

A System for Recording Air Concentrations of Zinc Sulfide Fluorescent Pigment on a Real-Time Scale¹

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The great majority of samples taken during atmospheric diffusion studies are of the bulk variety. The pollutant or tracer in the atmosphere is collected over some period of minutes, hours, or days on or in a collecting device which has time resolution only to the extent that it is known when the sampler is turned on and off. Thus, an increasing volume of experimental results is being published with regard to mean concentrations or dosages that can be expected from pollutant sources. However, minimal data are available concerning the time history of concentration contributing to the means.

A device capable of monitoring and recording air concentrations of a phosphorescing tracer (U. S. Radium Corporation zinc sulfide pigment No. 2210) on a real-time scale has been developed at Hanford. A prototype sampler was first field tested in 1962. The models presently used were put into field use in the fall of 1963. Within the technical limitations of the sampler, param-

eters such as source height, meteorological conditions, terrain, vegetation, and distance from the pollutant source can be related to time-dependent variables such as arrival and departure of the contaminant, per cent of time the contaminant is detectable, or peak-to-mean air concentration ratios.

Fig. 1 shows the real-time sampler set up for field use. A schematic drawing of the sampling system is shown on Fig. 2. Tracer laden air is drawn through the intake 1) to an irradiation chamber 2) where the tracer particles are caused to phosphoresce by exposure to a mercury vapor lamp 3). The glowing tracer passes through a light trap 4), past a photomultiplier tube 5), and through a flow control orifice 6). Vacuum required to maintain orifice control of flow rate can be monitored by the vacuum gage 7).

Up to 1400 V dc is supplied to the photomultiplier by a battery-operated, corona-regulated power supply 8). Anode current of the phototube, which is proportional to tracer concentration, is monitored by a strip chart recorder 9). An attenuator 10) attached to the recorder permits a selection of over three orders of magnitude in

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FIG. 1. Real-time sampler system assembled for field use.

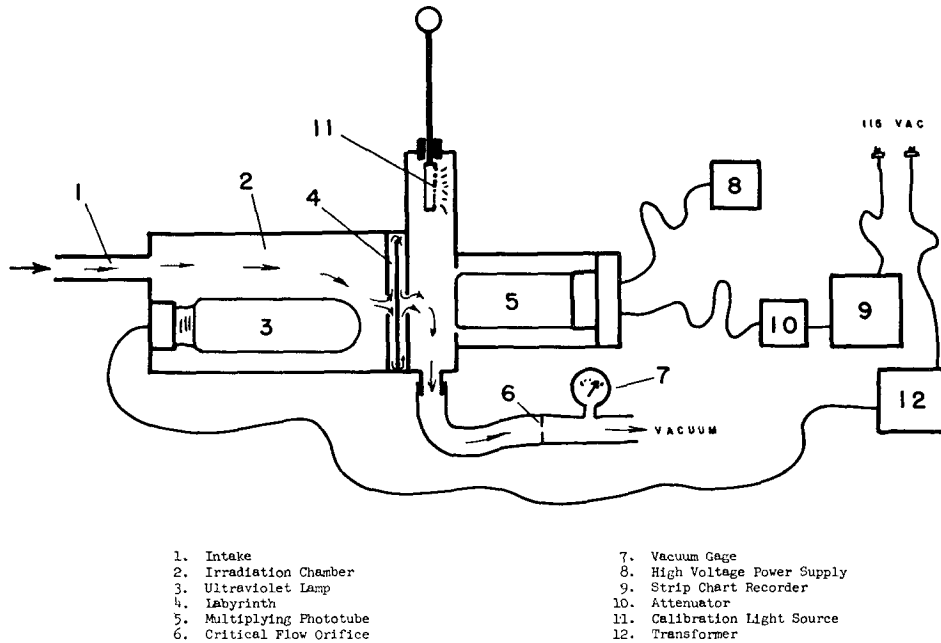


FIG. 2. Schematic drawing of zinc sulfide real-time sampler.

full scale signal level. A transformer 12) supplies 220 V ac to the mercury vapor lamp.

