). Close sample valve and gradually open air control valve on O₂ analyzer, Figure 9, to obtain a flow indication of 0.5 on the flowmeter.
5. Purge the system with compressed air for several minutes.
6. The infrared meter pointers should then read zero. If not, turn the meter adjust screws shown in Figure 10 to properly position the pointers. If necessary, mechanically adjust recorder pens to read zero.
7. With the RANGE switch of the O₂ analyzer on high (air check) position and the ZERO (fine) and RANGE dials at mid point, Figure 8, the O₂ recorder pen should track on or about the red A (air) line. Should the pen not approach the air line to within $\pm 5\%$ of scale, it is then necessary to adjust the ZERO (coarse) rheostat on the back of the analyzer to position the pen on the air line. Normally, ZERO (coarse) adjustment is checked daily.
8. The following routine for ZERO (fine) setting should be carried out daily. Place magnet shorting rod in OUT position for 1.5 minutes. Be sure that the shorting rod is completely out (against stop). At the end of 1.5 minutes, carefully adjust ZERO (fine) rheostat to balance recorder pen on red Z_A line. Place magnet shorting rod in the IN position and wait for about 10 minutes until the system stabilizes. Adjust RANGE rheostat until recorder pen balances at red A line. Repeat the above procedure for ZERO (fine) setting until pen tracks between and dead stops at red A and red Z_A lines on strip chart recorder.

Span Gas Calibration - CO₂ and CO Analyzers

The calibration of the infrared analyzers for CO₂ and CO respectively is performed separately, but the procedure is the same for both except that the span gas used is the specific component of interest, i.e. CO₂ span gas in CO₂ analyzer and CO span gas in CO analyzer.

1. Connect span gas of interest (CO₂ or CO) to gas manifold (G).
2. Close zero toggle valve (Z); close sample-gas toggle valve (SG); open span gas valve (S).
3. Pass span gas through the system at a flow rate of 2 SCFH, allowing at least 30 sec to purge.
4. Set span controls, shown in Figure 10, at settings specified on the CO₂ and CO calibration curves, Figures 11 and 12.
5. Turn span control until the meter indicates a value in agreement with the calibration curves and the known concentration of the span gas.

