• Recovery of weighed amounts of halogenated hydrocarbons has been within 95-100 percent.

Source—

Not commercially available. Contributed by: Dow Chemical Company. Approximate cost—$200.00.

Construction Details

Figure 1 is a drawing of the fritted glass absorber used in conjunction with the combustion apparatus. The apparatus was assembled as shown in Figure 2.

Operating Instructions

1. Prior to sampling, the furnace must be heated to about 900°C. Approximately twenty to thirty minutes is required for a warm-up period.
2. Connect the furnace to a sample point by means of a Saran line joined with rubber and glass joint connections.
3. Pipette 25 ml of trapping solution (1 percent sodium carbonate, 1 percent sodium formate solution) into the absorber. Turn the pump on and adjust the air flow rate (1.0 lpm proven efficient). The length of time of sampling will depend on the estimated concen-
4. Transfer the contents of the absorber to a 50 ml volumetric flask. It is necessary to blow air through the inlet of the absorber to remove liquid below the fritted glass. Wash absorber several times with distilled water and make t volume. The sample can now be analyzed or transferred to separate sample bottles for later analysis.

Calibration Instructions

To insure correct rates of air flow the flow meter should be periodically checked against a wet test meter.

Maintenance Instructions

1. Proper lubrication of pump should be maintained.
2. Fresh dessicant should be maintained in the drying tube.
3. Flow meter must be kept clean to insure accurate readings.
4. Temperature of combustion furnace should be checked periodically.

Bibliography

Determination of Chloride: A Modification of the Volhard Method. Caldwell and Moyer. Ind. Eng. Chem. Anal. Ed. 7: 38 (1935).

HALOGENATED HYDROCARBON ANALYZER

Uses

The halogenated hydrocarbon analyzer is used to record continuously in the parts per million range the concentration of halogenated hydrocarbon gases in the air throughout a plant.

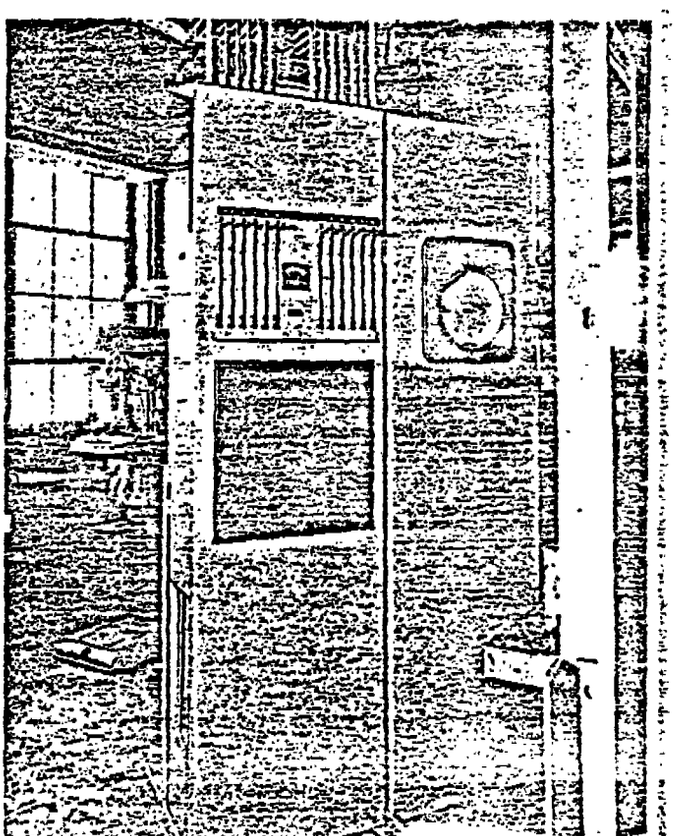
Operating Principle

A continuous sample of air is drawn from each of twelve plant areas through Saran tubing and is metered through twelve rotameters located on the front panel. The air is then passed through a furnace containing twelve quartz tubes operating at approximately 1000°C. The halogen in the presence of water vapor in the air is converted to the halogen acid. From here the acid is mixed with water through absorber tubes, the water being metered to each absorber by means of a rotating orifice operating under a constant head tank. Two 6-record Foxboro Dynalog recorders are used to measure the resulting conductivity.

