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Accuracy and Precision of Several Portable Gas Detectors

Additional Studies, A Supplement to RI 7811

UNITED STATES DEPARTMENT OF THE INTERIOR

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Accuracy and Precision of Several Portable Gas Detectors

Additional Studies, A Supplement to RI 7811

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ACCURACY AND PRECISION OF SEVERAL PORTABLE GAS DETECTORS

Additional Studies, A Supplement to RI 7811

by

H. B. Carroll, Jr.,[1] and F. E. Armstrong[2]

ABSTRACT

The performance of commercially available portable instrumentation for detecting nitrogen dioxide, sulfur dioxide, and hydrogen sulfide was evaluated. Length-of-stain detector tubes from several manufacturers were included in the study. The instruments were evaluated in atmospheres with 50- and 80-percent relative humidities at 75° F and containing test gas concentrations of 0.1, 0.25, 0.50, 1.0, 1.5, and 2.0 times the threshold limit values. The results from the gas analyzers were correlated with the known contaminant concentration by calculating and plotting an estimated line of regression, confidence limits, and correlation coefficient for each detector system. An increase in the relative humidity from 50 to 80 percent at 75° F changed the instrument response to the contaminants. The uncertainties in detection precision reported are for the observer-instrument system. The main difference or inconsistency in toxic gas concentrations determined with length-of-stain tubes resulted from the observer's interpretation of the results rather than from a predominant difference in the tubes.

INTRODUCTION

Monitoring and controlling airborne contaminants require reliable and reproducible methods of instrumental measurement. The Federal Bureau of Mines and other government agencies have contributed to this development because they have recognized the need for rapid and accurate instrument systems for detecting airborne contamination.

One of the most widely used portable instrument systems is length-of-stain detector tubes. These tubes are used to make rapid, simple measurements of toxic gas concentrations in work atmospheres. Although the speed and ease of detector tubes are undeniable advantages, the accuracy of such measurements has been questioned.

The reliability of these devices was questioned so frequenty that studies were prompted to evaluate them. Comprehensive studies of the detector systems

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[1] Research physicist.

[2] Project leader.

were made and reported; however, development of new or improved devices quickly outdated these reports (10).[3] More recently, Kusnetz, Saltzman, and Lanier (11) reported the calibration and evaluation of some detector tubes for gases such as arsine, carbon monoxide, nitrogen dioxide, stibine, phosgene, chlorine, chlorine dioxide, and mercury vapor. In 1962, Saltzman (15) presented theoretical mathematical expressions for indicator-tube calibrations. He concluded that "The accuracy, limitations, and applications of indicator tubes are highly dependent upon the skill with which they were manufactured." In 1970, Morgenstern, Ash, and Lynch (13) reported results of a study on detector tubes for carbon monoxide, carbon tetrachloride, and sulfur dioxide. Ash (4) reported the accuracy of the carbon monoxide tubes to be "±25 percent." In 1971, Ash and Lynch (5) reported that carbon tetrachloride and sulfur dioxide detector tubes have similar precision ranges. Johnson (9) published work on hydrogen sulfide detector tubes in 1972 and stated that only one set of detector tubes met performance standards.

The objective of this study was to evaluate the performance of several length-of-stain detector tubes and to provide new or updated information on their accuracy and precision for determining specific gases by simulating the work atmospheres of mining and mineral industries. Instrumentation studied was limited to "off-the-shelf," commercially available (8)[4] units for detecting nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S). Instruments were evaluated in atmospheres with 50- and 80-percent relative humidities at 75° F, and containing test gas concentrations of 0.1, 0.25, 0.50, 1.0, 1.5, and 2.0 times the threshold limit value (TLV)--the minimum amount constituting a health hazard.

This report describes the apparatus and technique used for preparing gas mixtures, establishing gas concentrations, and reading the tubes, and presents an evaluation of the data.

Test limits or ranges for NO_2, SO_2, and H_2S used in this research were fractions of limit values adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) (1). These limits are designated TLV and are related to a health-hazard condition.

EXPERIMENTAL APPARATUS

To evaluate detectors in a typical work atmosphere, it was necessary to design and construct a system for controlling the test atmosphere at a desired temperature, humidity, and toxic gas concentration. This was accomplished by assembling a gas-blending system (4, 6-7) and coupling it to a large, glove-box-type test chamber.

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[3] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

[4] Reference to specific makes and models of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

Sample Manifold

In the test range at 50- to 80-percent relative humidity and 75° F, concentrations of gaseous contaminants were generated by means of a dynamic blending system (6). Models 602 and 603 rotameters obtained from Matheson Instrument Co. were used to monitor dilution airflows in the range of 50 to 4,500 cm^3/min. These rotameters were calibrated for airflow at atmospheric pressure and ambient temperatures. Calibrations of the rotameters using a "soap bubble" meter for flow rates and a calibrated wet-test meter for higher flow rates showed that the manufacturer's airflow calibration was not exact for all rates under present experimental conditions. All rotameters were calibrated under conditions of use, and correction curves were plotted for each.

Concentrations of NO_2, SO_2, or H_2S were dynamically generated by means of a permeation-tube system that has been described in previous Bureau publications (6-7). The standard-rate permeation tubes were ordered from Metronics Associates in Palo Alto, Calif. Metered steams of compressed air, conditioned by passing through an ascarite trap, then through a bubbler system to adjust the humidity, were used as a diluent for the contaminants. Because of the reactive properties of the contaminant gas, only glass, stainless steel, and Teflon tubing were used upstream of the permeation tubes.

The test chamber, an integral part of the blending system, was constructed from a 310-liter stainless steel tank by installing a viewing window and a rectangular flange that contained glove ports (6). Standard, black, one-piece neoprene gloves were used in the chamber.

A Honeywell model W611A portable relative-humidity indicator was installed on the exit airstream to monitor the chamber humidity. The unit uses resistive sensing elements as one leg of a bridge circuit network. Several of the sensing elements covering a range of relative humidities were combined into an aluminum holder mounted in thermal contact with the chamber.

Detector-Tube Systems

Equipment could not include every commercially available detection device; consequently, representative instrumentation of each type available for detection of the contaminants of interest was selected, based upon availability, detection range, and manufacturer's advertised precision and accuracy. Table 1 lists the detectors included in this evaluation.

TABLE 1. - Commercial detectors surveyed in this test series

Manufacturer and instrument	Model	Range
H_2S DETECTORS, PPM		
Mine Safety Appliances Co.: Gas detector tube........	87414.....	1 - 800
Bacharach Instrument Co.: Gas detector tube..........	19-5030...	1 - 650
Drager (distributed by National Mine Safety Co.):		
Gas detector tube..................................	6719001...	1 - 20
Kitagawa (distributed by Unico):		
Gas detector tube................................	120-b.....	5 - 160
Gas detector tube................................	120-c.....	50 -1,600
Gastec (distributed by Scott-Acme Co.): Gas detector tube..	8529......	1 - 240
NO_2 DETECTORS, PPM		
Mine Safety Appliances Co.: Gas detector tube........	83099.....	0.1- 50
Bacharach Instrument Co.: Gas detector tube..........	19-0156...	1 - 50
Drager (distributed by National Mine Safety Co.):		
Gas detector tube..................................	30001.....	.5- 10
Kitagawa (distributed by Unico): Gas detector tube...	117.......	1 -1,000
Gastec (distributed by Scott-Acme Co.): Gas detector tube..	8544......	2 - 100
SO_2 DETECTOR, PPM		
Mine Safety Appliances Co.: Gas detector tube........	92623.....	1 - 400
Bacharach Instrument Co.: Gas detector tube..........	19-5071...	1 -2,700
Drager (distributed by National Mine Safety Co.):		
Gas detector tube..................................	31701.....	1 - 10
Gastec (distributed by Scott-Acme Co.): Gas detector tube..	8531......	.5- 120

Depending upon the tube type, the concentration of the toxic gas is proportional to either the length of the colored zone or to the color intensity. Scales furnished by the tube manufacturer (fig. 1) were used to determine the concentration of the gas. Each manufacturer has a method or calibration scale for its detector system. Drager and Gastec detector tubes have graduated scales printed on the side of the tubes for direct reading.

Calibration and Standardization Measurements

Standard wet-chemical laboratory methods were used to confirm the concentrations set on the permeation-tube blending system. Hydrogen sulfide was detected using a tentative method, No. 701 proposed by the Intersociety Committee, based on the p-aminodimethylaniline reaction to form methyl blue (3). Nitrogen dioxide was detected using the standard Saltzman technique (18). These methods employ batch-sampling techniques and require consistent analytical procedures to obtain a high degree of precision. Confirming the toxic gas level by these methods throughout the test would require excessive time; therefore, only a few selected concentrations were measured before the testing program began.

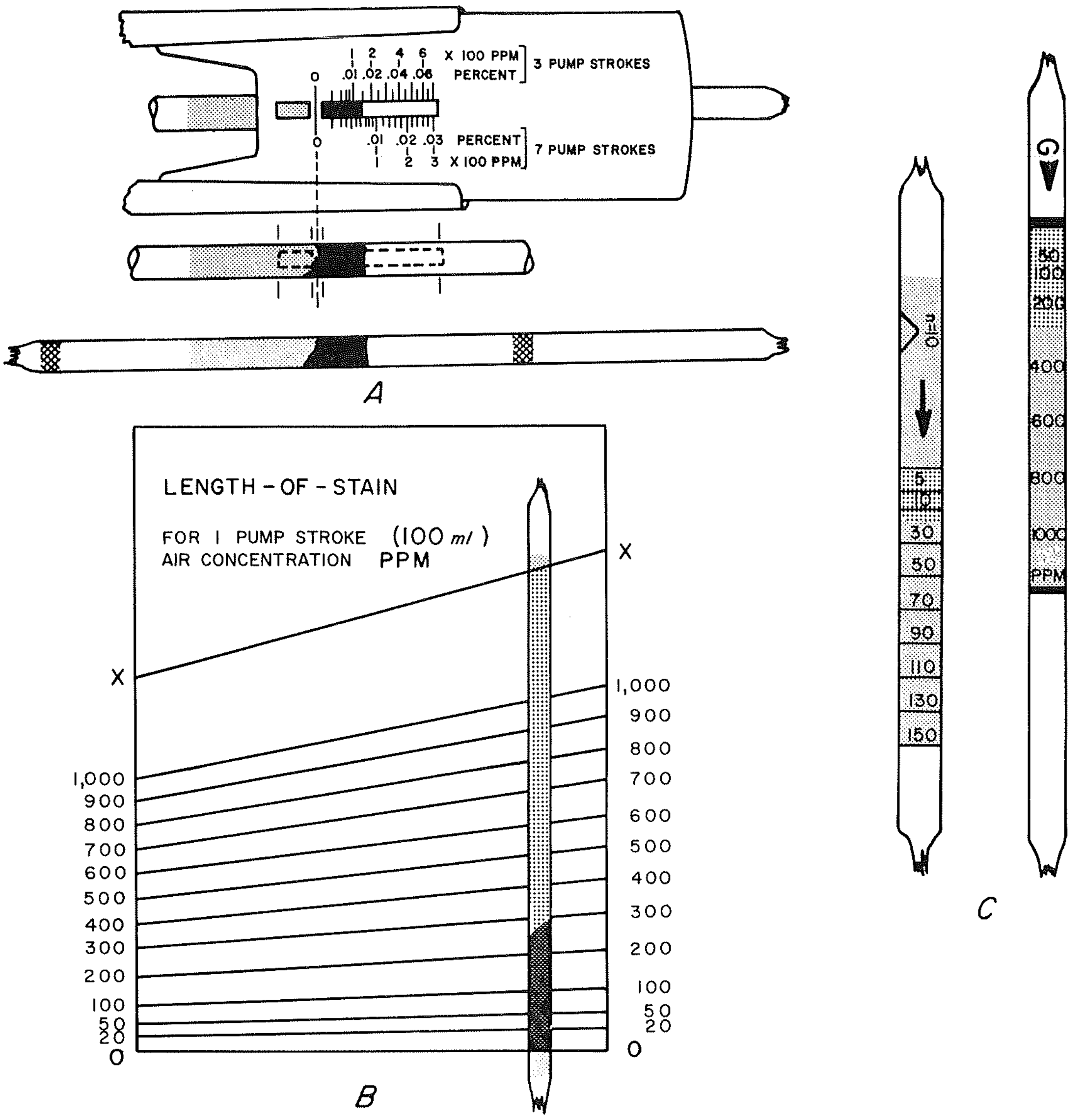

FIGURE 1. - Representative types of length-of-stain gas detector tubes and their calibration scales. *A,* Tube placed behind calibration card for reading; *B,* tube alined with calibration chart for reading; *C,* direct-reading tube.

In each of the methods, a standard sample was collected in a bubbler containing the absorbing solution. Figure 2 shows the sample collection apparatus. A small pump was used to pull the airflow through the reagent in the bubbler, then through a drying column and through the flowmeter. The contaminant concentration was determined by reading the optical density of the exposed reagent and comparing it to a calibration chart for the method.

