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THE TRICHLOROETHYLENE-SATURATED WATER AND THE TETRACHLOROETHYLENE CHEMICAL DOSIMETER SYSTEMS

Preparation and Response to Gamma Radiation

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ABSTRACT

Chemical dosimeter systems for measuring dose from about 5 to more than 1,000,000 rads in fast-neutron and gamma-radiation fields are presented. Experimental techniques for preparation and evaluation of these dosimeters and the effects of individual components are discussed. A simple two-band filter-photometer reader is described.

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CHAPTER 1

INTRODUCTION

Various methods which are available or under investigation for the measurement of dose from a mixed-radiation field have been the subject of recent publications (1). Dosimeters are needed which are capable of measuring the individual contribution of each component of the mixed radiation to the total dose and which are energy and dose-rate independent throughout the region of interest. For biological systems, the dosimeter must be capable of measuring the dose delivered to tissue and, for certain purposes (e.g., depth-dose determinations), be physically small enough that the dosimeter itself does not perturb the dose to the system being studied.

Chemical dosimeters at the present stage of development appear to offer distinct potential for fulfilling these requirements. The chemical dosimeters chosen for initial investigation in this Laboratory were prepared essentially by the procedures described by Sigoloff[a] (2). Two types of dosimeters are involved -- one which responds to both gamma radiation and fast neutrons and another which responds significantly only to gamma radiation.

Chemical chain reactions induced by radiation liberate acid in both types, and the amount of acid formed is directly proportional to dose. The response may be evaluated by titration of the acid produced, by change in conductivity of the solution, or by change in pH measured electrometrically or colorimetrically. In the present study, a pH indicator was always used. The dosimeters which respond to both fast neutrons and gamma rays consist of trichloroethylene-saturated water containing a pH indicator; this one-phase solution is essentially all water. The dosimeters sensitive to gamma radiation only consist of tetrachloroethylene, which contains a small amount of free-radical chain-reaction retarder, overlayered with an aqueous phase containing the pH indicator. The sensitivity of both types depends on the concentration of chain-reaction retarders and, with spectrophotometric evaluation, on the presence of buffers and the initial pH of the aqueous phase.

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[a] We are grateful for many personal communications with Mr. Sigoloff.

The container for the solutions may be any convenient size or shape, although there is undoubtedly a lower size limit with respect to processes involved in energy absorption. It must be capable of excluding its environment, incapable of releasing significant amounts of acids or bases into the solution, and optically satisfactory when spectrophotometric methods are used.

The systems appear generally applicable in the dose range of approximately 5 to 10^6 rads. The amounts of acid produced are small (about 10^{-11} mole per rad), and consequently due precautions must be taken with low-dose types concerning the purity of reagents and cleanliness of apparatus. In this investigation some of these parameters have not been thoroughly investigated; certain precautions and procedures may not be necessary. Many of the initial attempts by this group to prepare dosimeters met with difficulties and failures. The causes were eliminated, as evidenced by success, although not always adequately explained or understood.

This report attempts to present directions and techniques which can serve as guides for the preparation and evaluation of these types of chemical dosimeters. It may be that some descriptions are unnecessary or discussed in too much detail, but it is hoped they will prove helpful. It is realized that better, more satisfactory methods will develop as more experience is gained by various investigators.

CHAPTER 2

PRODUCTION OF CHEMICAL DOSIMETERS

2.1 Preparation of Ampuls

The ampuls(b) were washed with 5 per cent nitric acid, thoroughly rinsed with distilled water,(c) and steam-cleaned.(d) As an alternative to steam cleaning, the ampuls may be boiled twice in a beaker with distilled water, care being taken to ensure cleanliness. The ampuls were placed

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(b) Kimble Neutraglass Ampuls, Type 12005-S28, "Treated," 7.5 x 43 x 76 mm. These ampuls are very uniform as to size and optical quality and have extremely thin walls which facilitate sealing.

(c) Syringes and hypodermic needles are useful in these operations.