Field calibration of the detection system is readily accomplished by insertion of a self-scintillating calibra-

tion light source 11) in front of the photomultiplier and adjustment of the high voltage until the recorded photomultiplier output reaches a prescribed level. Fig. 1 shows the calibration source in the "calibrate" position. Fig. 2

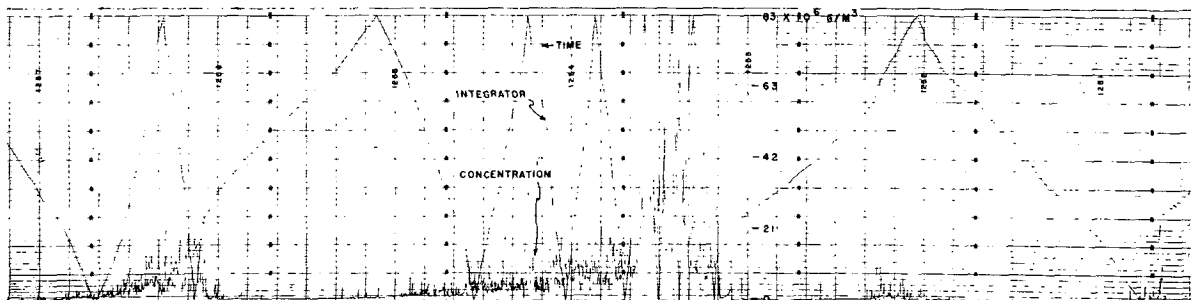
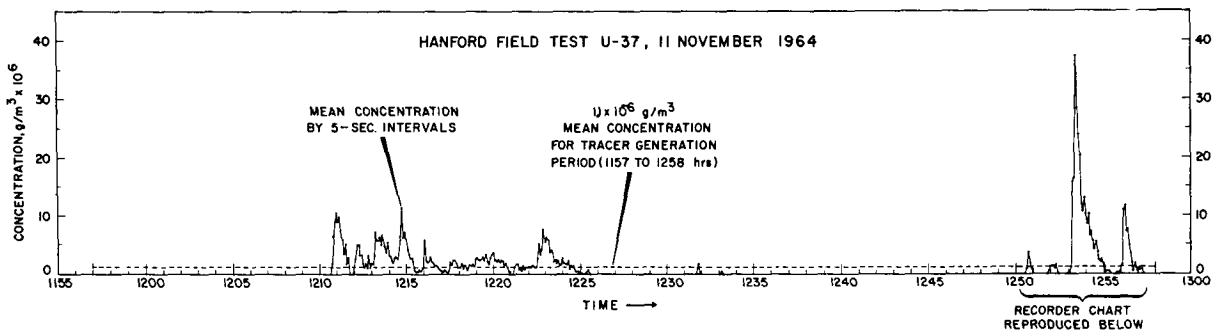


FIG. 3. Tracer concentration observed during a 1-hr release on 11 November 1964.

depicts the source in the "operate" position. This 0.005 microlambert calibration source was manufactured by the Minnesota Mining and Manufacturing Company. The activator in the self-luminous paint is Pm-147.

The following components and dimensions of the sampling system are not necessarily optimum, but they have been used in the described operable system. The cylindrical irradiation chamber is 3 inches in diameter and 10 inches long. Irradiation is supplied by a 100 W, ASA H4AB mercury lamp. The photomultiplier used is an EMI 9536B. The light trap, which fits into the end of the irradiation chamber, consists of two circular discs with protruding concentric ribs which mate to form a labyrinth. They are painted flat black and the spacing between the discs can be adjusted by four set screws which protrude from one of the discs. Tracer laden air passes around the outside edge of one disc, travels the labyrinth, and exits through a $\frac{1}{2}$ -inch diameter hole in the center of the second disc.

The use of an integrating recorder with the system greatly facilitates the averaging of concentration over any time increment of more than a second or two duration. As seen on the reproduced recorder chart at the bottom of Fig. 3, the integrating pen traverses across the chart at a rate proportional to the signal level of the "instantaneous" signal.