Continuous monitoring of the chamber atmosphere was necessary throughout the testing; the technique used would have to be convenient, reliable, simple, and not require constant maintenance by an operator. To achieve this, two modified Mast ozone meters were used to continuously measure NO and NO_2, or

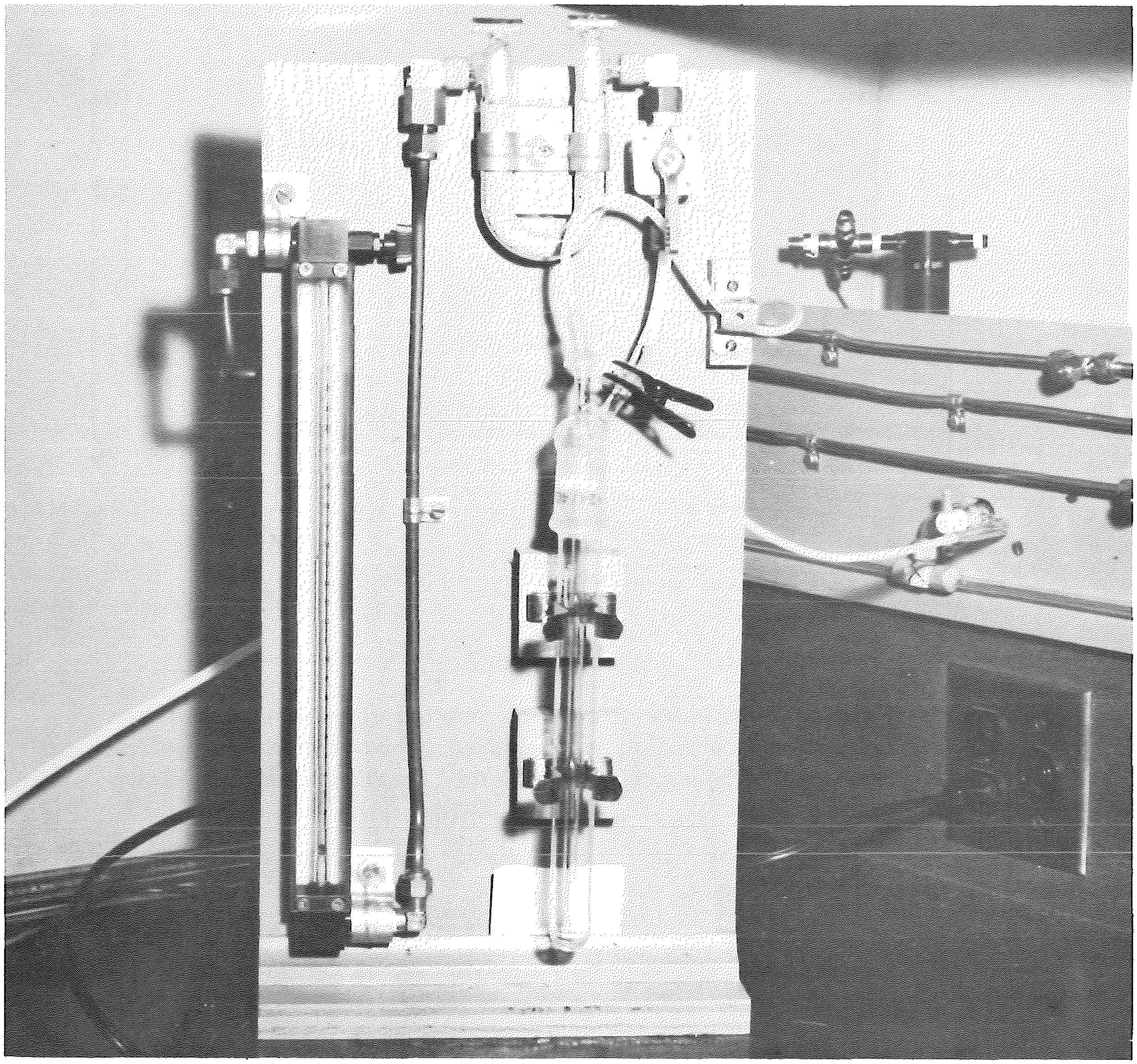

FIGURE 2. - Sampling system for wet-chemical laboratory techniques.

SO_2 (12, 14). Sensitive measurements of NO and NO_2 on the Mast meter require a solution flow over the electrode of 2.5 ml/hr rather than the 1.25 ml/hr for ozone measurements (14). This greater solution flow was achieved by replacing the standard-speed motor on the solution pump with one of higher speed. Concentrations of SO_2 were measured on the other Mast meter by changing reagent solutions and by sealing the fresh solution reservoir to diminish exposure to ambient air (12). Typical gas sampling rates of 140 ml/min on each instrument were adequate for NO, NO_2, and SO_2 measurements.

Concentrations of NO and NO_2 can be measured on the same meter because the Mast cell responds selectively to NO_2. After the NO_2 is measured, dichromate-impregnated papers are inserted in the sample stream, converting the NO to NO_2, and thus producing an instrument response proportional to the sum of NO and NO_2. The NO measurement is then obtained as the difference between the first NO_2 reading and the final one.

Batch samples of H_2S were analyzed on a flame photometer detector mounted on a Micro-Tek GC-2700 gas chromatograph. Periodically, a 30-cm^3 sample was injected into the gas chromatograph for comparison with a gas standard.

Each of the Mast meters and the flame photometric detector were calibrated periodically with known concentrations of the toxic gas obtained by dynamically blending air with effluent from the permeation tubes. The precision with which a desired concentration could be maintained during blending depended upon the reproducibility of setting and flow accuracy of the flowmeters. Errors in the flow rate were evaluated by repetitive settings to a given point on the flowmeter and then measuring the resulting flow with a wet-test meter or a soap-bubble meter. Repetitive settings were made periodically at two or three points in the calibration range while the calibration curve was being prepared for the rotometers. The maximum deviation from the average flow was 2 percent for the 603 rotometer and 3 percent for the 602. This suggests a probable error in setting a concentration level of 3 to 4 percent.

EXPERIMENTAL PROCEDURE

Before the instruments were evaluated in the simulated work atmosphere, they were tested and checked to insure proper performance. Test atmospheres were prepared at desired experimental conditions of gas concentration, temperature, and humidity. The experiment then consisted of operating the instruments in the simulated work atmosphere (comprised of known levels of humidity and predetermined concentrations of H_2S, SO_2, or NO_2) in the test chamber.

Preparing the Test Atmosphere

After selecting the experimental conditions for a particular test, the chamber temperature was set, and the instruments to be evaluated were placed inside the chamber. When the chamber and instruments reached a temperature equilibrium, usually overnight, the chamber background was measured.

The chamber was brought to the proper concentration by injecting calculated volumes of the pure gas. A calculated amount of deionized water was injected to bring the relative humidity to the desired level. The chamber contents were thoroughly mixed, then measured for proper contaminant concentration, humidity, and temperature. During the experiment, the contaminant levels were continuously monitored, and the humidity was periodically checked.

The injected toxic gas level in the chamber was not constant because of losses from instrument sampling and reactive chamber surfaces. The toxic gas level was held constant by a continuing flow of makeup air containing the proper concentration of contaminant to offset the loss. Matheson-cylinder air flowed over a permeation tube at a calculated rate to give the proper contaminant concentration in the flow going to the chamber.

Testing Gas Detector Tubes

Five separate gas detector tubes were used from each detection system at each selected fractional TLV value. The tips were broken off each end of the detector tube, and the proper end was inserted into the sample pump. The sampling cycle was started by making the required number of strokes on the pump and waiting for the time specified by the tube manufacturer after each stroke. As the work atmosphere was drawn through the tube at a controlled rate, a color change indicated the presence of the toxic gas. The exposed tube was then removed from the chamber through a 3/8-inch port for the reading.

A panel of three observers read the tubes using the scales provided by the manufacturers. These observers read the tubes independently under two lighting conditions--in the fluorescent room light and with a miner's light in a darkened room. The observers read the manufacturer's instructions before the tests began but were unaware of the test gas concentration in the work atmosphere until the test was completed. Also, the fractional TLV were chosen randomly to prevent the observers from recognizing a pattern that might bias their readings. Each observer made five readings for each detector-tube system and each fractional TLV.

RESULTS AND DISCUSSION

Preparation for the tests conducted in this study involved establishing and maintaining low concentrations of reactive gases at reasonably constant concentrations during instrument evaluations. Maintaining the low concentrations at a constant value, even with a makeup airstream, was a problem. Instrument surfaces, chamber surfaces, and glove surfaces were reactive to SO_2, H_2S, and NO_2, and significant losses were evident. This problem was solved by maintaining, as closely as possible, contaminant concentration and humidity levels in the chamber while sampling the makeup airstream from the permeation tubes with the laboratory instruments.

The makeup airstream was set at the current test concentration level for both humidity and toxic gas concentration, and was then introduced into the chamber through the arrangement shown in figure 3. The sample was pulled through the tube inserted at point A while the excess effluent flowed into the chamber through the exit at point B. This system was used to maintain the

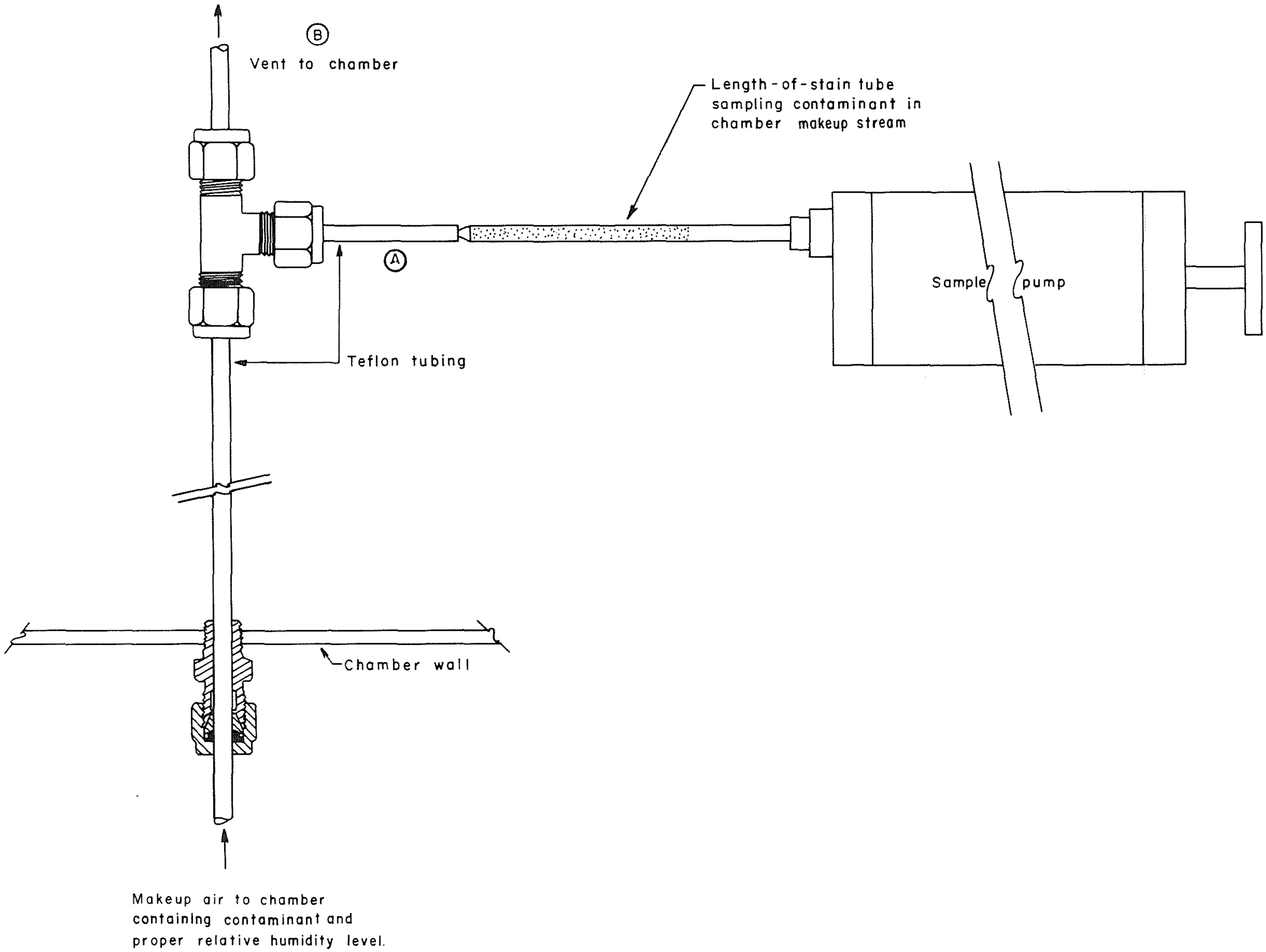

FIGURE 3. - Sampling "T" inside the test chamber.

proper work atmosphere surrounding the instrument while maintaining an accurate contaminant concentration for instrument sampling.

The accuracy of the permeation-tube system is such that it is used to calibrate the accepted standard wet-chemical methods for determining such contaminants as NO_2, SO_2, and H_2S in the atmosphere (3, 16-17, 19). Thus, using the permeation-tube effluent to test the detector tubes insures an accurate contaminant concentration in the sampled atmosphere.

Standard wet-chemical methods were used to verify the contaminant concentration in the permeation-tube effluent airstream. These methods require considerable caution to get the accuracy and precision specified in their procedures, and are therefore somewhat time consuming. Because of the time involved, these methods were used to spot check contaminant concentrations at particular rotameter settings, not at every point for each test.

Simulated work atmospheres were sampled with five gas detector tubes, which each observer read first in a darkened room using a miner's light, then in the room lights. Each average of five tabulated determinations was then considered as an independent determination of the contaminant in the work atmosphere. When testing began, problems on interpretation of the levels indicated by the tubes were observed immediately. The problems were of three major varieties: (1) The color front was not sharp and not perpendicular to the longitudinal axis of the tubes; (2) color changes were difficult to detect for several systems; and (3) color often bleached before the observers read the tube.

Most length-of-stain detector tubes have a color change relatively easy to detect from the background. However, one system varied between close shades of yellow and orange, and presented slight difficulties in perception of color change. The line of demarcation at the stain front (color front) in most of the tubes was diffused or broad at an angle to the longitudinal axis of the tubes, making it difficult to choose a plane at which to read. The broad, diffuse color front apparently caused more uncertainty for each observer than did the angle at which it lay. Causes for these diffuse and angular color fronts have been discussed (11, 15), and no further comments will be made at this point. However, there is one cause for the broad, diffuse color fronts found in the tubes examined in this research that has not been mentioned, and that is broadening caused by diffusion or continued reaction in the tubes before they are read. This occurs when the tubes are not read immediately upon exposure.

Most length-of-stain detector-tube systems have calibration charts with relatively large increments, as do the scales on the direct-reading system. Since the color front is broad and the scale increments are large, interpolation between scale markers was difficult and caused significant variation in each observer's data.

Each observer's readings was treated in a standard way; averages, standard deviations, and the 95-percent confidence limits on the averages were calculated. These calculations are summarized in table 2. Several entries in table 2 show the experimental scatter about the mean at the 95-percent confidence level as zero for a particular observer. All of that observer's readings for that particular test were the same; that is, each tube was read as indicating the same gas concentration. However, readings from the other observers of the same tubes show experimental scatter about the mean at the 95-percent confidence level to be greater than zero for that particular system.

Each observer's readings on the tubes under both lighting conditions are shown averaged in the tabulation. The effects of lighting conditions upon tube readings, if present, are not readily apparent in the data for the detector tubes. Observers experienced more difficulty and hesitated longer when reading the tube in miner's light than in room light.

Even with the experimental scatter, the resultant contaminant level of H_2S, SO_2, or NO_2 indicated by the detector tubes was generally shown to be influenced by the relative humidity of the atmosphere sampled. Examination of the data in table 2 shows that each detector-tube system was affected to various degrees by changes in relative humidity. Plots of the detector-tube readings versus the prepared contaminant level are shown in the appendix, and depict the effect of humidity on the performance of the detector tubes. The equation for the linear regression and correlation coefficient is listed on each graph.

