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Date September 16, 1974
Originating Dept. Engineering
Subject Air Monitoring Systems for Vinyl Chloride - TEC-74-13

Gentlemen:

Attached is technical report TEC-74-13 authored by Mr. G. L. Baker. The report is an excellent synopsis of SID's participation in the recent vinyl chloride monitoring problem, starting in early April 1974 and terminating with our present activities. Gary outlines the culling process used in the selection of the final analyzer for this measurement, after which he provides a brief description of the total system and some of the tests that have been made to verify its specificity to vinyl chloride.

For those individuals who desire additional information on this subject the following list of internal correspondence is recommended as reference material. It will provide a more in-depth examination of areas which have only been touched lightly in the attached technical report.

SID Proposal P-74-45
Date: April 23, 1974
Subject: Area Air Monitoring System for Vinyl Chloride

R&D Report No. 910A20
Date: June 4, 1974
Subject: Vinyl Chloride Monomer: Use of Miran I Portable Infrared Gas Analyzer for Continuous Area Air Analyses

SID Evaluation Report E-74-11
Date: August 13, 1974
Subject: Data Acquisition and Reduction Systems for Vinyl Chloride Analyzers

SID Proposal P-74-110
Date: September 12, 1974
Subject: Data Acquisition and Reduction Systems for Vinyl Chloride Analyzers

Manuals:

(1) Model 1200 (CMVII VFA)
Maintenance and Operation Manual

(2) Application Data for Carbide Model 1200
Vapor Fraction Analyzer, Code No. 514C-90

If there are any questions or comments concerning this report or any aspect of this entire monitoring program, please feel free to contact either Mr. Baker (extension 4482) or me (extension 5333).

Sincerely yours,

J. H. Brubaker
Measurement and Control Technology
CHEMICALS AND PLASTICS

JHB:jb
attachment

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TEC-74-13

Technical Report

Engineering Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia

SUBJECT: Air Monitoring Systems for Vinyl Chloride

WRITTEN BY: G. L. Baker DATE: September 16, 1974

REVIEWED BY: J. H. Brubaker

SUMMARY

As one part of the continuing efforts of Union Carbide Corporation Chemicals and Plastics to assure compliance with the requirements of the Emergency Temporary Standard for Exposure to Vinyl Chloride published by OSHA on April 5, 1974, five area monitoring systems for vinyl chloride monomer have been installed: three at the South Charleston Plant and two at the Texas City Plant. Each analyzer is measuring 0-100 ppm vinyl chloride on twenty sample points, requiring two minutes per analysis.

The results have been very good. The hardware has been reliable, and the data obtained has been useful in locating and reducing vinyl chloride emissions into working areas.

INTRODUCTION

An Emergency Temporary Standard for Exposure to Vinyl Chloride was published by OSHA in the Federal Register on April 5, 1974. On that date, Mr. R. N. Wheeler, South Charleston Plant, and Messrs, H. R. Guest, N. H. Ketcham and F. H. Small (R&D Environmental Protection Section) met to outline the technical capabilities required for compliance and to assure that the requirements would be met promptly. Multiple sample point, continuous air analyzers adaptable ultimately to computer data handling for at least five plant locations (three at South Charleston and two at Texas City) were listed as an urgent requirement. Mr. Ketcham was asked to coordinate efforts to determine the most suitable system and to facilitate installation at the earliest possible date.

On April 8, Messrs. J. H. Brubaker and G. L. Baker (Special Measurement Development), Mr. G. F. Hurley (R&D Environmental Helath Group), Messrs. Ketcham and Wheeler met to initiate the required review of currently available sampling and analytical systems, to select the most appropriate, and to expedite the procurement and installations. Installation of at least one system at the South Charleston Plant within ten days was established as one of the objectives. The immediate and long

term uses to be made of the analyzers were considered at this time, reviewed with others as opportunities permitted, and subsequently defined as follows.

(1) Provide automatic measurement of airborne vinyl chloride monomer throughout the work locations, with alarm capability, to identify where and when the ceiling limit of 50 ppm by volume in air is exceeded.