(d) The ampuls were inverted on a manifold of twenty 18-gage needles. Steam was supplied (at 80 p.s.i., which dropped to about 60 p.s.i. during the minute steam was being released) from a 6-kw electric steam generator (Sussman Hot Shot, Automatic Steam Products Corp., New York). Stainless steel piping and a porous stainless steel filter (5 μ pore size, Micro Metallic Corp., Glen Cove, New York), which was electrically heated, were used.

in drying racks,(e) rinsed with quadruply distilled water, dried at 110°, and finally baked at 300° for several hours. After cooling, about 0.5 ml of a 3 per cent solution of Dow-Corning 200 Silicone Fluid, 350 cs viscosity, in tetrachloroethylene (or 1,1,1-trichloroethane or trichloroethylene) was added to each ampul (the rack being inverted so that the ampuls were upright), distributed on the interior of the ampuls by swirling, and finally removed by shaking the rack of inverted ampuls over the sink. The ampuls were allowed to drain for 30 minutes, dried at 110° for 30 minutes, baked 3 hours at 300°, and stored in dust-free containers.

All other apparatus, flasks, bottles, syringes, needles, etc. (pipettes and burettes excepted) were cleaned and siliconed similarly.

2.2 Preparation of Reagents

Water used in all solutions and for rinsing glassware was quadruply distilled (ordinary distilled water which was distilled from alkaline permanganate, then from dilute sulfuric acid, and then distilled again). Precautions were taken to exclude carbon dioxide during and after the process.

(e) The racks utilized fuse clips for supporting the ampuls in an inverted position (which proved very convenient).

Trichloroethylene(f) (T_3CE) was washed with dilute hydrochloric acid and several times with water, dried over calcium sulfate, and distilled through a 25-cm Vigreux column. The reagent was stored under a layer of water in a refrigerator; immediately before use it was washed with water.

Tetrachloroethylene(g) (T_4CE) was washed twice with concentrated sulfuric acid, twice with fuming (20 per cent) sulfuric acid, twice with concentrated sulfuric acid, and finally about 10 times with water.(h) The water washings were done in the storage bottle by using vacuum to remove the water. The reagent was stored under water in a refrigerator.

2,6-Di-tert-butyl-p-cresol(i) (DBC) was recrystallized from 95 per cent ethanol.

(f) Eastman Kodak Company, No. 1300.

(g) Eastman Kodak Company, No. 2418 (stabilized with ethanol).

(h) This procedure is much less time-consuming than distillation as previously advocated (2) and furnishes a product of equal sensitivity. The present investigators were unable to obtain a satisfactory product by distillation through a 1-meter, helices-packed Todd Column.

(i) Shell Chemical Corp. Ionol, or Catalin Corp. Antioxidant CAO-1.

Chlorphenol red (CPR) and phenol red (PR)(j) were recrystallized from 95 per cent ethanol. Stock solutions, 0.02 M, keep indefinitely.

MacIlvaine's buffer(k) (citrate-phosphate) solutions were mixed to desired pH values as determined with a pH meter.

2.3 Conventional One-Phase Dosimeter Solutions

To a 5 x 10^{-5} M solution of CPR containing the appropriate amount of buffer and retarder for the desired range (Table I) was added about 1 per cent of T_3CE. The mixture was shaken and allowed to stand with occasional shaking for several hours or more. The aqueous solution was decanted from the undissolved T_3CE into an Erlenmeyer flask, and the pH was adjusted to ~5.9(l) with dilute sodium hydroxide and hydrochloric acid solutions.

2.4 Carbon Dioxide-Free One-Phase Dosimeter Solution

In an apparatus designed to exclude carbon dioxide,

(j) Eastman Kodak Company.

(k) Ref. 3; the citric acid and disodium phosphate solutions were not adjusted as prescribed in the reference since adjustment was made with a meter.

(l) Details will be discussed in later sections.