Generally, for each of the detector-tube systems, a reasonably high correlation coefficient resulted from the regression analysis, and no optimization of the best fit by maximizing the correlation coefficient was attempted. The high correlation coefficient was assumed to be an indication that the linear fit is the best.

Hydrogen Sulfide Detectors

Significant broadening of the color front was found in the contaminant concentration indicated by each detector system, and this introduced error because of the observer's uncertainty in determining the end-point. The greatest uncertainties appear in the readings of the Kitagawa tube No. 120-c. The H_2S concentration range was at the extreme lower end of the tube sensitivity, thereby causing a very short, light length of stain. The large uncertainty arose primarily because of the large divisions on the calibration chart, and the very short length of stain in the tubes.

Most of the uncertainties reflected in the data from the Scott/Gastec detector tubes arose from a delay in reading the tubes. This resulted in slight bleaching and loss of sharp demarcation of the color front. The delay was not only between exposure time and time to first reading, but also time between observers.

TABLE 2. - Average toxic gas concentrations measured with detector tubes

Instrument system	Test concentration, ppm	50±5 percent relative humidity Values are averages of five readings from each observer with 95-percent confidence limits						80±5 percent relative humidity Values are averages of five readings from each observer with 95-percent confidence limits					
		Room light			Miner's light			Room light			Miner's light		
		Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3
		H_2S, PPM											
Drager tube No. 6719001	1.0	0.0± 0.0	3.0± 0.0	2.0± 0.0	0.0± 0.0	3.0± 0.0	0.0± 0.0	1.3± 0.3	0.5± 1.0	0.3± 0.4	1.1± 0.7	0.8± 0.6	0.5± 0.5
	2.5	2.5± 1.5	5.8± 3.2	6.0± .0	2.0± .0	6.0± .0	4.0± .0	1.8± .4	1.8± .6	2.1± .7	1.9± .5	1.9± .3	1.8± .6
	5.0	3.0± .5	1.4± .1	3.1± .8	3.0± .6	1.3± .2	2.9± .6	1.8± .4	8.8± 1.2	7.8± .6	2.0± .0	8.5± 1.2	8.8± 1.2
	10.0	7.3± .9	8.0± 1.5	8.8± 1.0	6.9± 1.4	7.2± 1.4	8.0± 1.2	7.2± 1.6	16.8± 1.4	6.9± 1.3	6.8± 1.0	17.2± 1.4	7.0± 1.2
	15.0	13.0± 1.3	13.8± 1.2	14.5± 1.6	13.2± 1.5	13.5± 1.6	13.4± .9	10.6± 2.1	11.2± 2.2	11.0± 2.0	10.4± 2.1	11.6± 2.6	10.4± 2.3
	20.0	18.7± 1.6	18.8± 2.7	20.0± .9	19.1± .9	19.0± 2.8	20.0± .8	10.8± 1.4	10.4± .7	10.8± 1.4	9.8± .6	10.0± .0	10.0± .0
Bacharach tube No. 19-5030	1.0	.0± .0	.0± .0	.0± .0	.0± .0	.0± .0	.0± .0	3.4± .6	3.3± .6	2.1± .3	2.8± .5	3.0± .0	2.3± .6
	2.5	3.3± .7	3.0± .9	2.9± 1.1	2.9± .9	2.6± .7	2.9± .3	4.5± .6	4.0± .9	4.2± 1.0	4.6± .8	4.2± 1.0	4.7± .8
	5.0	3.8± .2	4.0± .0	3.4± .3	3.7± .2	3.8± .6	3.3± .4	4.6± .7	4.0± 1.2	4.4± .7	4.4± .7	4.4± .7	4.1± .7
	10.0	8.2± .5	8.4± .7	8.8± .6	7.7± .6	8.6± .7	7.8± .7	6.8± .6	5.4± 1.4	5.2± 1.0	6.6± .7	5.2± 1.0	5.0± .9
	15.0	10.5± .4	11.0± .9	10.4± .5	10.7± .7	10.6± .7	10.3± .6	11.3± 1.1	11.2± 1.4	10.4± 1.4	10.8± 1.4	11.0± .9	10.4± 1.4
	20.0	19.0± 1.2	18.0± 3.4	17.8± 1.6	19.6± 1.9	18.0± 3.4	17.2± 2.7	14.8± 1.6	15.0± 1.7	14.2± 1.9	15.2± 1.6	15.2± 1.6	14.2± 1.6
MSA tube No. 87414	1.0	---	.8± .6	1.0± .9	---	.8± .6	1.2± 1.0	2.0± .4	1.7± .3	1.8± .4	2.1± .2	1.8± .4	1.7± .3
	2.5	2.3± .6	2.2± .6	2.7± .4	---	2.3± .3	2.2± .6	2.9± .2	2.5± .4	3.0± .8	2.8± .3	3.0± .8	2.9± .3
	5.0	3.2± 1.0	7.2± 1.0	5.0± .9	3.0± .0	7.4± 1.1	4.8± .6	3.2± .6	2.9± .3	3.2± .7	3.1± .7	2.8± .6	3.2± .6
	10.0	7.5± .5	7.0± 1.8	7.0± 1.1	6.5± .7	6.8± .6	6.9± 2.4	7.8± 1.8	7.8± 1.0	7.0± .9	7.3± 1.5	7.4± 1.4	6.6± 1.4
	15.0	13.2± 2.0	13.2± 2.0	13.2± 2.2	13.0± 2.9	12.4± 2.6	13.0± 2.3	11.0± .9	10.4± .7	10.4± .7	10.6± 1.1	10.0± .9	10.0± .0
	20.0	15.5± .7	15.4± 4.5	17.0± 1.0	15.8± 1.9	15.0± 4.4	20.0± 2.0	15.4± 2.7	16.6± 2.1	14.0± 1.8	15.2± 2.4	17.4± 2.3	14.8± 3.4
Scott/Gastec tube No. 8529	1.0	1.0± .1	0.9± .1	1.0± .1	1.0± .0	.9± .1	1.0± .0	1.7± .4	1.3± .6	1.2± .3	1.6± .6	1.3± .6	1.2± .2
	2.5	2.0± .2	1.8± .3	2.1± .1	2.0± .1	1.9± .3	2.1± .1	2.0± .6	1.8± .4	1.8± .4	2.0± .6	1.8± .6	1.8± .4
	5.0	4.3± 1.4	2.6± .8	5.0± 1.5	4.5± 1.4	2.5± .0	4.5± 1.4	4.1± .7	3.8± 1.0	3.3± 1.5	4.4± 1.2	4.0± .8	3.8± 1.1
	10.0	6.3± 1.1	6.5± 2.8	9.4± 1.5	7.1± 1.8	7.0± 3.4	7.9± 1.8	8.6± 1.1	8.6± 1.4	7.4± 1.4	9.2± 1.0	9.2± .6	7.8± 1.8
	15.0	15.0± 3.6	15.8± 5.5	15.0± 4.2	15.0± 2.9	15.8± 5.5	15.2± 4.4	8.8± 1.6	9.0± 1.5	9.0± 2.1	9.8± 1.4	9.4± 1.1	9.0± 1.8
	20.0	21.0± 1.3	21.0± 1.8	15.3± .9	21.4± 1.7	21.4± 3.9	14.3± 1.2	17.8± 2.8	16.0± 3.8	14.6± 4.1	17.0± 3.6	16.8± 4.8	15.4± 4.4
Kitagawa tube No. 120-b	1.0	1.1± .3	1.6± .7	1.0± .0	1.2± .6	1.6± .7	1.4± .5	1.9± .3	1.6± .7	2.1± .3	1.8± .3	1.8± .6	1.6± .7
	2.5	1.5± .2	1.4± .7	2.1± .3	1.4± .5	---	2.2± .3	2.4± .7	2.3± .3	2.6± .7	2.3± .3	2.2± .3	2.4± .7
	5.0	3.0± .0	2.8± .5	3.0± .0	3.7± .0	3.0± .0	2.5± .7	2.3± .4	3.0± .0	2.8± .4	2.3± .4	2.8± .6	2.3± .4
	10.0	5.2± 5.6	5.8± 1.4	7.0± .8	7.2± 1.0	6.2± 2.0	6.8± 1.0	7.6± 1.1	9.2± 1.4	8.6± 1.7	8.0± 1.5	8.4± 2.1	8.0± 1.5
	15.0	9.9± .9	9.6± 2.1	10.4± 1.1	10.3± 1.2	9.6± 1.1	10.4± 1.1	7.8± 1.0	7.6± 1.1	6.2± 1.0	8.4± 1.4	7.8± 1.6	5.6± 1.1
	20.0	10.4± .7	9.6± 1.1	10.0± .0	10.6± 1.1	9.8± .6	9.8± .6	11.6± 1.1	11.6± 1.4	11.0± 1.2	11.6± 1.4	10.6± 1.1	10.6± .7
Kitagawa tube No. 120-c	1.0	.0± .0	.0± .0	1.0± .0	.0± .0	.0± .0	1.0± .0	11.0± 2.7	20.0± .0	12.0± 5.6	10.0± .0	10.0± .0	14.0± .7
	2.5	11.0± 2.8	10.0± .0	18.0± 5.6	13.0± 5.6	---	---	12.0± 5.6	16.0± 2.7	18.0± 5.6	11.4± .3	14.0± .3	18.0± .6
	5.0	18.0± 2.6	14.0± 6.8	18.0± 5.6	18.0± 2.6	18.0± 5.6	18.0± 5.6	18.0± 3.4	20.0± .0	19.0± 2.7	17.0± .7	20.0± .0	17.0± .3
	10.0	24.0± 2.8	20.0± .0	32.0± 7.1	28.0± 3.4	22.0± 5.6	28.0± 5.6	30.0± .0	32.0±13.7	36.0± 6.8	30.0± .0	26.0± 1.1	34.0± .7
	15.0	30.0± .0	30.0± .0	36.0± 6.8	28.0± 3.4	30.0± 8.8	32.0± 5.6	31.0± 6.8	32.0± 5.6	32.0± 5.6	31.0± .7	32.0± .6	30.0± .4
	20.0	47.0± 5.6	42.0± 5.6	46.0± 6.8	49.0± 2.8	40.0± 8.8	36.0± 6.8	32.0± 5.6	30.0± .0	34.0± 6.8	32.0± .6	30.0± .0	32.0± .6

TABLE 2. - Average toxic gas concentrations measured with detector tubes--Continued

Instrument system	Test concentration, ppm	50±5 percent relative humidity						80±5 percent relative humidity					
		Values are averages of five readings from each observer with 95-percent confidence limits						Values are averages of five readings from each observer with 95-percent confidence limits					
		Room light			Miner's light			Room light			Miner's light		
		Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3
		NO_2, PPM											
Drager tube No. CH 30001	0.50	0.5± 0.1	0.5± 0.2	0.5± 0.1	0.4± 0.1	0.5± 0.1	0.4± 0.1	0.4± 0.1	0.4± 0.1	0.5± 0.0	0.5± 0.1	0.4± 0.1	0.3± 0.1
	1.25	.5± .0	.6± .3	.5± .1	.5± .0	.5± .0	.4± .1	.5± .0	.5± .1	.6± .1	.5± .0	.5± .0	.5± .0
	2.50	1.9± .3	1.2± .3	1.2± .3	1.9± .3	1.1± .3	1.2± .2	.9± .3	1.0± .0	1.1± .3	1.0± .2	.9± .3	1.0± .0
	5.00	4.0± .0	4.3± .7	3.5± .4	4.0± .9	4.3± .7	3.4± .5	1.0± .4	.8± .3	1.1± .3	1.0± .1	.5± .0	1.0± .7
	7.50	4.4± 1.4	3.8± .6	4.0± 1.0	4.1± 1.3	4.2± 1.0	4.1± 1.1	1.6± .3	1.3± .3	1.7± .3	1.4± .3	1.0± .0	1.6± .5
	10.00	6.4± 1.1	6.6± 1.5	5.5± 1.1	6.5± .6	7.0± 1.2	5.6± 1.1	5.9± .4	5.6± .7	5.5± .4	5.8± .3	5.6± .7	5.4± .3
Bacharach tube No. 19-0156	.50	.9± .3	.3± .3	1.4± .5	.2± .3	.1± .0	1.0± .0	.6± .3	.8± .2	1.0± .0	.6± .2	.7± .4	.5± .0
	1.25	1.5± .4	1.6± .5	1.3± .3	1.0± .1	1.8± .6	1.1± .1	.5± .2	.6± .3	.5± .1	.4± .3	.6± .3	.3± .2
	2.50	.9± .3	3.2± .6	1.2± .6	1.1± .7	3.2± .6	1.6± .7	.7± .3	.9± .3	.6± .2	.6± .2	.8± .3	.5± .0
	5.00	5.2± 1.0	5.4± .7	4.6± .7	5.4± 1.1	5.4± .7	4.8± .6	1.0± .1	3.6± 1.1	5.2± 1.4	.9± .3	4.2± 1.0	5.2± 1.0
	7.50	5.8± 1.0	5.0± 1.8	5.4± 1.1	5.6± .7	5.2± 2.0	5.4± 1.1	3.5± .9	.9± .1	3.2± .6	3.6± .7	.9± .1	4.0± .0
	10.00	8.4± .7	7.8± 1.6	8.2± 1.0	8.3± 1.5	7.8± 1.4	8.6± 1.4	9.1± 1.1	8.6± 1.1	7.3± 1.3	8.3± 1.2	8.6± 1.1	7.9± 1.5
MSA tube No. 83099	.50	.3± .2	.3± .1	.4± .1	.2± .3	.3± .1	.2± .2	.5± .2	.7± .3	.8± .3	.0± .0	.5± .1	.7± .1
	1.25	1.0± .3	.8± .3	.7± .2	.9± .1	.8± .2	.7± .3	.8± .1	.7± .1	.8± .1	.8± .1	.8± .1	.8± .1
	2.50	1.4± .5	1.2± .3	1.0± .4	1.7± .6	1.5± .4	.9± .3	.7± .1	.6± .1	.7± .1	.7± .1	.5± .1	.6± .1
	5.00	4.4± .7	3.7± .7	3.8± .9	4.4± 1.4	3.6± .5	3.9± 1.0	1.0± 1.2	1.6± .7	2.1± .7	.4± .8	1.0± .0	1.2± 1.4
	7.50	4.5± 1.1	4.6± .7	4.7± .6	4.5± .4	4.6± .7	4.7± .5	2.4± .8	1.6± 1.2	3.4± 1.1	2.5± .9	.0± .0	2.2± 1.0
	10.00	8.8± 3.4	12.2± 4.2	6.6± 1.1	9.0± 2.2	12.6± 2.1	7.4± 1.9	4.9± 1.4	4.9± 1.8	4.8± .9	4.8± 1.4	5.0± 1.5	4.7± 1.3
Scott/Gastec tube No. 8544	.50	.7± .3	.4± .2	.6± .4	.7± .3	.4± .3	.5± .2	.5± .4	.2± .1	.4± .3	.3± .2	.2± .2	.2± .2
	1.25	2.0± .0	2.0± .0	2.0± .1	2.0± .0	2.0± .0	1.8± .3	1.8± .3	3.0± 5.0	1.6± .5	1.8± .3	---	1.7± .5
	2.50	3.0± .0	3.0± .0	2.6± .7	3.0± .0	3.0± .0	2.6± .7	2.4± .5	2.6± .7	2.6± .7	2.2± .1	2.6± .7	2.6± .7
	5.00	6.0± .9	6.2± 1.0	5.4± .7	6.2± 1.0	6.4± 1.1	5.6± .7	3.7± .3	3.8± .6	3.8± 1.0	3.4± .5	3.4± .7	3.8± 1.0
	7.50	10.2± .6	10.0± .0	9.0± 1.2	10.0± .0	10.0± .0	9.0± 1.2	5.2± .6	5.4± .5	5.0± .0	4.6± .7	5.2± .6	4.8± .6
	10.00	14.2± 1.4	15.0± 2.3	10.8± 1.0	15.4± 3.1	14.2± 1.6	12.2± 2.7	12.8± 2.6	11.8± 1.6	10.5± 2.1	11.3± 1.9	11.3± 1.2	9.3± 1.2
Kitagawa tube No. 117	.50	1.4± .7	.8± .1	.4± .3	.6± .5	.8± .1	.3± .4	.9± .3	.9± .1	.3± .2	1.0± .0	.9± .1	.2± .1
	1.25	7.0± 1.4	6.8± .6	1.0± .0	2.6± 3.1	6.8± .6	.0± .0	3.2± 4.8	3.0± 5.0	1.0± .0	.6± .7	---	.2± .3
	2.50	9.0± 5.2	7.6± 3.1	10.8± 8.2	7.5± 3.1	7.2± 3.9	9.8± 6.2	20.8± 5.2	15.0± .0	9.0± 2.8	2.0± 2.0	14.0± 2.8	6.6± 4.7
	5.00	8.0± 1.5	7.8± 2.2	7.2± 3.2	8.4± 1.9	7.4± 1.7	6.6± 2.6	17.5± 3.6	15.5± 4.1	14.3± 3.7	17.5± 3.6	17.5± 3.6	12.5± 3.6
	7.50	32.6±23.0	22.0±20.9	21.0±21.7	32.5±23.2	22.0±20.9	21.0±21.7	20.0± 4.4	18.0± 3.4	14.0± 2.8	14.0± 5.2	14.0± 5.2	13.0± 3.4
	10.00	27.6±20.7	28.4±14.7	22.0±19.7	18.0± 5.6	26.4±13.3	22.6±19.4	51.0±30.2	43.0±28.9	33.6±17.3	43.0±28.9	38.0±20.4	34.6±18.2