(2) Identify and document the work locations which are consistently below the ceiling limit of 50 ppm, hence are in compliance with the emergency temporary standard.

(3) Help identify any work locations in which the ceiling limit is frequently or regularly exceeded. These will require first level priority action to correct the condition or to protect persons when they must be in such locations.

(4) Help identify the locations in which unusual conditions occur only infrequently with the result of approaching or exceeding the ceiling limit. These will require second level priority action to correct the condition or to protect personnel.

(5) Generate data showing the locations and/or operations which would be out of compliance if the allowable limit of exposure were to be reduced, i.e., to 20 ppm, 10 ppm, or 5 ppm.

(6) Document measurements to show that the monomer vapor does not travel past the perimeter of the unit area in concentrations exceeding the ceiling limit, or identify the circumstances under which this does occur.

(7) Provide potential capabilities for computerized data processing of area exposure measurements to facilitate the generation and recording of exposure histories for each individual employee, should that become necessary or desirable at a later date.

DISCUSSION

Recently the R&D Environmental Health Laboratory evaluated the Miran I Portable Infrared Gas Analyzer (manufactured by the Wilkes Scientific Corporation) for use as a continuous air analyzer for vinyl chloride. Favorable results led to its installation at the Vinyl Dispersion Unit at South Charleston. It was installed in the control room and equipped with 100 feet of movable sample line. The Miran I

has performed well, although it was not designed for unattended operation. A sister instrument, the Miran II, is built especially for permanent installations and is suitable for use with multiple sample points. Accordingly, the Miran II was considered along with several other possible instruments for the permanent installations.

Manufacturers of potentially suitable instruments and sampling systems were contacted by telephone. Other companies known to be using or acquiring multisampling point, area monitoring systems were also contacted and/or reports of their systems were reviewed. The most important factors considered were reliability, sensitivity, specificity, ease of maintenance, delivery times and cost. The search quickly narrowed to two analytical techniques: infrared spectrometry and gas chromatography. As a result of firsthand experience by various Union Carbide instrument users with these types of analyzers, the choice was narrowed to three specific instruments: the Wilks Miran II Infrared Monitor, the Union Carbide Model 1200 process chromatograph, and a Honeywell process chromatograph. Table I is a compilation of important instrument parameters for comparison of these analyzers.

After considering all the pertinent factors, chromatographs were concluded to be the best analyzers for the vinyl chloride measurement in plant atmospheres, primarily because of their superior sensitivity and specificity over infrared analyzers. Immediate availability and better plant capability for maintenance were additional advantages which apply to the Model 1200 chromatograph. It has proved to be very reliable in numerous applications throughout Union Carbide. It is also capable of very high sensitivity and excellent specificity for vinyl chloride. Since several of these analyzers were already in use at both South Charleston and Texas City, the instrument servicemen at both locations were trained to maintain them and spare parts were readily available facilitating any necessary repair work. Therefore, the Union Carbide Model 1200 chromatograph was selected for the vinyl chloride measurement.

General System

Five air monitoring systems for measuring vinyl chloride emissions are now in use at the South Charleston and Texas City Plants. Each system is equipped with a UCC Model 1200 chromatograph, a 20 point stream selector, and a strip chart recorder with an adjustable high level alarm, all mounted on a 24 by 52 inch panel (Figure 1). A stream switching station, including a sample pump and stream switching valves, is also provided with each system (Figure 2).

Each analyzer has been initially ranged for 0 to 100 ppm full scale, although the capability exists to expand the range to 0 to 20 ppm full scale or lower if required.

The stream selector permits any of the 20 sample points to be sampled sequentially. The systems are now programmed to sample and analyze each point in two minutes. The vinyl chloride concentration from each point is presented on the recorder in bargraph form (Figure 3). Each sample point is also identified in bargraph form prior to the component readout.

Model 1200 Chromatograph

The Model 1200 chromatograph is a compact process analyzer equipped with solid state circuitry, including an electronic automatic zero. It is equipped with a flame ionization detector which is very sensitive to most organic compounds including vinyl chloride. It is purged with air and provided with a purge-power safety interlock system permitting safe operation in operating areas which can sometimes be hazardous (Class I, Group D, Division 2).