Physical Description

	Measuring Unit	Panel
Weight—	Approx. 500 pounds	Approx. 150 pounds
Height—	8 feet, 10 inches	7½ feet
Width—	2 feet	2 feet
Depth—	1 foot, 10 inches	1 foot

The sampling and measuring unit is designed for permanent installation but the panel containing the two Dynalog recorders may be mounted remotely with respect to the



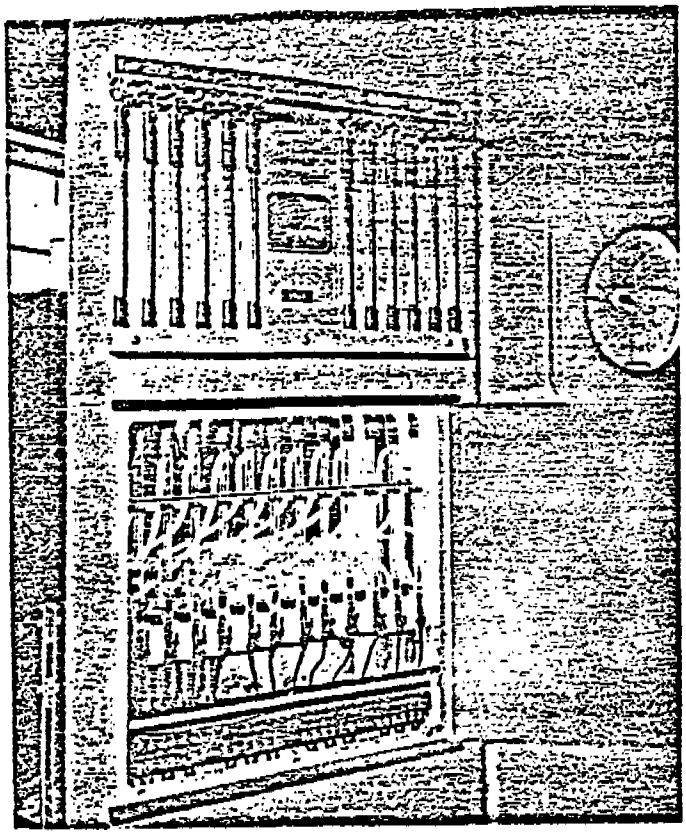


Figure 2 — Enlarged Front View Showing Rotameters, Absorbers, and Conductivity Cells.

Performance Data

This instrument has been used successfully over a period of time on methyl chloride, ethyl chloride, methyl bromide, carbon tetrachloride, vinyl chloride, and vinylidiene chloride. Its range is limited by the purity of water available, range of recorder, and CO_2 or other interfering gases present in air deemed as "zero."

Range:

Range limitations of this instrument have not fully been investigated. Air rates, water rate, recorder range and cell constants all may be varied, giving this instrument abundant flexibility. Extreme ranges have not been required in the Dow applications. Toxic limits have somewhat determined ranges f instruments now in use; i.e., vinyl chloride 0-1000 ppm; vinylidiene chloride 0-500 ppm; ethyl chloride 0-1000 ppm; carbon tetrachloride 0-300 ppm. Experimental units have been operated at both lower and higher ranges with excellent results and further investigation is in progress. The accuracy of all instruments now in operation is within 10 percent of analyzed gas samples.

Source—

Not commercially available. Contributed by: Dow Chemical Company.