TABLE 2. - Average toxic gas concentrations measured with detector tubes--Continued

Instrument system	Test concentration, ppm	50±5 percent relative humidity Values are averages of five readings from each observer with 95-percent confidence limits						80±5 percent relative humidity Values are averages of five readings from each observer with 95-percent confidence limits					
		Room light			Miner's light			Room light			Miner's light		
		Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3	Obs. 1	Obs. 2	Obs. 3
		SO_2, PPM											
Drager tube No. CH 31701	0.50	0.0±0.0	0.0±0.0	---	0.0±0.0	0.0±0.0	---						
	1.25	.1± .0	.0± .0	0.0± .0	.0± .0	.0± .0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
	2.50	1.4± .5	1.6± .7	1.7± .6	1.5± .6	1.6± .7	1.6± .7	.0± .0	.0± .0	.0± .0	.0± .0	.0± .0	.0± .0
	5.00	4.4± .8	4.4± 1.2	4.3±1.2	4.4± .8	4.4±1.2	4.5±1.2	4.7±1.4	5.0±2.2	4.2±1.1	5.0±1.6	5.3±2.9	4.5±1.2
	7.50	9.1±1.8	8.6±1.7	9.8±1.6	9.1±1.8	8.6±1.7	9.6±1.9	8.0±4.1	7.8±3.2	7.4±3.1	8.0±4.0	7.8±3.0	7.4±3.1
	10.00	8.8±2.0	8.2±1.6	8.0±1.5	8.5±1.8	8.6±2.2	8.3±1.5	12.5±2.5	11.5±2.2	10.0± .0	11.9±1.6	11.5±2.2	10.3± .6
Bacharach tube No. 19-5071	.50	.3± .2	.0± .0	---	.1± .1	.0± .0	---						
	1.25	1.2± .7	1.7± .8	1.4± .7	1.2± .7	1.5± .6	1.6±1.4	1.3± .6	2.2± .6	2.6± .7	1.5± .6	2.4± .7	2.5± .9
	2.50	2.8± .6	3.4± .7	3.8± .6	3.4± .7	3.6± .7	4.6± .7	2.6± .7	4.0± .0	3.6± .7	2.8± .6	4.2± .6	4.2±1.0
	5.00	9.2±2.2	10.0±2.3	9.4±2.1	9.2±2.2	10.0±2.3	9.4±2.1	7.4±2.4	8.8±2.0	8.6±2.9	7.4±2.4	8.4±1.9	9.4±2.7
	7.50	11.2±1.0	10.6± .5	11.0±2.2	11.2±1.4	10.8± .6	11.4±2.1	8.5± .7	8.5± .7	9.0±1.0	8.5± .7	8.3± .6	8.8±1.2
	10.00	14.8±3.2	16.0±3.6	16.8±4.2	14.8±3.2	16.2±3.6	17.6±4.1	12.0±4.3	13.3±4.0	13.3±5.2	13.0±4.3	13.7±4.7	13.7±5.0
MSA tube No. 92623	.50	.0± .0	.0± .0	---	.0± .0	0± .0	---						
	1.25	1.2± .2	1.3± .2	7.0± .9	1.2± .1	1.3± .2	7.0± .9	.8± .4	.9± .3	.8± .4	.8± .4	.8± .4	.6± .6
	2.50	1.9± .4	1.6± .5	1.6± .5	1.9± .4	1.6± .4	2.0±1.2	1.1± .5	1.1±1.2	1.3±1.0	1.0± .5	.9± .7	1.2±1.1
	5.00	3.4± .0	3.4± .0	4.0± .4	3.8± .5	3.5± .5	3.5± .4	3.1±1.2	3.9±1.9	3.4±1.0	2.7±1.2	4.1±1.8	3.4±1.0
	7.50	5.2± .4	5.1± .8	5.3± .7	5.1± .3	5.6± .6	5.2±1.5	3.5± .4	3.8± .5	3.4± .0	3.4± .0	3.3± .7	3.4± .0
	10.00	6.9±2.6	7.3±1.8	7.5±1.9	6.8±2.3	7.3±1.8	7.0±1.1	8.6±1.1	9.3±1.4	8.7±1.3	8.7±1.1	9.1±1.5	9.0± .9
Scott/Gastec tube No. 8531	.50	.5± .1	.5± .1	---	.5± .1	.5± .1	---						
	1.25	1.4± .4	1.4± .4	1.4± .4	1.3± .3	1.4± .4	1.4± .4	1.3± .2	1.3± .1	1.3± .1	1.3± .2	1.3± .1	1.3± .0
	2.50	2.5± .1	2.4± .3	2.6± .3	2.4± .3	2.5± .2	2.5± .0	2.4± .3	2.5± .8	2.4± .3	2.3± .3	2.7± .3	2.4± .3
	5.00	4.6± .5	4.8± .6	4.8± .6	4.8± .3	4.8± .6	4.8± .6	4.0± .9	3.9± .7	4.3± .5	4.2± .7	3.8±1.0	4.3± .5
	7.50	6.3± .6	6.6± .8	6.4±1.4	6.3± .6	6.8± .4	6.0±1.0	6.0±1.2	6.0±1.2	5.8± .9	6.0±1.2	6.0±1.2	5.6± .7
	10.00	9.2±1.4	9.4±1.1	9.1±1.3	9.2±1.4	9.4±1.1	9.1±1.5	9.6± .7	9.6± .7	10.0± .0	9.6± .7	9.6± .7	10.0± .0

The two experimental variables, illumination and humidity, do not appear to affect the uncertainties in the H_2S detector-tube systems. An examination of the data showed no significant change in the 95-percent confidence limit on the mean for each observer as the humidity changed from 50 to 80 percent. Neither was there any increase or decrease in the uncertainty because of the two different illumination sources.

The sensitivity of the detector tubes to H_2S decreased as the humidity increased. An examination of each of the plots shown in figures A-1 through A-6 shows that the slope of the least-squares line decreases with an increase in humidity. Ideally, the slope would be 1.0, but because of errors in the detector-tube/observer system, the slope varies significantly from the ideal. Analyzing the results at 50-percent relative humidity and 75° F, then arranging the tubes in order of their smallest prediction limit width at TLV gives the following order:

Rank	Manufacturer and tube number	Width, ppm	
		Confidence limit	Prediction limit
1	Kitagawa tube No. 120-b.............	0.9	4.0
2	MSA tube No. 87414..................	1.1	4.8
3	Bacharach tube No. 19-5030..........	1.2	5.4
4	Scott Gastec tube No. 8529..........	1.7	7.4
5	Drager tube No. 6719001.............	1.9	8.1
6	Kitagawa tube No. 120-c.............	4.7	20.2

Nitrogen Dioxide Detectors

The uncertainties in each observer's readings of the NO_2 detector tubes appeared to be unaffected by the illumination change or by the 30-percent change in relative humidity. The NO_2 detector tubes were slightly paler in their color changes than the H_2S tubes. The pale color and the rapidity of bleaching account for the broad confidence limits and, in many cases, the low readings. The rather large confidence limits around the mean readings of the Kitagawa detector tube No. 117 resulted from significant dispersion of the color front caused by delays in reading the tubes.

Plots of the observer's average readings, shown in figures A-7 through A-11, indicate that the detector-tube systems decreased in sensitivity to NO_2 as the humidity of the test atmosphere increased. The Kitagawa tube No. 117 appears to be an exception; however, the large 95-percent confidence limits for this data mask a distinct slope change.

The detector-tube sensitivity to NO_2 decreased as the humidity of the test atmosphere increased. As with the hydrogen sulfide detectors, the slopes of the least-squares lines decreased with an increase in humidity. Arranging the tubes tested at 75° F and 50-percent relative humidity in the order of their response to NO_2 and, consequently, their smallest prediction limit width at TLV, the following order results:

Rank	Manufacturer and tube number	Width, ppm	
		Confidence limit	Prediction limit
1	Drager tube No. 30001..............	0.5	2.0
2	Bacharach tube No. 19-0156..........	.8	3.3
3	Scott/Gastec tube No. 8544..........	.9	4.0
4	MSA tube No. 83099..................	1.3	5.6
5	Kitagawa tube No. 117...............	4.6	19.9

Sulfur Dioxide Detectors

Wide confidence limits occurred on two of the detector-tube systems--the Drager SO_2 detector tubes and the Bacharach SO_2 detector tubes. At low SO_2 concentrations, but within tube operating ranges, no discernible change occurred in the Drager SO_2 detector tubes. At higher SO_2 concentrations, the observers were uncertain of the position of the color front. Uncertainty of the position of the color front on the Bacharach tubes increased with increasing SO_2 concentration. An examination of the data showed no significant change in the 95-percent confidence level in the mean for each observer when the humidity was increased from 50 to 80 percent.

Readings of the same tubes under both lighting conditions were statistically similar. Therefore, effects of lighting conditions on the tube readings, if present, are not readily discernible in the data for SO_2 detector tubes.

The 30-percent increase in humidity affected the SO_2 detector tubes by increasing SO_2 sensitivity for the MSA and Drager detectors, but decreasing it for the Bacharach and Scott/Gastec tubes. The plots in figures A-12 through A-15 indicate the following response to SO_2 for each of the systems:

MSA tubes.--Even though the slopes of the lines in figure A-14 generally increase with humidity, a significant decrease in the slope would be apparent for SO_2 concentrations of <10 ppm if the last point were discarded.

Drager tubes.--Although the slopes of the lines in figure A-12 generally increase, two regions of sensitivity are prominent. The tubes were not sensitive to low concentrations of SO_2.

Scott/Gastec tubes.--Little slope change with humidity was noted; however, a discernible increase in sensitivity was evident.

Bacharach tubes.--A definite slope change was noted, although data fitted had large 95-percent confidence limits on the mean.

Ranking the tubes and observers in order of their smallest prediction limit width at TLV provides the following order:

Rank	Manufacturer and tube number	Width, ppm	
		Confidence limit	Prediction limit
1	Scott/Gastec tube No. 8531..........	0.2	1.0
2	Bacharach tube No. 19-5071..........	1.1	4.5
3	Drager tube No. 31701...............	1.2	5.1
4	MSA tube No. 92623..................	1.6	6.6

CONCLUSIONS

1. Under the conditions of this investigation, changing the illumination of the tubes from room light (fluorescent) to miner's cap lamp did not significantly affect the observer's readings of the length of stain.

2. The width of the 95-percent confidence limit on the least-squares line generally increased with the increase in humidity.

3. Humidity influenced the indicated toxic gas concentration to some extent for all of the length-of-stain tubes evaluated in the program.

4. Evaluation of the length-of-stain detectors shows that the type of gas being detected will affect the selection of a manufacturer's tube for that gas.

5. The uncertainties in precision reported are for the observer-instrument system and result from the observer's interpretation of the indicated toxic gas level, as well as the lack of instrument precision. These are not separated in this report.