Table I. ONE-PHASE DOSIMETERS[a]

Range[b]	Conc.[c] of buffer[d]	Conc.[c] of thiourea
20-400	0	0
100-1000	0	0
300-3000	0.15	0
$2000-2 \times 10^4$	0.25	0.1
$1.2 \times 10^4-1.5 \times 10^5$	0.6	0.4
$5 \times 10^4-2 \times 10^6$	5	0.4

[a] The indicator at 5×10^{-5} <u>M</u> is CPR in all systems except the first, in which it is PR (CO_2-free).

[b] Dose range (photometric evaluation, $0.1 < \Delta R \leq 2$) is approximate and is expressed in roentgens of Co^{60} gamma radiation.

[c] Concentration in per cent.

[d] MacIlvaine's buffer, pH 6.0.

the solution was prepared by saturating carbonate-free 5×10^{-5} $\underline{M}$ PR solution with T_3CE.(m)

2.5 Two-Phase Dosimeter Solutions

The lower phase consisted of T_4CE containing the appropriate amount of retarder and overlayered with water or upper phase. The upper phase was 5×10^{-5} $\underline{M}$ CPR solution containing the appropriate concentration of buffer (Table II); the pH was adjusted with dilute acid and base. Equilibration of the two phases was not necessary but, when convenient, both were often contained in the same flask.

2.6 Dosimeter Preparation (Filling, Sealing, and Aging)

For the conventional CPR systems the dosimeter solution, 0.75 ml, was placed in the ampuls with the aid of a syringe and needle. With one-phase dosimeters the volume used need not be precisely measured unless titration is to be used for evaluation. With the two-phase dosimeters, however, the ratio of volumes of lower phase to upper phase must be kept constant (a ratio of 4:1 was generally used, i.e., 0.60 ml of T_4CE and 0.15 ml of upper phase). This was a compromise

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(m) Details will be discussed in later sections.

Table II. TWO-PHASE DOSIMETERS(a)

Range(b)	Retarder conc.,(c) lower (T_4CE) phase	Buffer conc.,(d) upper (H_2O) phase
2-12	EtOH, 0.1(e)	0
10-200	DBC, 0.2	0
50-500	DBC, 0.2	0.1
100-1000	DBC, 0.2	0.25
500-6000	DBC, 0.2	1.5
1500-2.5×10^4	DBC, 0.2	4
5000-1.5×10^5	DBC, 0.5	10
4×10^4-7×10^5	DBC, 0.5	10(f)
5×10^4-8×10^5	DBC, 0.5	50
8×10^4-2×10^6	DBC, 0.5	100

(a) Indicator is aqueous CPR at 5×10^{-5} M containing 0.2 per cent thiourea. Ratio of volumes of upper to lower phase is 1:4 [except in one example (f)].

(b) Dose range (photometric evaluation, $0.1 < \Delta R < 2$) is approximate and is expressed in roentgens of Co^{60} gamma radiation.

(c) Concentration in per cent (w/v) of lower phase.

(d) Concentration of MacIlvaine's buffer, pH 6.0, in per cent (v/v) of upper phase.

(e) Partition of this retarder greatly favors the aqueous phase; however, its concentration is expressed as indicated.

(f) Ratio of volumes of phases is 1:1.

among sensitivity, optical, and mechanical considerations. After filling, the ampuls were centrifuged briefly in a small clinical centrifuge to remove droplets adhering to the ampul walls and neck and, with two-phase dosimeters, to force the T_4CE below the water layer. They were then flushed with carbon dioxide-free nitrogen to remove organic vapors which would produce acid if pyrolyzed during sealing. Flushing was done on a manifold of hypodermic needles which extended almost to the surface of the solution. The time required depended on the flow rate; insufficient flushing resulted in excessive and variable acid production on sealing.