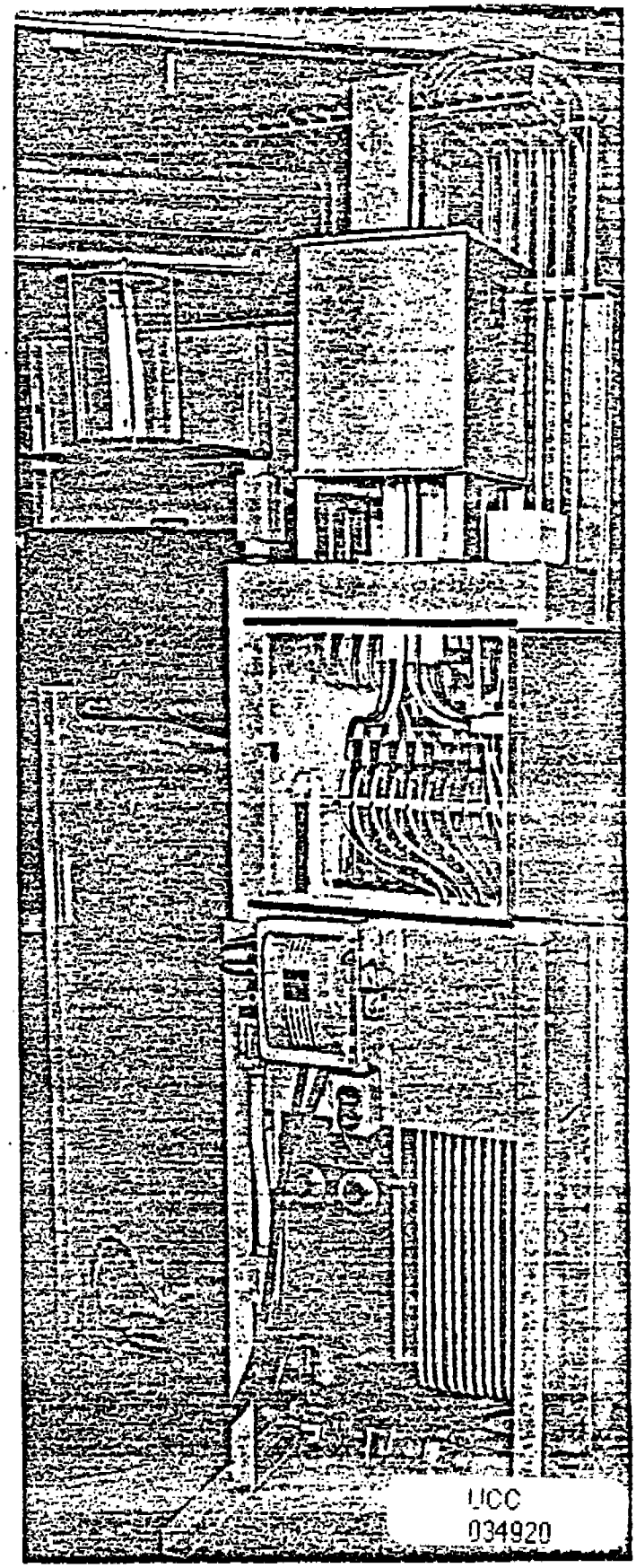


Figure 3 — Rear View of Analyzer Showing Measuring Unit and Recorder Panel (From Top of Photo). A. Measuring Unit—(1) Sample Line Inputs (12 in this Case), ¼" Pipe; (2) Furnaces; (3) Quartz Tubes Passing Through

Construction Details

Following are the essential components used in the construction of this instrument:

12 points # Req'd.	6 points # Req'd.	
1	1	Heavy Duty Pyrometer
1	1	Heavy Duty Furnace
1	1	Heavy Duty tap changing transformer
1	1	Vacuum pump
1	1	Bodine motor
1	1	Constant level water chamber
24	12	Needle valves
12	6	Rotameters
4	4	Fittings (Crouse-Hinds)
1	1	Switch box
		Tygon tubing
4	2	Terminal strips
6		Elbows 45° brass ⅛ inch
6		Couplings brass ⅛ inch
12	6	Quartz tubes
1	1	Steam condenser or ion exchange tower
2	1	Foxboro Dynalog conductivity recorder

Operating and Maintenance Instructions

1. Check pyrometer at top of front panel on measuring unit. This may vary from 1000°C to 1090°C. At no time should this temperature vary from these limits.
   a. If in excess of 1090°C, adjust taps located on transformer. An adjustment decreasing the "fine" control 1 or 2 divisions should be sufficient.
   b. If less than 1000°C, check furnace fuse. (Located on right facing rear of panel, in fuse box.) Check thermocouple, check taps on furnace and increase "fine" adjustment 1 or 2 divisions.
2. Check rotameters. Balls should ride with their bottoms adjacent to top of marking tabs. Adjustments are made by needle valves on top header. Any oscillations may be damped by adjusting needle valves on water leg located inside panel. Check to insure constriction is not too great so as not to allow the allotted quantity of water to reach the cell. This may be done by removing rotating arm and filling leg in question, replacing the arm and checking to see whether or not the water level decreases. Rotameters should be cleaned periodically when the end of sample tube is subjected to a dusty atmosphere or when dust or oil film accumulation is noticed in tube.
3. Remove rotating arm from water distributor and check flow.
4. Check vacuum pump for oil level in trap on vacuum side of pump. This oil is used for lubrication. No fluid should be present in the trap on pressure side of pump.
5. Check absorption tubes and rubber tubing.
6. Check conductivity cells for bubble formation on plates. If present, partially remove cell allowing inrushing air to remove bubbles.
7. Clean pens on recorder and replace ink pads when needed.
8. When instrument has been shut down and is again to be put into operation, allow the water system to run 10 minutes before starting pump so the water legs will be full. Also check the ball in the vacuum release valve to insure free operation.
9. In case of pump failure and a replacement pump is not available immediately, voltage on furnace should be reduced by changing taps on transformer to lowest possible value to avoid operating the furnace at higher than rated capacity.