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APPENDIX

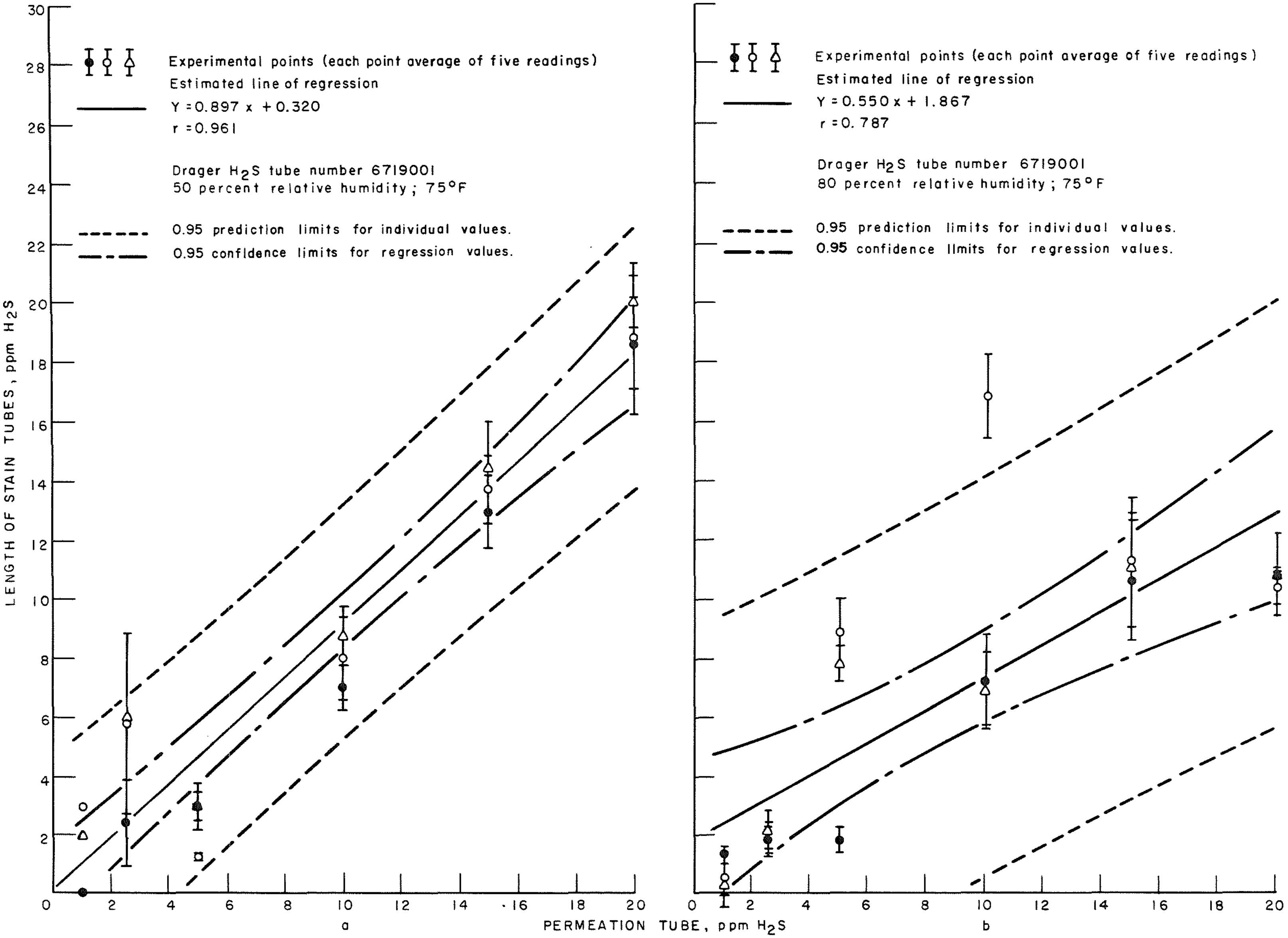

FIGURE A-1. - Determination of H_2S concentration with a Drager length-of-stain detector system.

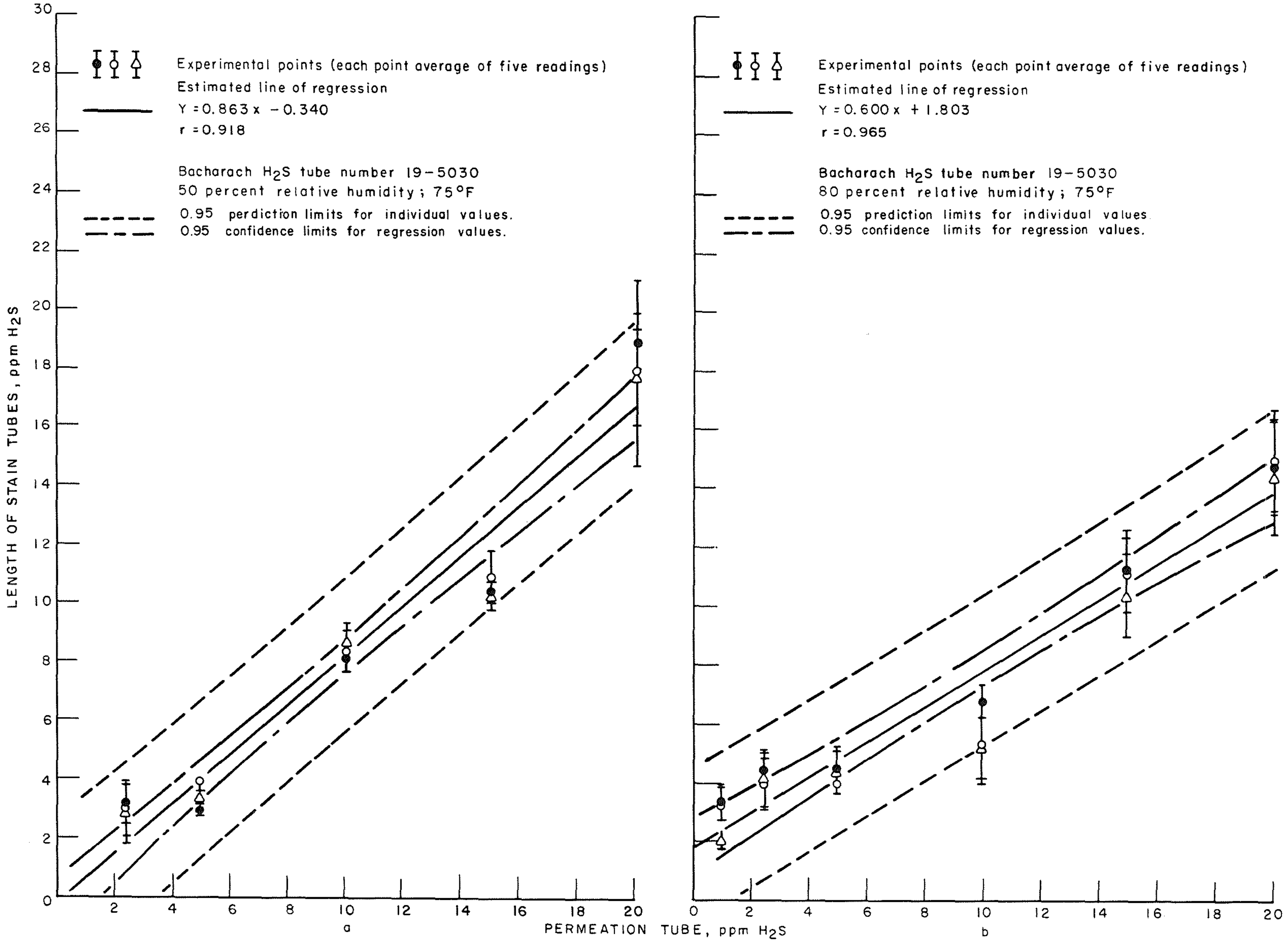

FIGURE A-2. - Determination of H_2S concentration with a Bacharach length-of-stain detector system.

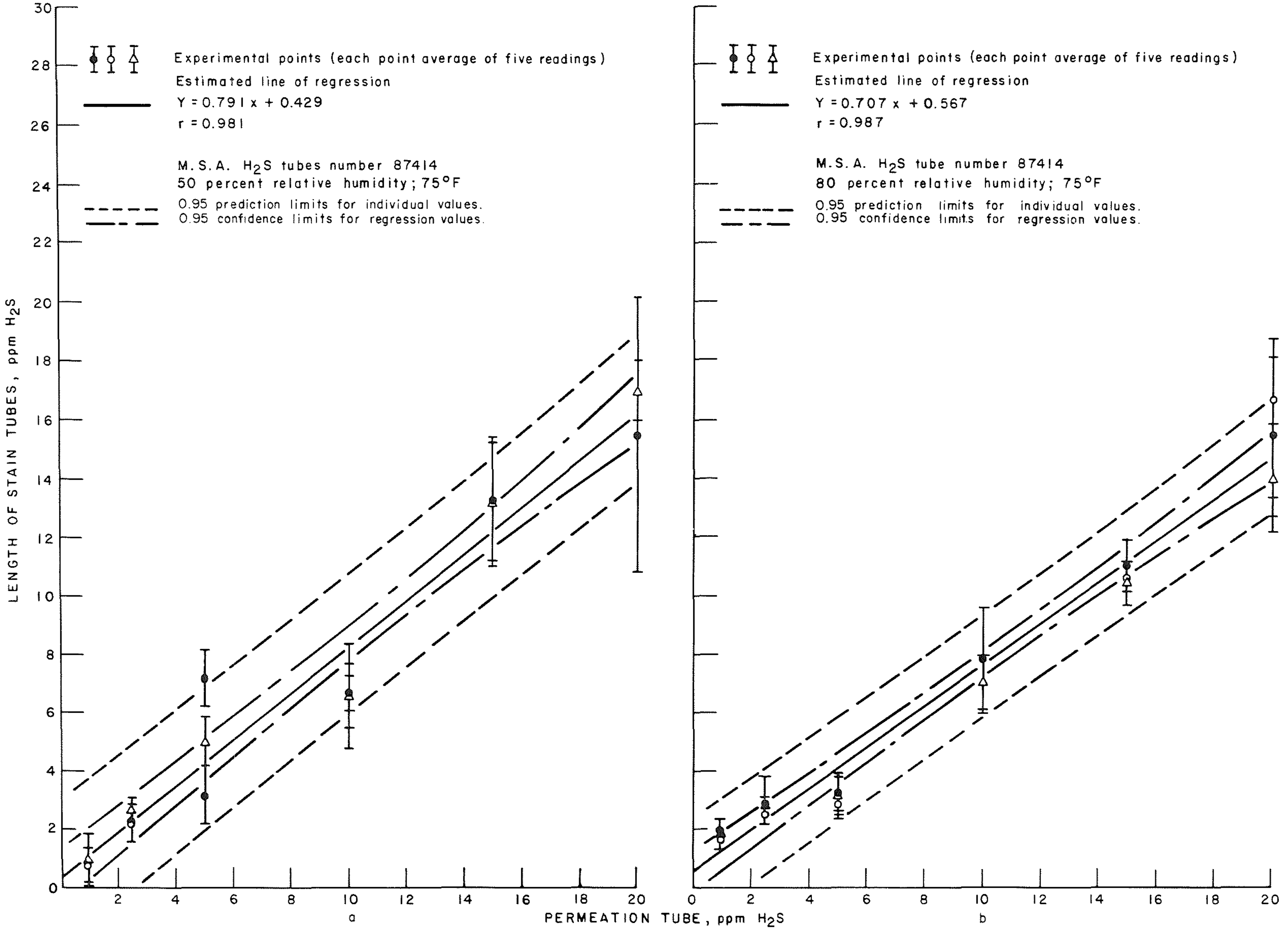

FIGURE A-3. - Determination of H_2S concentration with an MSA length-of-stain detector system.

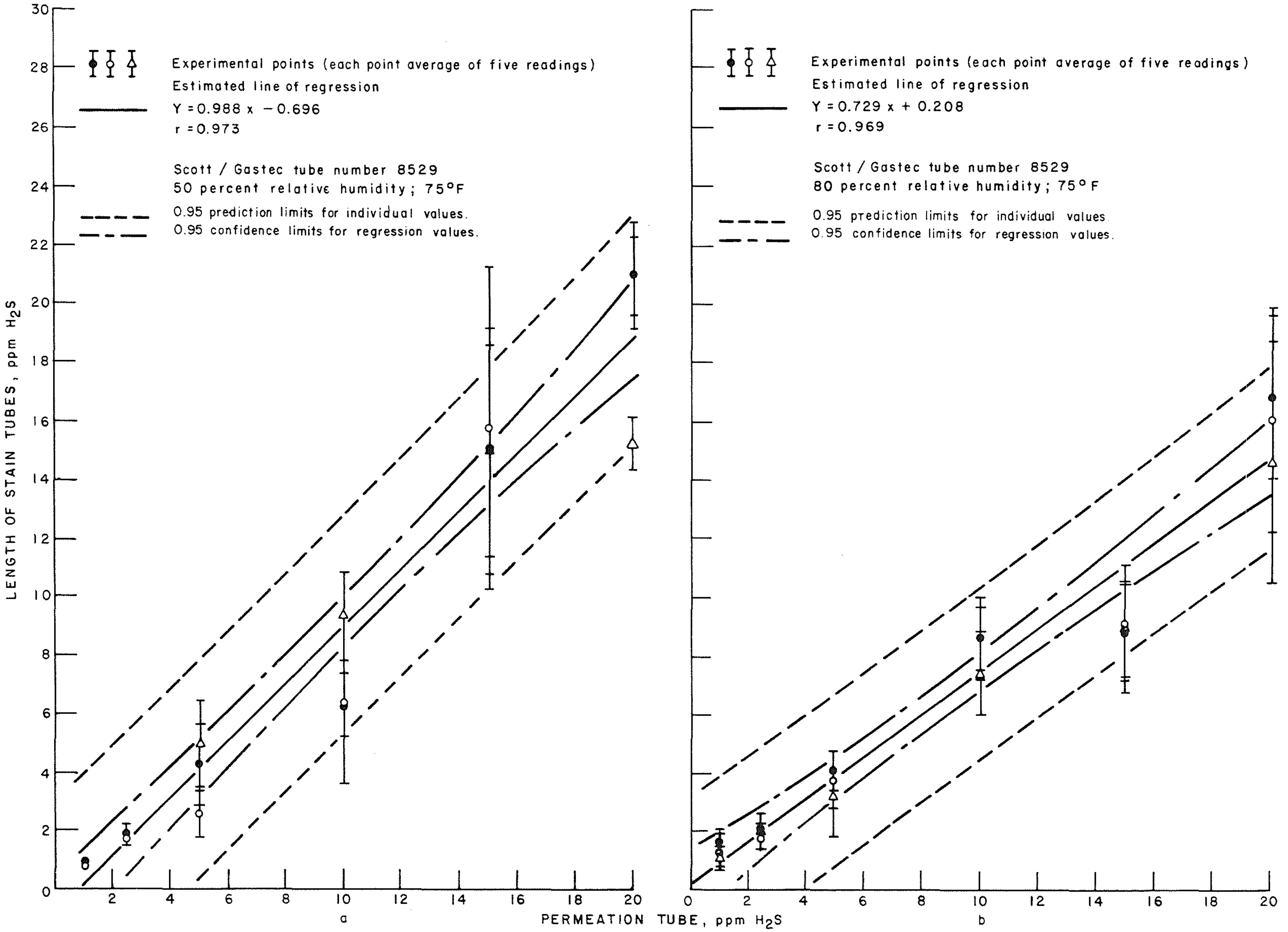

FIGURE A-4. - Determination of H_2S concentration with a Scott/Gastec length-of-stain detector system.