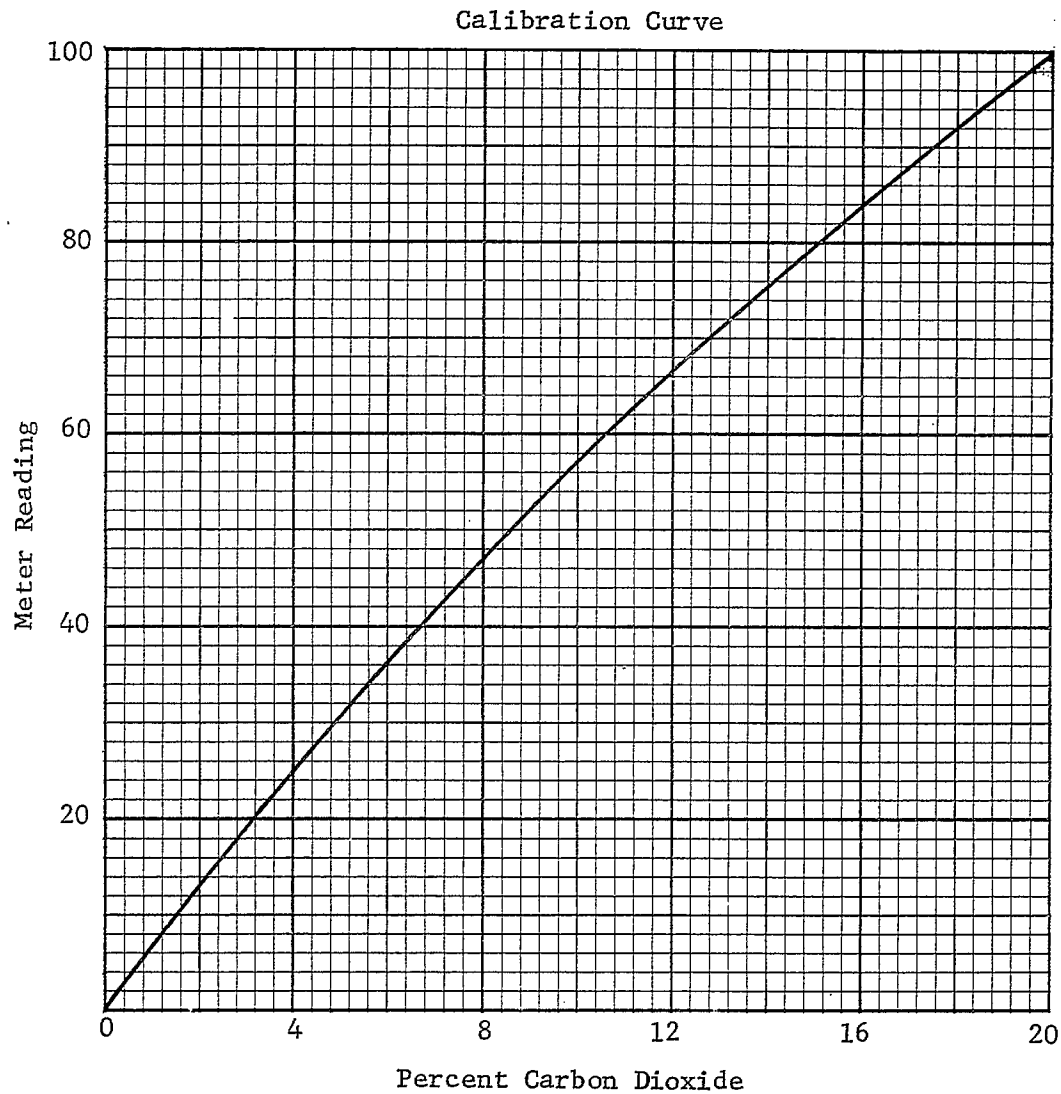


(a) CO₂ analyzer



(b) CO analyzer

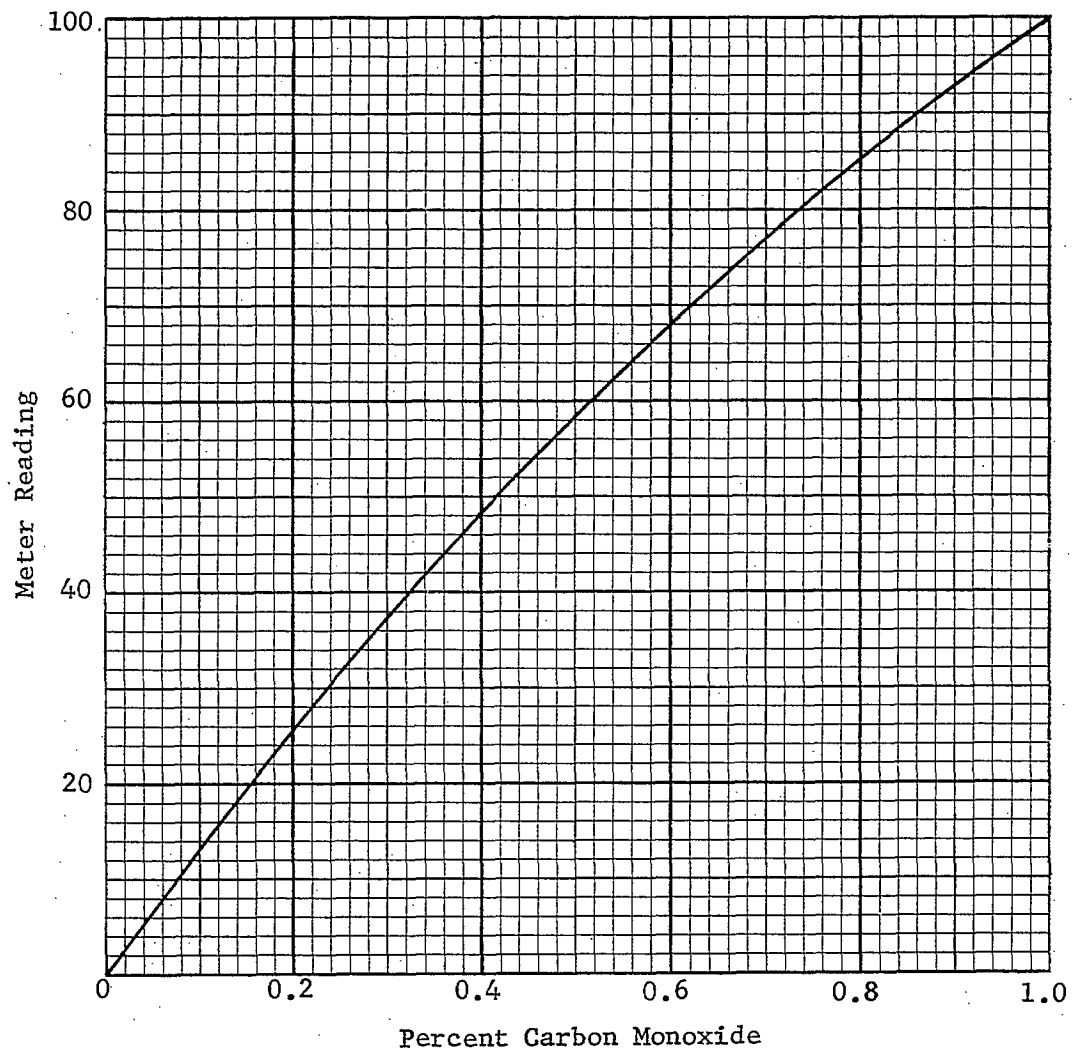
Figure 10. Infrared analyzers for CO₂ and CO, front panel.