A sample valve in the analyzer injects a 0.5 cc sample into a two-column system every two minutes. The first column separates the vinyl chloride from virtually all the other organic compounds expected to be present in the air sample. A column valve diverts the unwanted compounds to vent, and at the proper time, diverts the vinyl chloride to the second column where it is separated from any remaining interferants.

The first column is a section of tubing filled with 20 percent Igepal CO-880 on a Chromasorb "P" support. The second column is a section of tubing filled with 20 percent Octoil "S" on a Chromasorb "P" support.

Samples of the compounds most likely to interfere with the vinyl chloride were prepared at 100 ppm concentrations or higher and sampled by the analyzer; none produced any measurable interference. The compounds tested included all C_1 through C_4 hydrocarbons, 1-pentene, methyl chloride, ethyl chloride, hydrogen chloride, chlorine, and refrigerant 22.

Sampling System

The sampling system includes a Metal Bellows sample pump which pulls sample from up to twenty different sample points sequentially and delivers part of it to the analyzer. Most of the sample does not enter the analyzer but is vented outdoors. The excess volume is required to facilitate adequate purging of the sampling line. A sample flow switch is provided to give a warning for low sample flow. The system is equipped to automatically sample the calibration standard on the number 20 sample point if desired.

The sampling systems contain 1/4 inch O.D. polyethylene tubing which has relatively little effect on vinyl chloride. However, with very long sample runs and low sample flow rates, a small percentage of the vinyl chloride is absorbed by the tubing. For example, about 7 percent of the vinyl chloride is removed from a sample flowing at about two liters per minute through 1000 feet of the polyethylene tubing. At lower flow rates, much more is absorbed.

The length of the sample run affects the response time as well as the amount of vinyl chloride absorption. Tests with one of the monitoring systems showed that 93 percent of the ultimate response was obtained with a sample run of 250 feet, using a two-minute purge time at a sample flow rate of 5 liters per minute. About 89 percent of the ultimate response was obtained with a 500 foot sample run at a sample flow rate of 3.3 liters per minute. With longer runs, the percent response decreased drastically.

Additional tests made with 1/4 inch O.D. type 304 stainless steel tubing showed that no absorption (or adsorption) occurred. The stainless steel tubing would, therefore, give better results, but it is much more expensive than polyethylene. The polyethylene tubing should be satisfactory for sample runs of up to 300 to 400 feet if it is periodically tested for leaks and if a high sample flow rate is maintained. Testing is recommended at least once per month. Longer sample runs should be equipped with auxiliary pumping systems and with stainless steel tubing for best results.

Data System

An investigation of data logging and computing systems to be used in addition to the analog recorders now on the vinyl chloride analyzers has been completed. Daily, monthly, and annual averages for each sample point will be computed and logged in addition to other data pertaining to the specific shifts and to specific job functions. Appropriate data systems are expected to be obtained and installed within a few months.

CONCLUSIONS

The five monitoring systems for vinyl chloride have been in operation since June, 1974, and they have performed very well. The hardware has been reliable, and the data obtained has been useful in locating and reducing vinyl chloride emissions into the working environment.