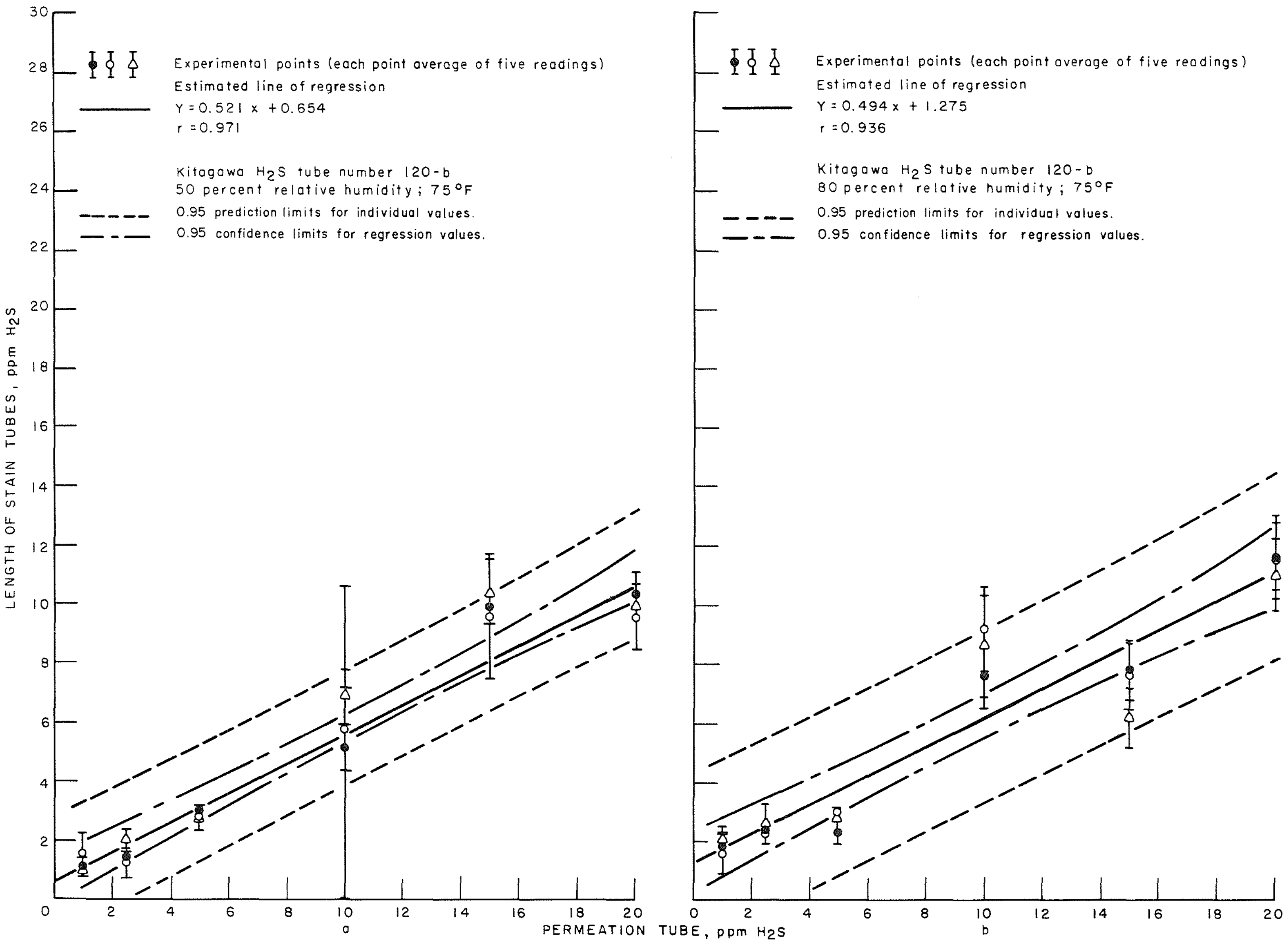

FIGURE A-5. - Determination of H_2S concentration with a Kitagawa 120-b length-of-stain detector system.

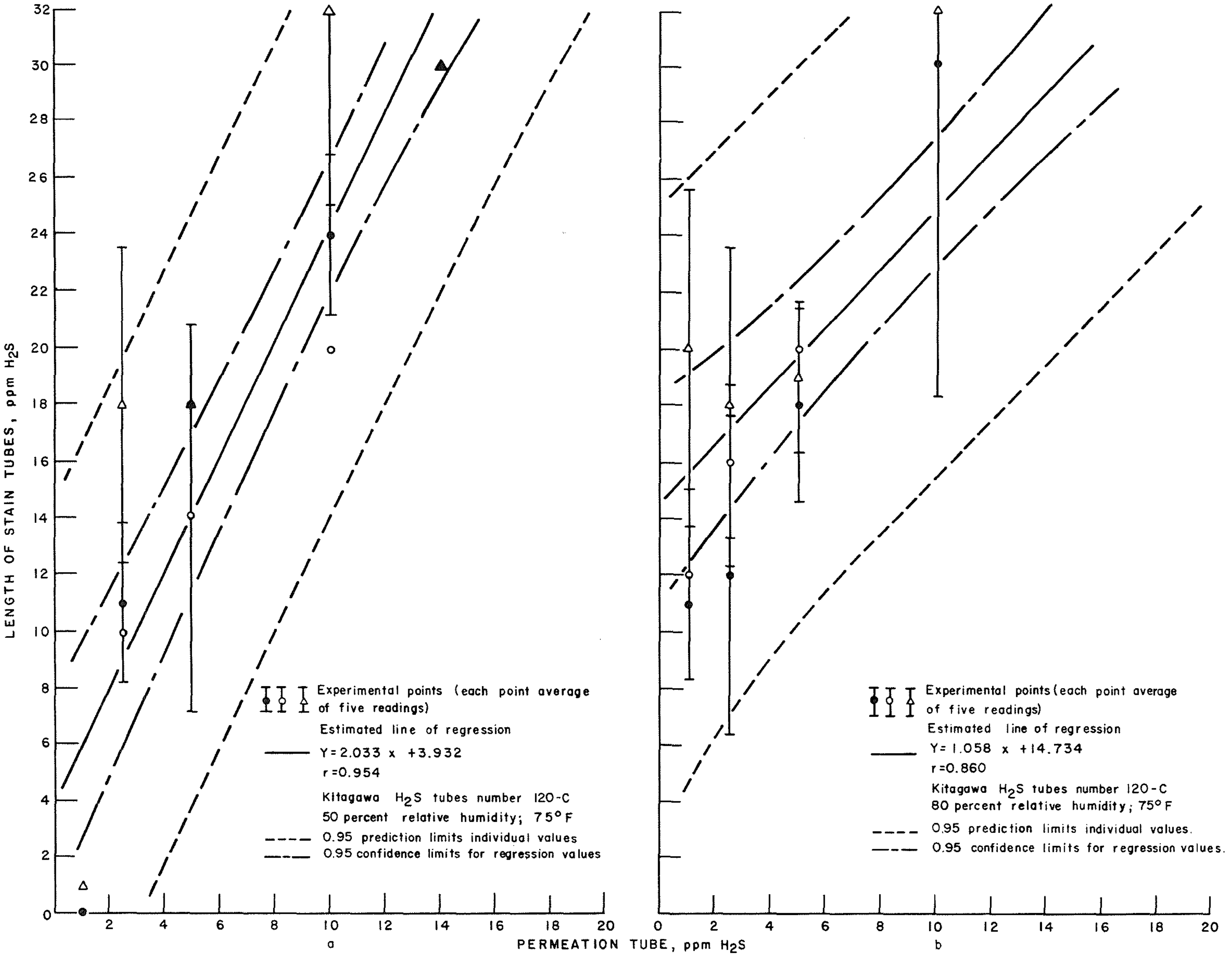

FIGURE A-6. - Determination of H_2S concentration with a Kitagawa 120-c length-of-stain detector system.

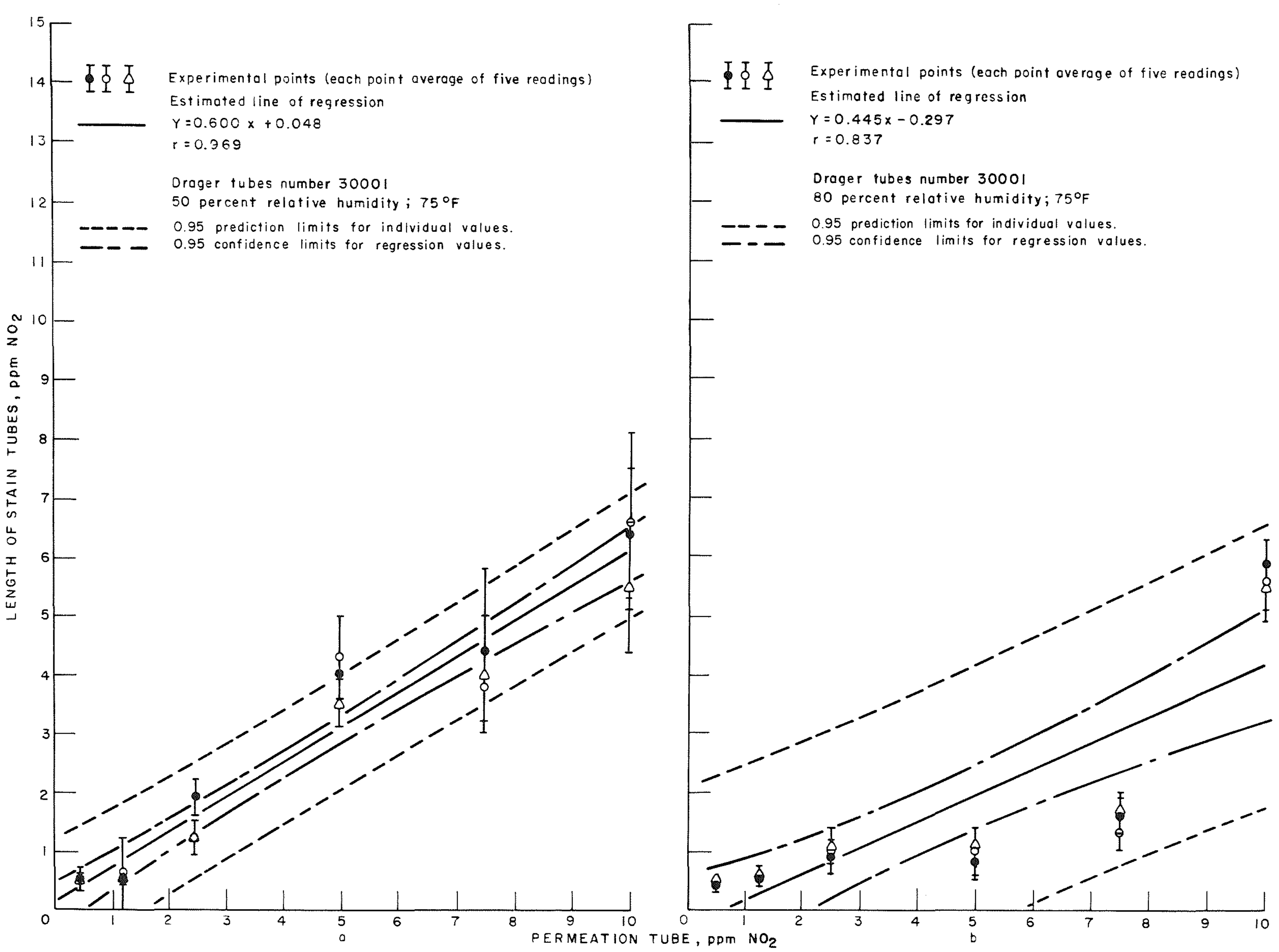

FIGURE A-7. - Determination of NO_2 concentration with a Drager length-of-stain detector system.

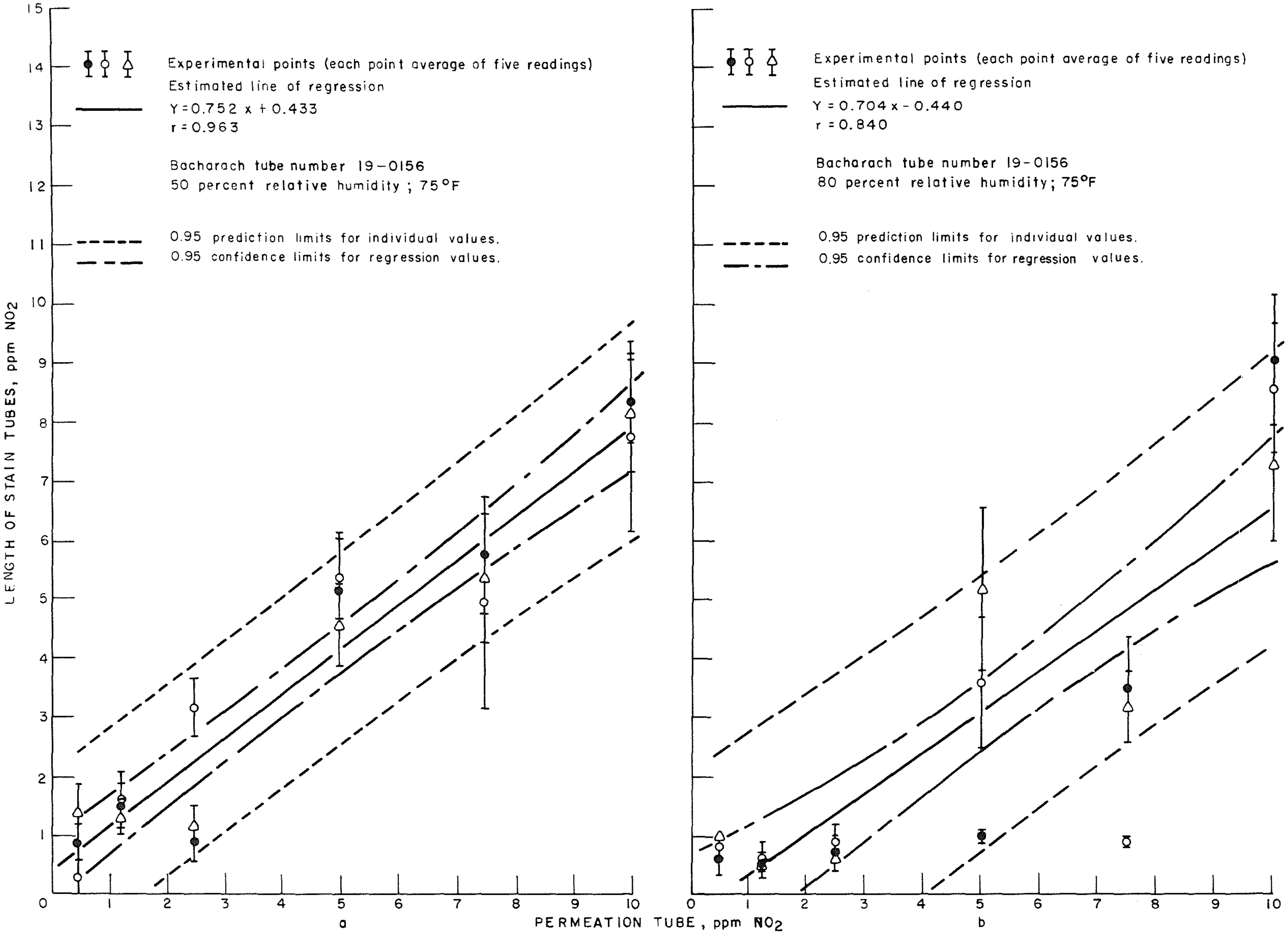

FIGURE A-8. - Determination of NO_2 concentration with a Bacharach length-of-stain detector system.