Calibration: 0-20% CO₂ in Steam
 Optics MSA Spec. -
 Zero: 26 OSC - VDC
 Span: 86 Gain -
 Thermostat: 160°F
 Non-linearity: < + 7%
 Source Tap: S - 2, C - 1
 Percent Absorption: 20
 Operating Pressure: 0 PSIG
 Cross Sensitivity of Background:
 3% H₂O = 0
 100% CO = 0
 100% CH₄ = 0
 1% SO₂ = 0

Figure 11. Calibration data for CO₂ analyzer.

Calibration Curve



Calibration: 0-1% CO in Flue Gas
Optics MSA Spec. 004
Zero: 35 OSC, 126 VDC
Span: 88 Gain 3
Thermostat: 160°F
Non-linearity: < + 9%
Source Tap: S - 1, C - 1
Percent Absorption: 14
Operating Pressure: 0 PSIG
Gross Sensitivity of Background:
3% H₂O = 0.5% F.S.
10% CO₂ = 0.5% F.S.
10% CH₄ = 0.5% F.S.

Figure 12. Calibration data for CO analyzer.

6. Pass zero gas through the analyzer, and check zero setting again. Zero and span should be rechecked after instrument reaches temperature stability. Lock the final settings of the zero and span controls with knob locks.
7. The recorder reading should coincide within $\pm 2\%$ of the reading of the analyzer meter. The only exception to this would be in the case where a special scale for the meter has been prepared to correct for the non-linearity of the signal from the analyzer. The analyzer meter and the recorder reading, however, should still coincide at both zero and full scale. If the recorder reading is different than the meter reading by more than $\pm 2\%$ at one-half or three-quarter scale, an adjustment must be made in the recorder adjust.

Span Gas Calibration - O₂ Analyzer

Span calibration of the thermomagnetic analyzer may be carried out using any of the three methods outlined below.

Thermomagnetic Method for 'Low Range' Calibration

Having first calibrated the O₂ analyzer on zero setting, it is then necessary to calibrate the analyzer for the oxygen-bearing gas being sampled. The following routine should be repeated with every change in level of oxygen in the sample gas stream:

Close air valve on O₂ analyzer. Switch on pump and gradually open SAMPLE valve to provide a flow of 0.5 SCFH. Place the RANGE switch in LOW position and allow system to stabilize with sample gas in cells. Place magnet shorting rod in OUT position and at the end of 1.5 minutes adjust ZERO (fine) rheostat to balance recorder pen on the red ZG line. The magnet shorting rod is then returned to the IN position. The O₂ analyzer should now be calibrated for 'low range' (0 to 5%) levels of oxygen.

Thermomagnetic Method for 'High Range' Calibration

Generally, 'low range' calibration of the O₂ analyzer will suffice for continuous monitoring of oxygen levels in boiler flue gases under normal conditions of combustion. However, should monitoring of oxygen levels above 5% be desired, the following routine for calibrating the analyzer using the 'high range' sample gas is employed;

1. Span the O₂ analyzer on air as described above for 'low range' calibration.
2. With sampling pump on, close AIR valve on the O₂ analyzer and gradually open SAMPLE valve, Figure 9, to provide a flow of 0.5 SCFH.
3. Place the RANGE switch in HIGH (air check) position and allow system to stabilize with sample gas in cells.

4. Place magnet shorting rod in OUT position and at the end of 1.5 minutes adjust ZERO (fine) rheostat to balance recorder pen on the red Z_A line. Return magnet shorting rod to IN position.

The O₂ analyzer should now be operational in the 'high range' of oxygen monitoring where zero reading on the recorder scale represents 0% oxygen and the red A line represents the 20.9% oxygen content of air.

Readings on the recorder scale are then referred to the 'high range' calibration curve (Figure 13) for correct per cent of oxygen in the sample gas stream.

Orsat Method

Before attempting to check the calibration of the thermomagnetic analyzer by means of an Orsat or other analytical method, the thermomagnetic method should be employed. The thermomagnetic calibration may then be checked by comparing the results of independent analysis with the analyzer recorder readings. A sample for analysis can be withdrawn by making a connection to the bypass outlet, Figure 5. Any adjustments to make the recorder agree with the Orsat values should be made with the ZERO dial.

Tank Gas Method

The analyzer may also be checked with gases from tanks of known composition. For most accurate results the tank gases should include any background gases normally present in the gases being sampled.