Calibration Instructions

Calibration is accomplished by contaminating a metered air stream with a known amount of material. This stream is sampled, analyzed by the instrument and at the same time checked against a standard.

CARBON DIOXIDE INDICATORS

Uses

Carbon dioxide indicators can be used to determine the concentration of CO_2 present in the atmosphere of a closed space or compartment. Other uses include analysis of flue gases and combustion testing.

Operating Principle

A measured volume of air or flue gas under test is drawn into the absorption column by means of an aspirator bulb. Carbon dioxide in the sample is absorbed by a solution of potassium hydroxide contained in the absorption and manometer columns. The resulting reduction of gas pressure (the scale having been previously set to zero at the top of the liquid column) is an indication of the percentage of CO_2 present in the sample. Percent CO_2 is read directly from the scale.

upon the various ranges. The model shown in Figure 1, for example, weighs 1 pound and is 2½ by 1¼ by 9 inches high.

All models are built of acrylic plastic construction employing stainless steel for all metallic parts in contact with the fluid. The instruments are portable in design and provided with carrying cases and other accessories as needed to operate in the field.

Figure 2 is an enlarged drawing of the # 800-5 (0 to 5 percent) Carbon Dioxide Indicator showing the various components.

Performance Data

Various ranges and accuracy limits are available as follows. # 800-5 Carbon Dioxide Indicator, range 0-5 percent CO_2, minor divisions 0.10 percent accuracy at full scale

HALOGENATED HYDROCARBON ANALYZER

Raymond M. Donahue

Midland, Michigan

The Company has for many years been particularily concerned about the health and well-being of the employees who are directly involved in the manufacture of various chemical products.

In the manufacture of a product in which a halogenated hydrocarbon is involved, analyzing the ambient air within the plant buildings has been one method of safeguarding the employee against an exposure that might not otherwise be detected until upper threshold limit values were exceeded.

The Halogenated Hydrocarbon Analyzer was developed by for the purpose of recording the concentration of halogenated hydrocarbons in air in the parts per million range. It is usually a 6-point or 12-point instrument.

The operation of this instrument can be described as follows: A continuous sample of air is drawn from specified locations through Saran tubing and is metered through rotameters located on the front panel. This air is then passed through quartz tubes in a furnace at a controlled temperature, depending upon the particular compound being looked for. While passing through the furnace, the halogen in the presence of water vapor in the air is converted to the halogen acid such as hydrogen bromide or hydrogen chloride. From here the acid gas is scrubbed by deionized water in passing the absorber tubes. The water is metered to each absorber tube by means of a rotating orifice operating under a constant head tank. The conductivity of the resulting solution is directly proportional to the amount of a halogenated compound present

in the sample gas. This conductivity measurement is made by a Foxboro multi-record recorder which measures and prints out twelve sample points in 72 seconds.

The air and water flows are so adjusted that the chart readings may be interpreted directly in parts per million of a halogenated hydrocarbon in air. In this particular analyzer shown here, the range is 0-500 ppm of methyl bromide in air and is set to alarm when any one point exceeds 50 ppm. This analyzer is a 12-pointer with a range of 0-500 ppm of methyl chloride and alarm point set at 100 ppm. When the alarm system is activated, a horn is energized as well as a flashing beacon in the analyzer area. At the same time a similar light is in operation in other areas in the building including the office. This signal informs personnel in all areas of the building that a leak has occurred, and specific location of the leak is determined by the recorder printout. This general, or full area alarm system, is particularily helpful to minimum size operating crews at night at which time a leak in a remote storage area could be detected before the atmosphere accumulated over the threshold limit values. In addition to the alarm set point on parts per million concentration, there is also a device which detects furnace temperature failure. This alarm is necessary because if the furnace temperature falls off, then conversion is not complete and operating personnel would be unaware of an accidental leak.

This furnace is a vertical tube type with the sample inlet on top, and the outlet below feeds directly to the absorber where the gas is immediately scrubbed. Thus, with the use of a vertical tube furnace, there are no traps in the outlet which might accumlate residual concentrations of the halogen acids.

Pure water is essential to the proper operation of the analyzer. Steam is condensed, cooled, and then the condensate run through an ion-exchange bed and filtered to 25 microns before entering the constant level tank.