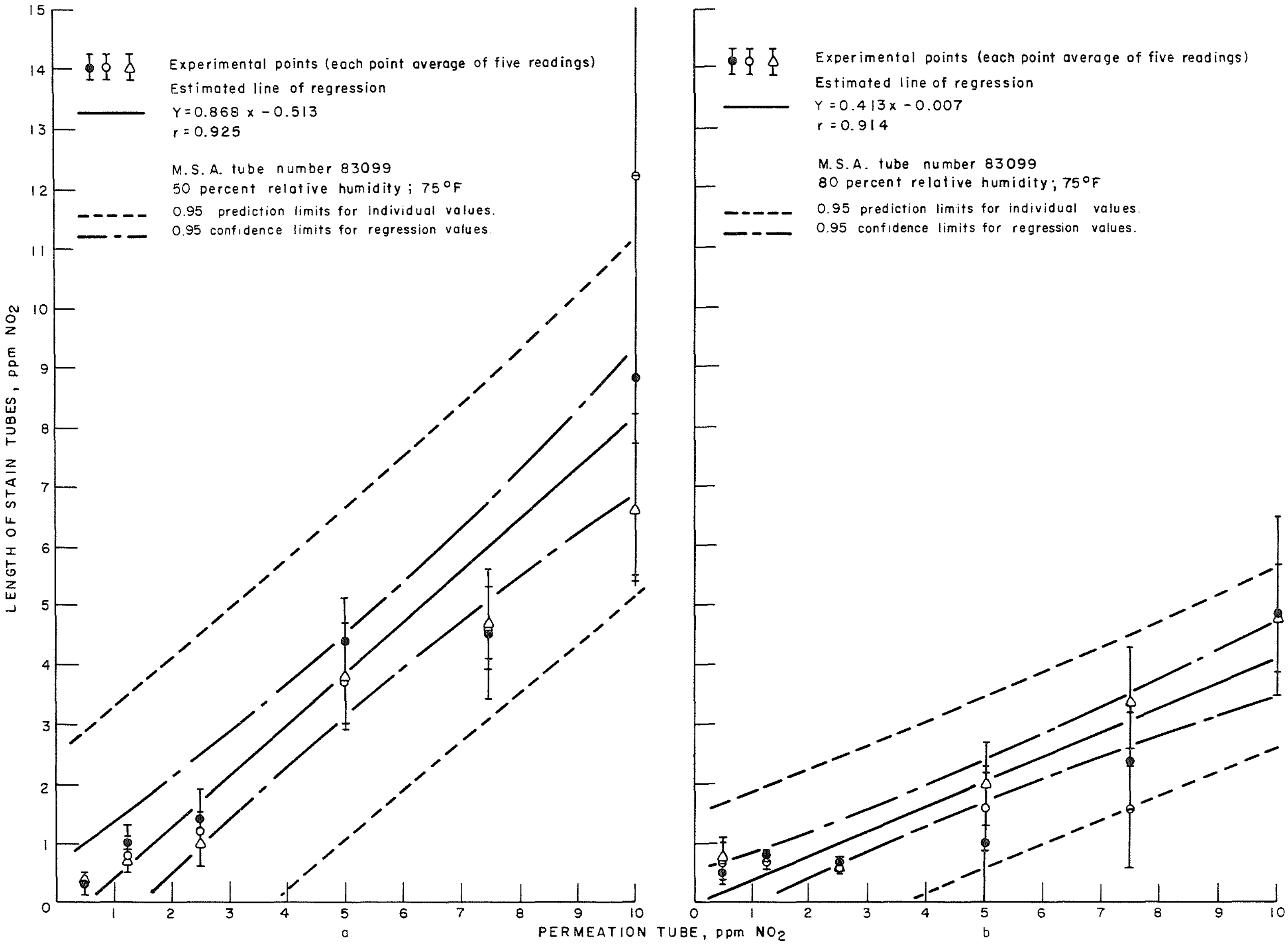

FIGURE A-9. - Determination of NO_2 concentration with an MSA length-of-stain detector system.

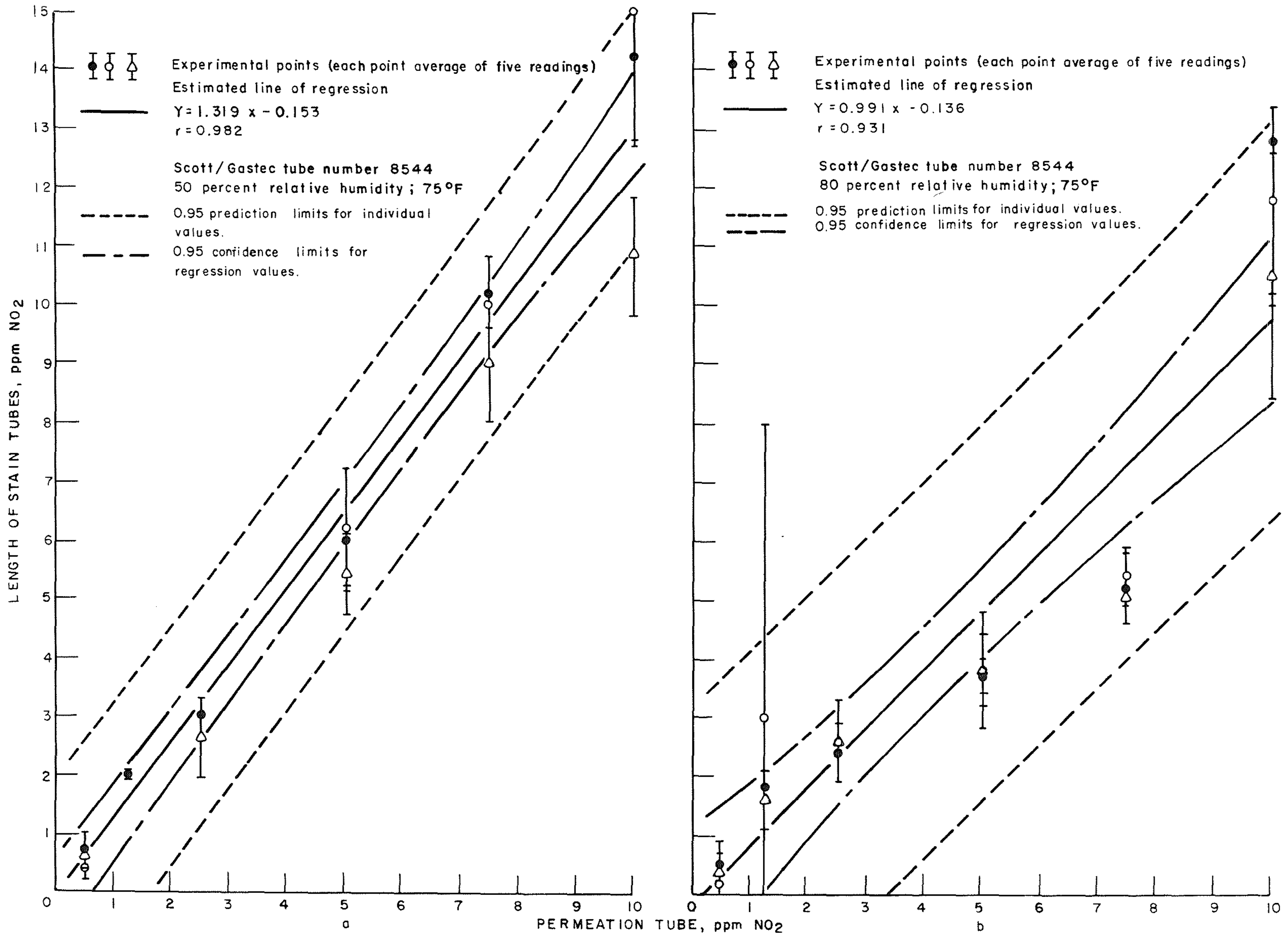

FIGURE A-10. - Determination of NO_2 concentration with a Scott/Gastec length-of-stain detector system.

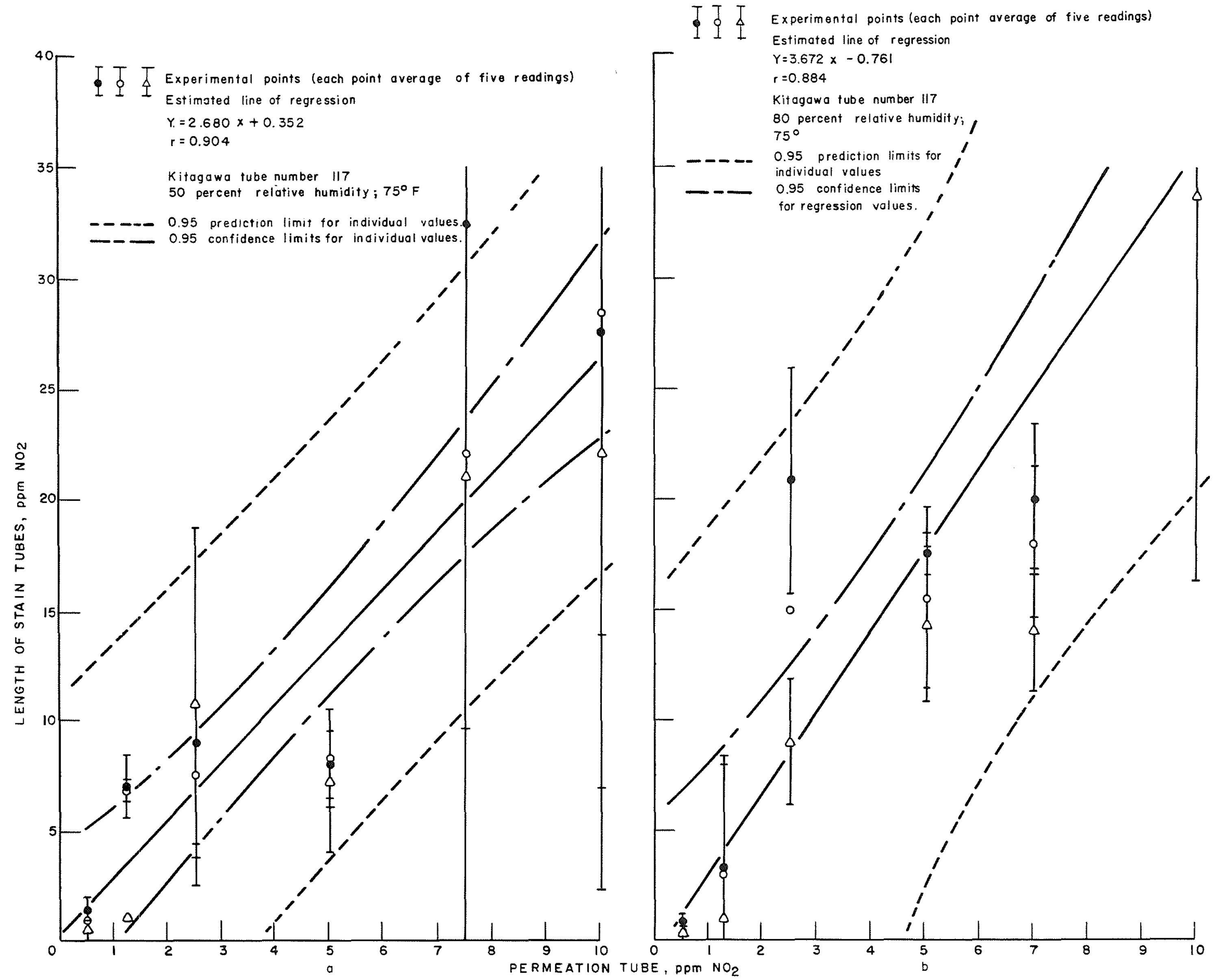

FIGURE A-11. - Determination of NO_2 concentration with a Kitagawa length-of-stain detector system.