A semiautomatic sealer(n) permitted greater uniformity of seals than did manual sealing by the average operator. The gas and oxygen flow rates were controlled by using simple, noncalibrated rotameters; ampul position and rotation were controlled by the sealing apparatus, and the length of time the ampul was in the flame was controlled by the operator. A good seal "burns" as little glass as possible. This does not necessarily require a "hot" flame or "fast" sealing; in the present case, seals were made in about 3.5 seconds. A

(n) Bench Model Ampul Sealer, Kahlenberg-Globe Equipment Co., Sarasota, Florida.

good seal will be uniformly rounded (almost hemispherical, not flattened) with a tiny hemisphere of solid glass at the top. Some acid was always liberated during the sealing process, most of which apparently came from decomposition of the vapors present above the solution (which was the reason for centrifugation and flushing before sealing). Small amounts of acid produced in this way did not interfere if the same amount was produced each time.

Immediately after sealing, the tip of the ampul was cooled by a jet of air. Aqueous phase was shaken into the tip of each ampul, and the dosimeters were "aged" in an oven at 80° for about 1 hour. This aging process hastens the leaching of small amounts of alkali present in the new glass surface at the seal. For example, it has been observed that the pH of an unbuffered, conventional one-phase dosimeter changes from 5.9 to $\sim$5.8 on sealing and back to $\sim$5.85 on aging.

Each dosimeter was numbered (diamond-point pencil or the like), and a file card for each was prepared on which would be entered subsequent spectrophotometric and exposure data.

For preparation of the low-dose, carbon dioxide-free, PR, one-phase dosimeters, quadruply distilled water containing $\sim$1 per cent sodium hydroxide was distilled into the apparatus (see Appendix, Illustration No. 6) with nitrogen flushing. Trichloroethylene and stock PR solution were added through a stopcock while the apparatus was under nitrogen pressure. All stopcocks were closed and the apparatus was shaken vigorously. After several hours or more, the excess T_3CE was withdrawn and the pH of the solution was adjusted to a value of ~7.5, which would give finished dosimeters having a starting pH of ~7.2. The ampul was flushed by nitrogen flowing from the outer needle of the apparatus, the solution was withdrawn into the ampul via the inner needle, and the ampul was quickly transferred to the sealer. The sealer was equipped with a flushing needle that extended just into the top of the ampul. After sealing, the dosimeters were treated as above. Owing to the sensitivity of this type of dosimeter, considerable color variation among dosimeters was common.

CHAPTER 3

EVALUATION METHODS

The most precise method for determination of the amount of acid produced in the dosimeters is generally by spectrophotometry, and in these studies a Beckman DK-1 was employed and, later, filter photometers. The indicators used have two widely separated absorption bands in the visible region of the spectrum. The acid form of chlorphenol red (CPR) exhibits an absorption maximum at 433 mμ and its conjugate base at 571 mμ. The respective values for phenol red (PR) are 432 mμ and 558 mμ. Over the useful pH range of the indicator (about pH 6.2 to 5.2 for CPR and 7.6 to 6.6 for PR), both these bands are present, and their relative transmittances are related to the pH. Theoretically, the transmittance (or absorbance) of either of these bands could be employed to determine the pH of a solution. However, with ampuls which do not have strictly uniform optical properties, a function which considers the magnitude of both the bands is much more satisfactory in that ampul-to-ampul variations, e.g., size, imperfections, and striations, tend to cancel. Such a function which is now in use is the ratio (R) of the transmittance of the band produced by the basic form of the indicator (T_B) to the transmittance of the band from the acid form (T_A).

The amount of acid produced by exposure to radiation is directly proportional to dose. The relationship of dose to spectral ratio ($R = T_B/T_A$) is somewhat more complicated. The curves obtained by plotting spectral data in two of the many possible ways are shown in Figs. 1a and 1b.

When a group of dosimeters are prepared, a rather wide range of pre-exposure R values may be obtained unless the system is buffered. This presents difficulties because of the nonlinear response. The method routinely used in this work and which was used by Sigoloff (2) employs a log-log plot of dose versus difference between pre-exposure and post-exposure ratios ($R_f - R_i = \Delta R$, Fig. 1b). Three different R_i values are illustrated. The falling off at large ΔR is produced by saturation of the indicator. The same data are plotted in a different manner in Fig. 1a.