The water distributor receives a constant head of water from a float tank and contains an orifice on the end of a rotating arm driven by a 60 rpm synchronous motor. As the arm revolves, the water stream is divided into either six or twelve portions by a segmental cup and delivered to the water traps. The "U" traps prevent sucking of air into the absorbers through the water lines to the absorbers. Anti-surge valves are one-eighth needle valves and serve to reduce pulsing of the water flow into the absorbers. The suction regulator is a ball type.

The glass absorbers and conductivity cells are connected to the nickel air and water header by means of bored out rubber stoppers. The air samples which have passed through the furnace enter into the top connection on the absorbers. Metered streams of water from the rotating orifice pass into the side arms at the top of the absorber assemblies. The air and water pass with parallel flow at high velocity through the three millimeter capillary tubes where most of the HBR and HCl is scrubbed out of the air. The air and water then separate, the air passing through the upper glass outlet and into the nickel header, and the water passing down through the conductivity cell and thence into the header. The absorbers have been dipped into a 10% solution of hydrogen flouride to facilitate wetting and to even flow along the walls of the capillary.

This instrument does not meet requirements for areas classified either as semi-hazardous or hazardous. The measurement unit must be located in an area where hazardous conditions never exist--even in an emergency. It is

impossible to make the instrument safe by shutting off the power, as the furnace will stay hot for a considerable period of time. Installations have been made where the measurement unit was located in a standard area and over 250 feet away from the sample points and recorders; the latter being installed in another direction in the operating panel area.

This analyzer requires a normal amount of instrument maintenance. The water flow to the absorbers and cells must remain constant if the instrument is to maintain its calibrated range. This, then, is checked frequently. Air sample flow rates, furnace temperature stability, alarm systems, and recorder operations are also checked periodically.

The Section makes a calibration check of each analyzer every six months. Preventive maintenance schedule calls for quartz tube and connecting rubber tubing replacement on six-month intervals also. This quartz and rubber replacement insures a high instrument measurement sensitivity. Sample lines are checked for leaks every month and repaired or replaced immediately if necessary.

The Halogenated Hydrocarbon Analyzer is obviously not specific for any one halogenated compound, so it can show the concentration of a particular compound only if it is the only one present which is contributing to the conductivity. Chlorinated as well as brominated materials as stated earlier have been analyzed with this instrument.

The range can be changed by:

1. Changing the conductance range of the recorder.
2. Changing the water rate to the cells.
3. Changing the air flow rate.

Furnace temperature control is more critical on some compounds than others. There is a several hundred degree spread between the efficient conversion of some halogenated hydrocarbon compounds than others. There is a noticeable fact evident to our Lab people who have developed, installed, and maintained these analyzers from their beginning, and that is: When there is a changeover of supervision in the plants where these analyzers are located, then there is a new, vigorous approach to safety, and the analyzer is soon equipped with an additional horn or flasher. Over a period of years and after several management changes, one can easily visualize a Halogenated Hydrocarbon Analyzer with alarms and redundancy on the alarm rendundancy.

The process operator who has lived through these changes and additions to the alarm system has been known to take steps in his own way to reduce the sensitivity and intensity of the system. This particular method is called the fresh air purge. Plant supervision has learned that the best method to reduce the number of alarms is to have a tight process--that is no pump seal leaks, valve packing gland leaks, etc.

At present there are nine analyzers in the Plant measuring through 102 sample points. In addition, there are two more in use in Plants, and one analyzer is operating in Europe.

There are several variations of this basic instrument in use at present in the Plant. Example: SO_2 is monitored in the and Power Houses by using 12-point analyzers without the furnace; that is, the sample of the ambient air is introduced directly to the absorber. $POCl_3$ has also been analyzed this way. In another, it is used solely as a process monitor where process cooling water is analyzed for a methylene chloride leak. Clean air is swept over an enclosed temperature controlled flowing sample, and that air is the influent sample to the Halogenated Hydrocarbon Analyzer.

The object in this case is to drive out the methylene chloride, if any, from the water sample by heating, and to sweep the air sample to the analyzer where it is pyrolyzed, scrubbed, and measured. This has been used as a clear water sewer monitor.

At one plant where methyl chloride in air is analyzed, the measurements of each sample point were fed to a computer where time weighted averages of each sample point in the plant area were recorded. Future plans are being considered in which the computer input from every sample point will result in analytical feedback to the Plant and the Group