GLB:jb

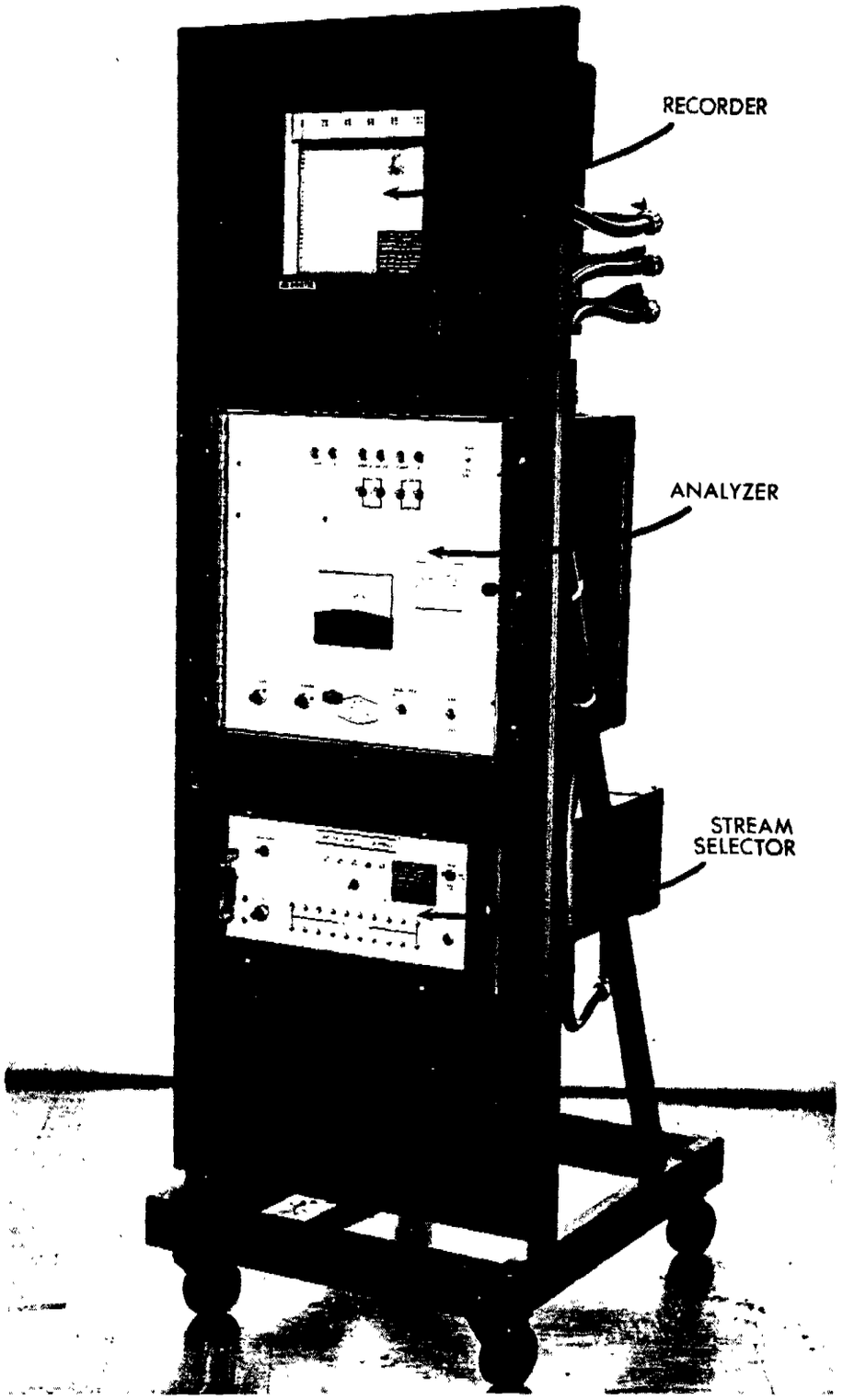
TABLE I

COMPARISON OF VINYL CHLORIDE
MEASUREMENT SYSTEMS

Features	Infrared Spectrometry MIRAN II	GAS CHROMATOGRAPHY	
		UCC MODEL 1200	Honeywell MODEL 100
Specificity	Good	Excellent	Excellent
Maximum Sensitivity (ppm full scale)	100	< 10	< 10
Minimum Detectability	≃1 ppm	≃0.05 ppm	≃0.05 ppm
Stability	?	±1%/week	±1%/week
Reliability (malfunctions per year)	?	1 - 5	?
Ease of Maintenance	Moderate (modular const)	Moderate	?
Trained Servicemen Available in Plants	No	Yes	No
Spare Parts Available	Can Buy	Yes	Can Buy
Analyses Per Hour	60	30*	60
System Availability			
(1 Unit)	8-12 weeks	2-3 weeks	4 weeks
(3 Units)	8-12 weeks	4-6 weeks	12 weeks
(5 Units)	8-12 weeks	4-8 weeks	?
Can Use with Data Logger	Yes	Yes	Yes
Contact Closure for Alarm	Yes	Yes	Yes
Suitable for Hazardous Area Division 2	Yes**	Yes	Yes

* May be able to obtain 60 analyses per hour if desired.