With the sampler flow rate of $0.1 \text{ m}^3 \text{ min}^{-1}$, approximately 0.6 sec is required for a parcel of sampled air to pass from the intake of the sampler to the photomultiplier viewing chamber. The span step response of the Texas Instruments recorder employed is less than 0.5 sec.

Calibration in units of tracer concentration versus recorder signal level was accomplished by first exposing the real time sampler within a few inches of a membrane filter of a type routinely used at Hanford in collection of particulate atmospheric tracers. The tracer was emitted in routine fashion at an upwind distance varying from 0.2 to 12.8 km. The filter was replaced after each "puff" of tracer passed, as was indicated by the real-time record. A knowledge of 1) flow rate through the filter, 2) mass of tracer collected by the filter, and 3) time interval during which tracer was collected, permitted calculation of concentrations which were considered representative for the adjacent real-time sampler.

Air concentrations during calibration ranged from 10^{-7} to approximately $6 \times 10^{-4} \text{ gm m}^{-3}$. (Since for pigment 2210 there are approximately 10^{10} particles gm^{-1} , concentrations thus ranged from 1000 to 6×10^6 particles m^{-3} .) Concentration computations were made for 62 "puffs" of from 10 sec to 5 min duration, and the mean recorder signal level during each puff was noted. Fitting a least squares regression line to the logarithms of the resultant points gave the equation

$$C = 2.90 \times 10^{-8} R^{0.965},$$

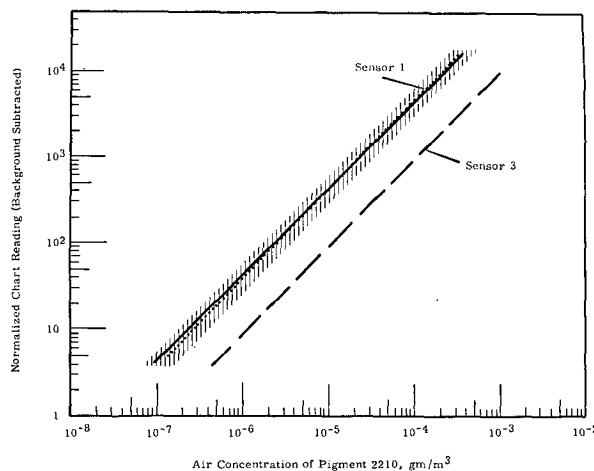


FIG. 4. Calibration curves for zinc sulfide real time samplers.

where C is concentration in gm m^{-3} , and R is a minor chart unit (0.04 nA) at the most sensitive range setting. This curve is the dotted line on Fig. 4. The standard error of this regression line is indicated by the shaded area. This error embraces the range of $C - 0.31C$ to $C + 0.44C$. The error includes variance due to actual differences in concentration existing between the real-time samplers and that of the nearby calibration filters.

The hypothesis that the computed exponent 0.965 is really 1.000 is readily acceptable on statistical as well as theoretical grounds. If this hypothesis is accepted, and the curve is drawn through the mean of the logarithms of the data points, the equation becomes

$$C = 2.35 \times 10^{-8} R.$$

This equation, which is considered more representative, is shown as the solid line on Fig. 4.

Specification of a precise detection limit is not easy. An atmospheric concentration of about $3 \times 10^{-8} \text{ gm m}^{-3}$ of tracer (300 particles m^{-3}) should result in one particle passing into the sampler each 1.7 sec. A series of "spikes" spaced at approximate 2-sec intervals has been observed superimposed on chart background at air concentrations (as computed from adjacent calibration filters) in the neighborhood of $3 \times 10^{-8} \text{ gm m}^{-3}$. One can speculate that the "spikes" are individual particles registering on the recorder and thus claim the ultimate detection limit of a single particle. However, during sampling at higher concentrations, some particles undoubtedly impact in the ultraviolet irradiation chamber. These particles can be sporadically knocked loose from the chamber to give an increase in background noise signal which is indistinguishable from true low-level atmospheric concentrations. Thus, a more realistic estimate of the detection limit of the instrument is set at $2.5 \times 10^{-7} \text{ gm m}^{-3}$ (2500 particles m^{-3}). The impaction problem results in the sampler being more reliable in detecting the first arrival of the tracer than in indicating its departure.