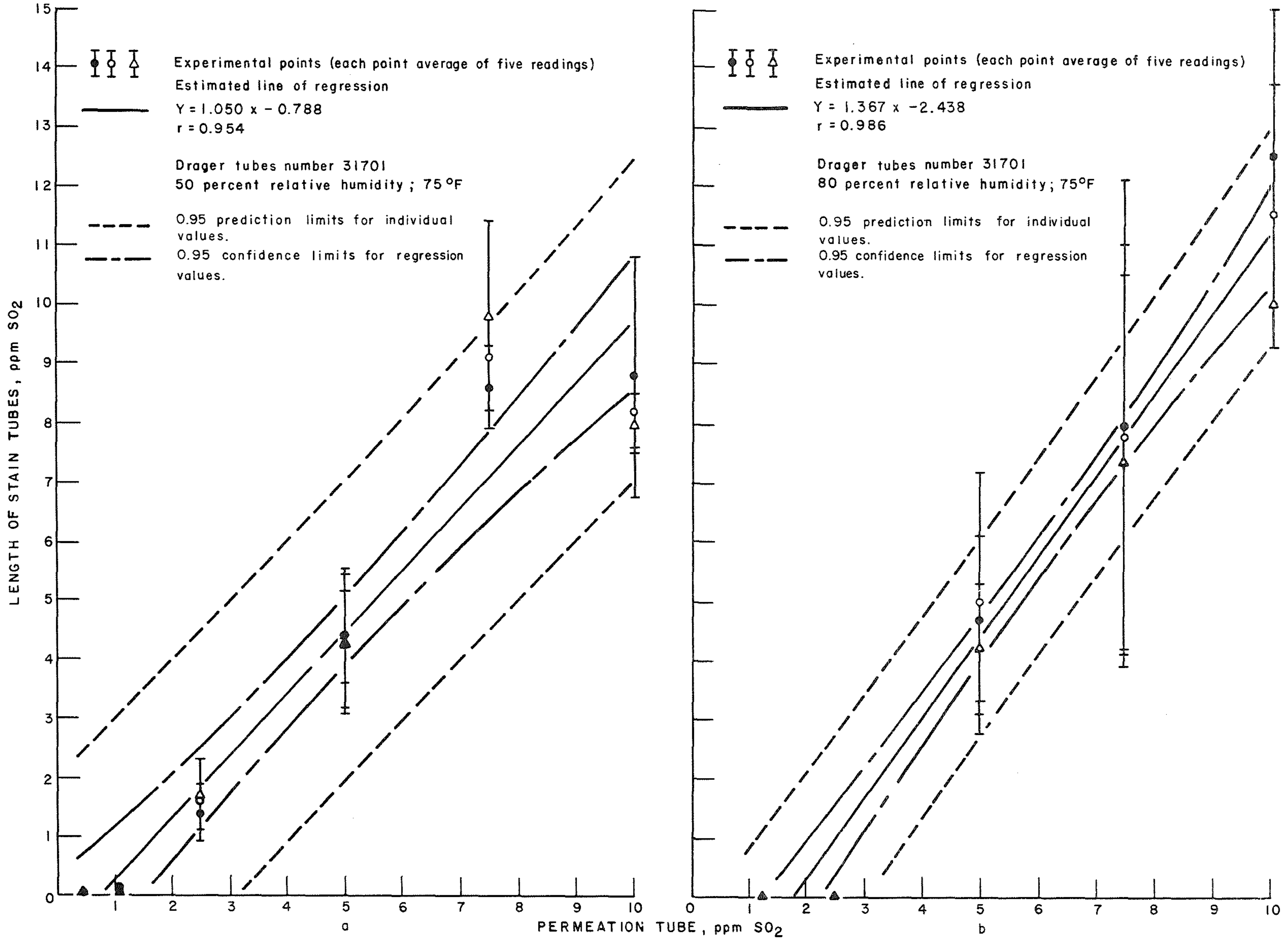

FIGURE A-12. - Determination of SO_2 concentration with a Drager length-of-stain detector system.

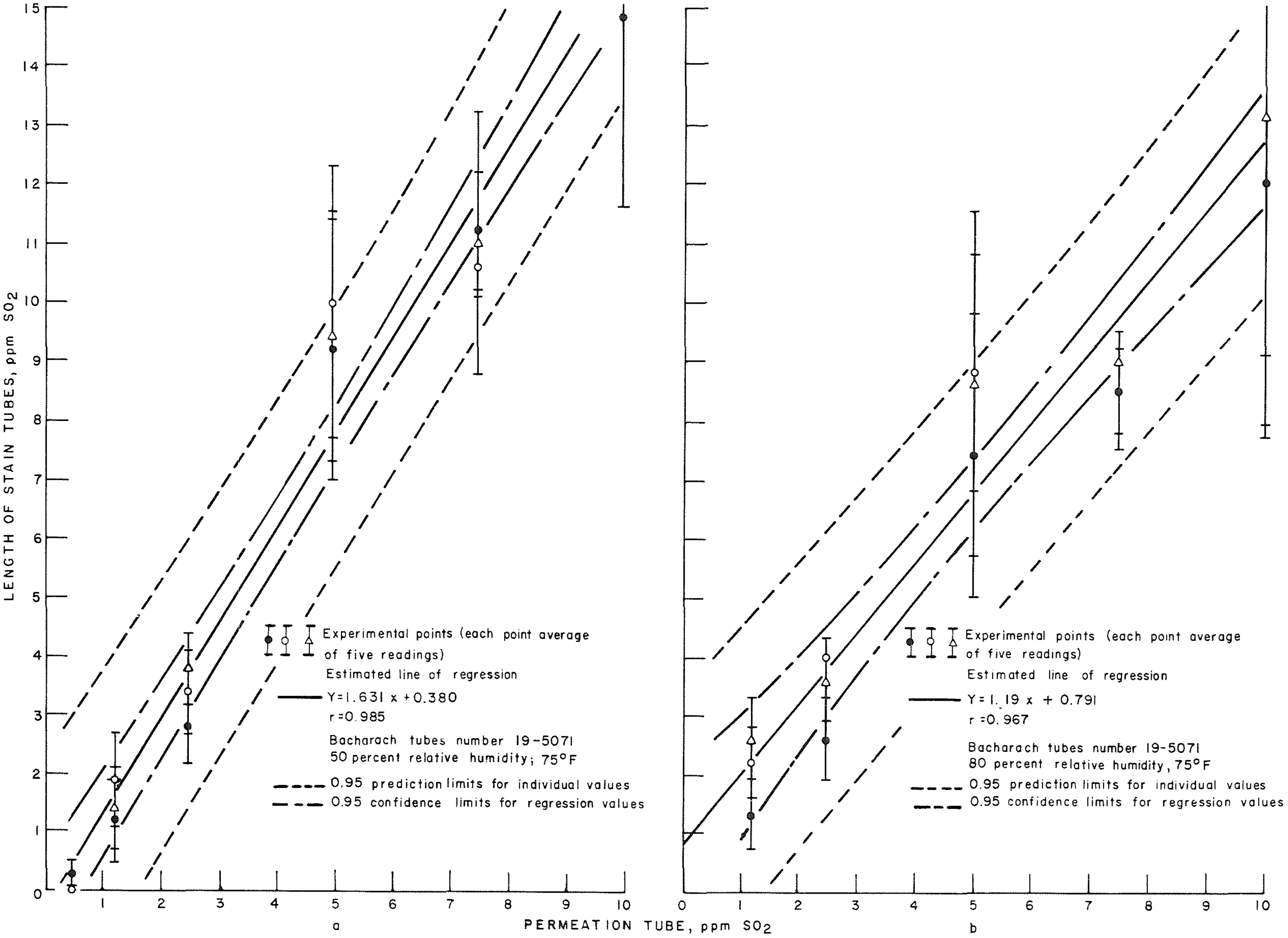

FIGURE A-13. - Determination of SO_2 concentration with a Bacharach length-of-stain detector system.

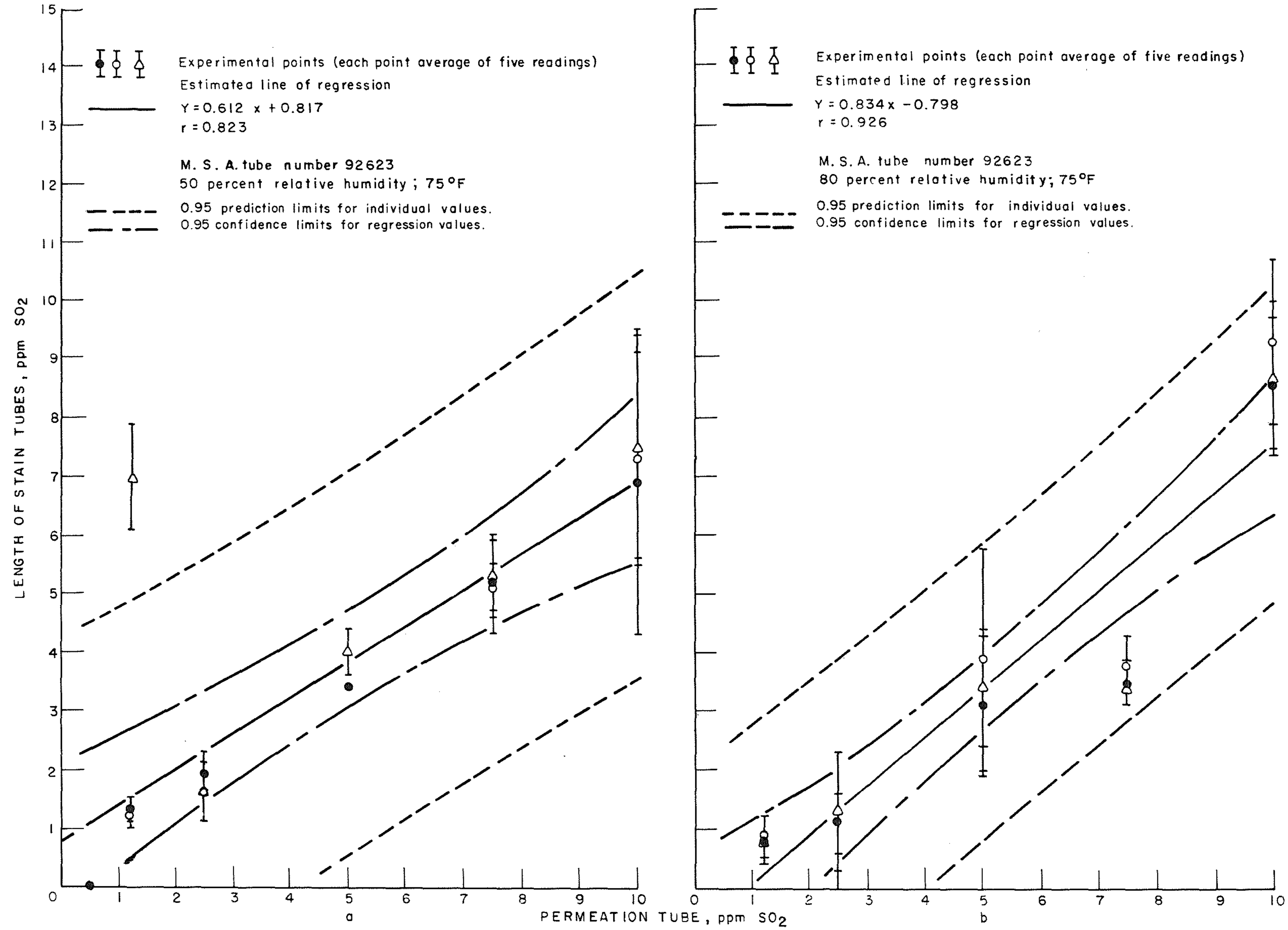

FIGURE A-14. - Determination of SO_2 concentration with an MSA length-of-stain detector system.

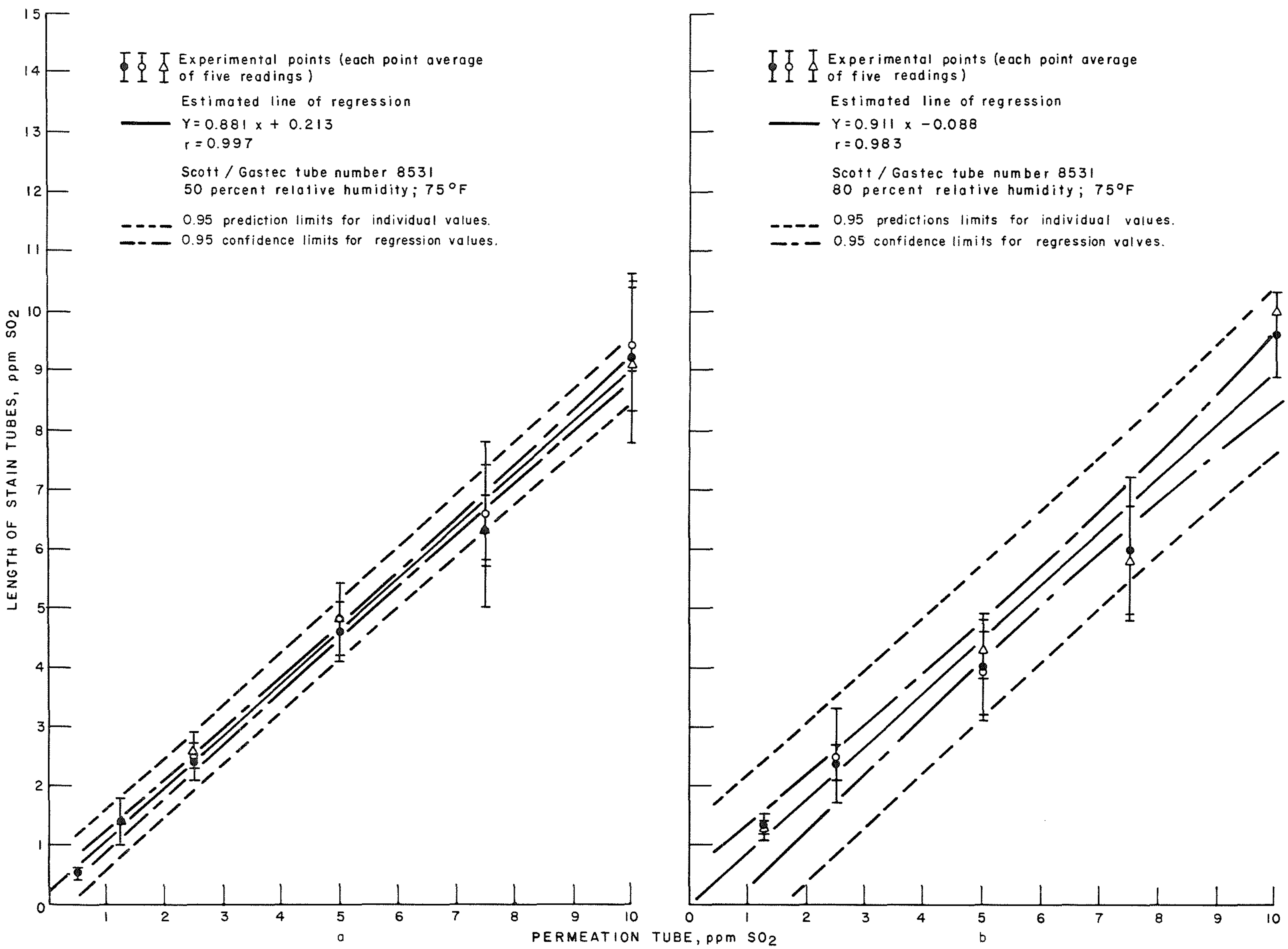

FIGURE A-15. - Determination of SO_2 concentration with a Scott/Gastec length-of-stain detector system.

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