** Applies to complete system in a purged housing.



AIR MONITORING SYSTEM

FIGURE 1

UCC 094460

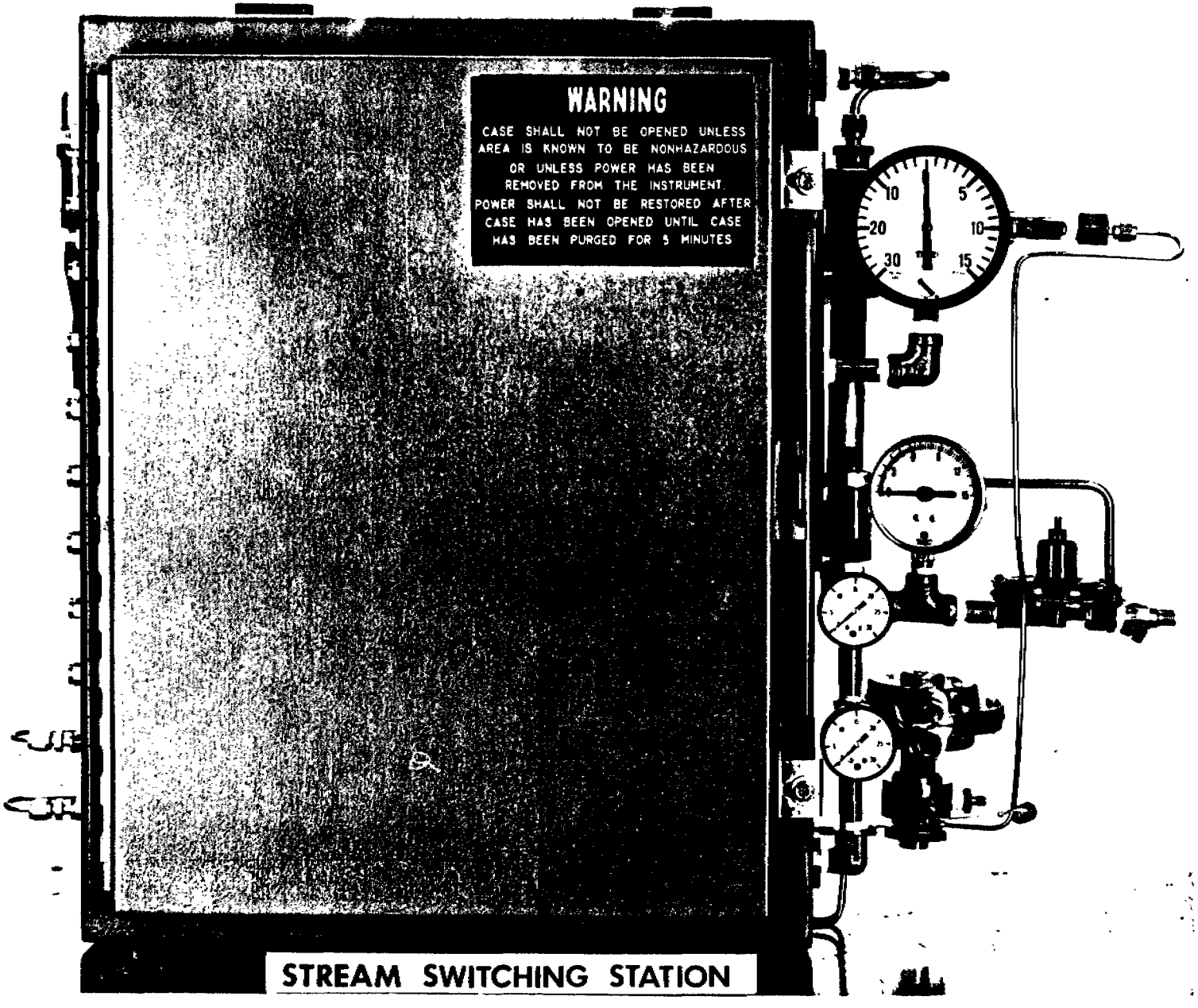