Differences in phototube characteristics, in geometry within the sensors, and in flow rates through the systems, result in differences in calibration from sampler to sampler. The computed regression curve for a second sampler is

$$C = 1.28 \times 10^{-7} R^{0.974}.$$

The computed standard error on this line was almost identical to that of the other, with the applicable figure being $C - 0.31C$ to $C + 0.45C$. As before, theory and reasonable statistics permit the acceptance of the hypothesis that the equation is

$$C = 1.12 \times 10^{-7} R.$$

This curve is the broken line at the right on Fig. 4.

Examples of data obtained from charts generated by a real time sampler are given in Table 1 and Fig. 3. On 23 October 1963, a real-time sampler was operated during a routine Hanford field diffusion experiment. Fluorescent tracer 2210 was generated at an elevation of 56 m for a period of one hour. Generation rate was 25 gm min⁻¹. Mean wind speed during the experiment was 5 m sec⁻¹ at an elevation of 2.1 m, and 8 m sec⁻¹ at an elevation of 61 m. Temperature at 0.9 m was 15.1C, and at 61 m, it was 12.9C. The sampling height was 1.5 m. The sampler was first operated for a period of 19 min at a ground distance of 600 m from the source. Subsequently, the sampler was moved and operated for 29 min at a distance 1600 m from the source. At 1600 m,

the sampler was, fortuitously, exposed at the location of the peak mean concentration for that distance; at 600 m, exposure location was at 70 per cent of the peak mean concentration.

The per cent of time the ratio of "instantaneous" concentration C to the mean concentration \bar{C} (for the appropriate 19- or 29-min period), equalled or exceeded a given value is listed in Table 1. For example, at 600 m, the instantaneous concentration equalled or exceeded the 19-min mean concentration 15.8 per cent of the time. C was at least twice \bar{C} 10.9 per cent of the time, and was at least three times \bar{C} 8.2 per cent of the time.

Data displayed in Fig. 3 were derived from measurements made during a tracer release from an elevation of 111 m on 11 November 1964. Tracer was released at a rate of 213 gm min⁻¹ for 61 min. The mean wind speed during the experiment was 5 m sec⁻¹ at an elevation of 122 m. Temperature was 8.3C at 122 m, 8.5C at 61 m and 9.8C at 2.1 m. The sampling elevation was 1.5 m at a distance of 1200 m from the source. The mean tracer concentration observed during the period of generation was 1.1×10^{-6} gm m⁻³ as determined from the real-time sampler record. This mean value is indicated by the dotted line in the top portion of Fig. 3. For comparison, a filter located within 3 ft of the real time sampler intake revealed a mean concentration of 1.3×10^{-6} gm m⁻³ during this field experiment. This concentration is 23 per cent of the value determined from the filter with the peak mean concentration observed at 1200 m from the source. The peak filter on this sampling arc was 126 m (along a circumference) from the real time sampler.

The bottom portion of Fig. 3 is a reproduction of a portion of the actual real-time sampler chart generated during Hanford Field Test U-37. The upper graph was constructed by plotting the mean concentrations for successive 5-sec increments. Also, as mentioned previously, the mean concentration for a 61-min period is suggested by the dotted line.

The data presented are not the results of exhaustive studies involving use of the Hanford real-time sampler, but are intended as examples of the type of data which can be generated by such a device. The collection of such data should help to fill a need of the diffusion meteorologist for information specifying the real-time history of diffusing contaminants.

TABLE 1. Per cent of time C/\bar{C} equals or exceeds the indicated ratio.

C/\bar{C}	Percent of time	
	600 m	1600 m
0	100.0	100.0
1	15.8	22.0
2	10.9	14.2
3	8.2	10.4
5	5.2	6.3
10	2.1	2.1
20	0.14	0.32
30	0.039	0.053
34.6	0 (Peak C)	0.041
40	0	0.022
50	0	0.006
58.5	0	0 (Peak C)