Preferably, at least two samples should be used, one near the low end of the scale range and one near the normal operating point. When changing from one sample to another, allow sufficient time for the system to stabilize before making any adjustments. The ZERO and RANGE dials in the analyzer should be adjusted to give the desired readings as the tank gases are sampled. Adjust the ZERO dial for the correct readings at the low end of the scale, and the RANGE dial for correct upscale readings. Unless the low-end sample contains no oxygen the low- and high-end adjustments will be interdependent and must be repeated until both are correct. If only one tank sample is used, the range adjustment should be made with air according to Step 7 of Zero Gas Calibration. If necessary, the ZERO dial should then be adjusted to give the correct tank sample reading. In this instance, the oxygen content of the tank sample should be near the normal operating point.

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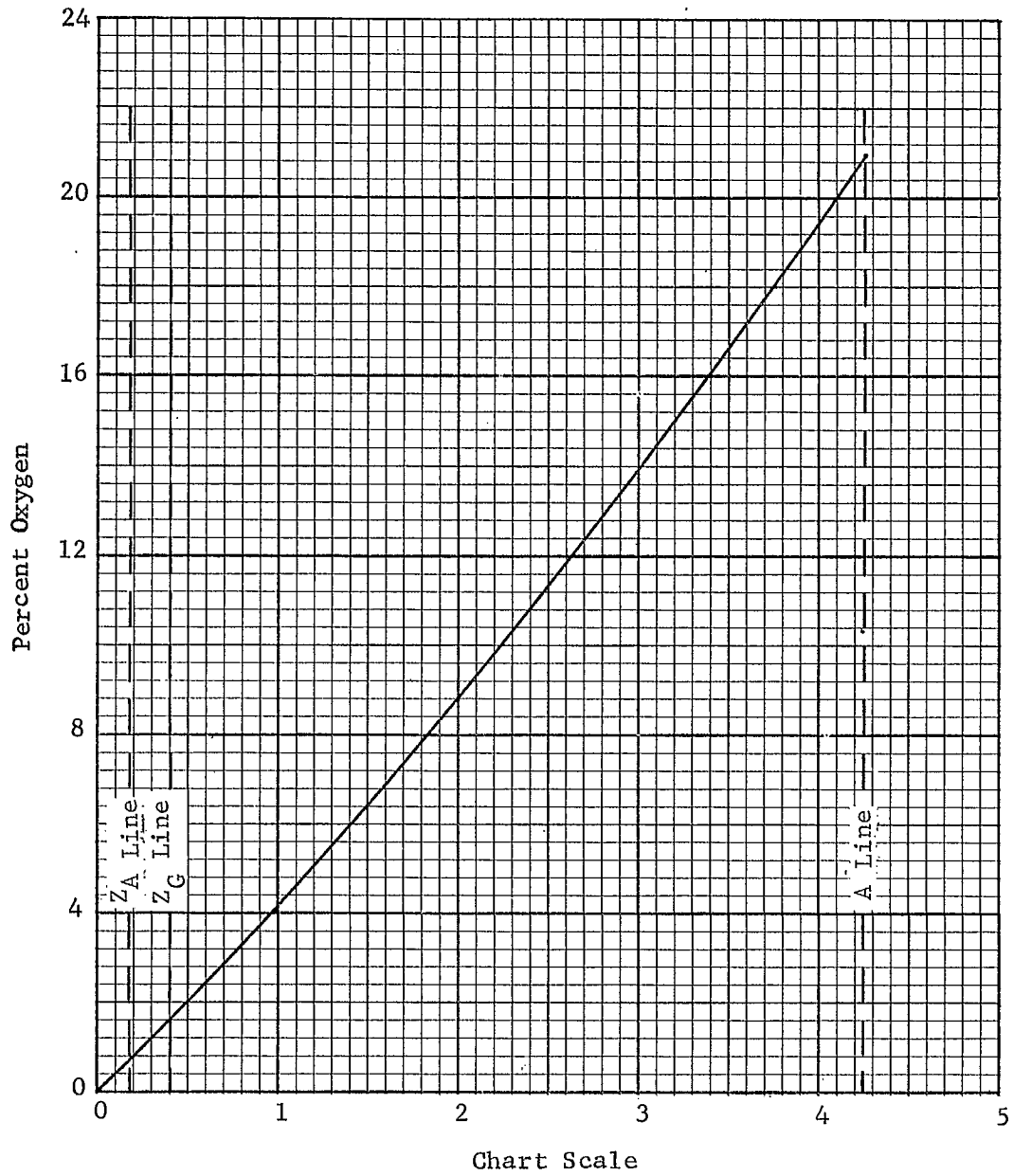


Figure 13. High-range calibration chart for thermomagnetic analyzer.