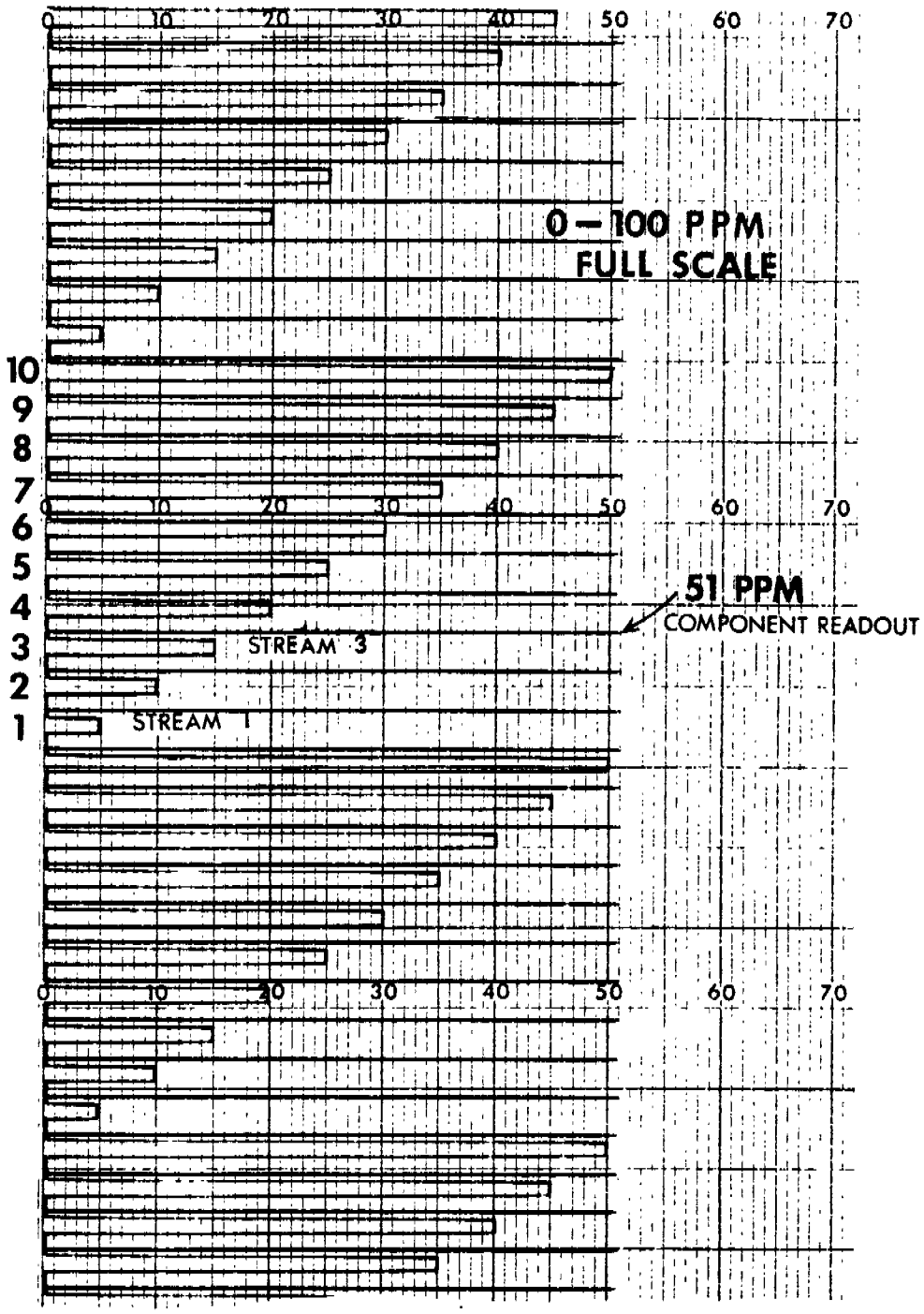


FIGURE 2

UCC 094461



RECORDER PRESENTATION

FIGURE 3

UCC 094462