This discussion illustrates a practical difficulty. Only a certain fraction of the dosimeters prepared fall within a given range of R_i values, and from Fig. 1b it is apparent that

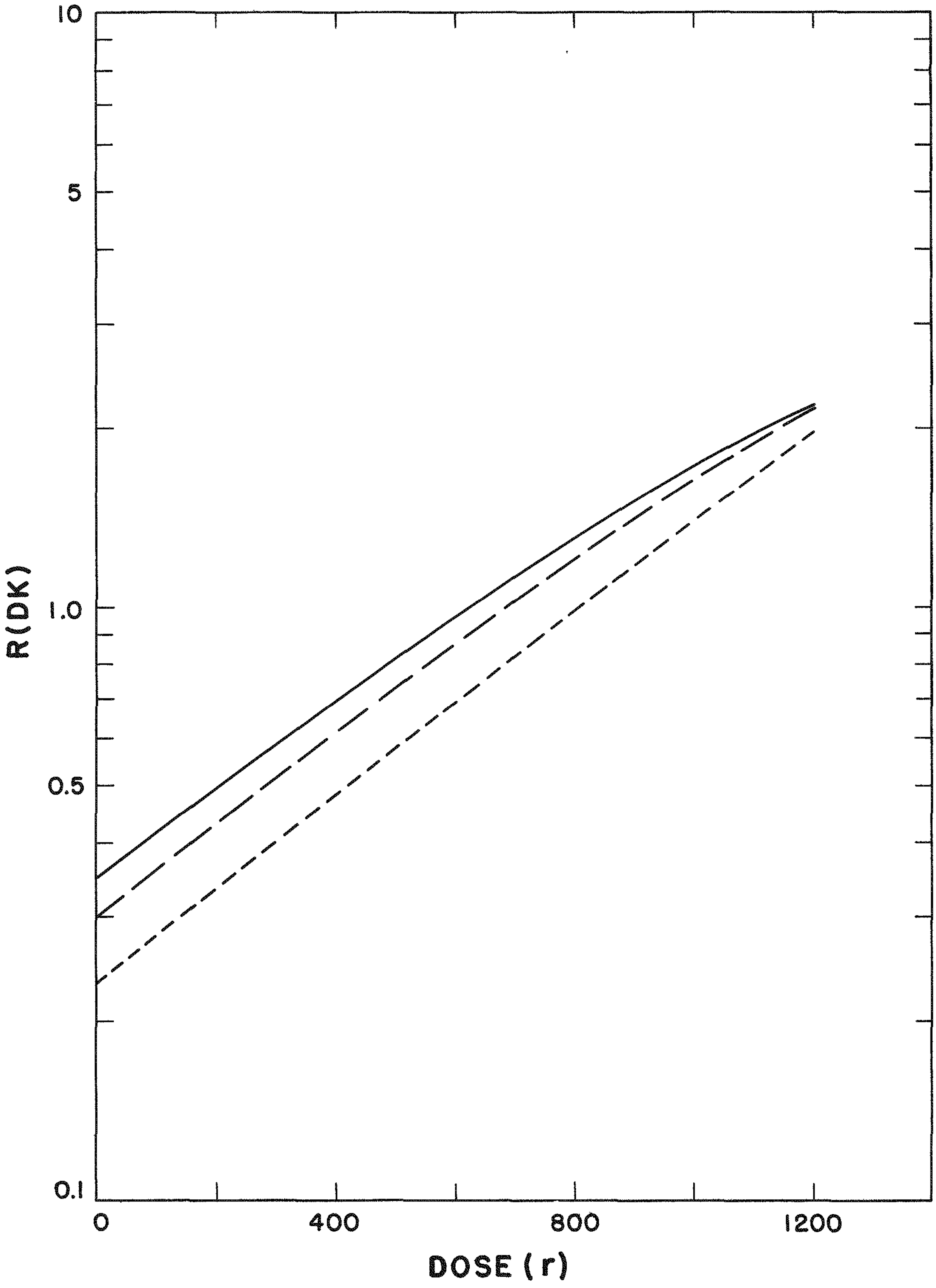

Fig. 1a. Representative response curves.

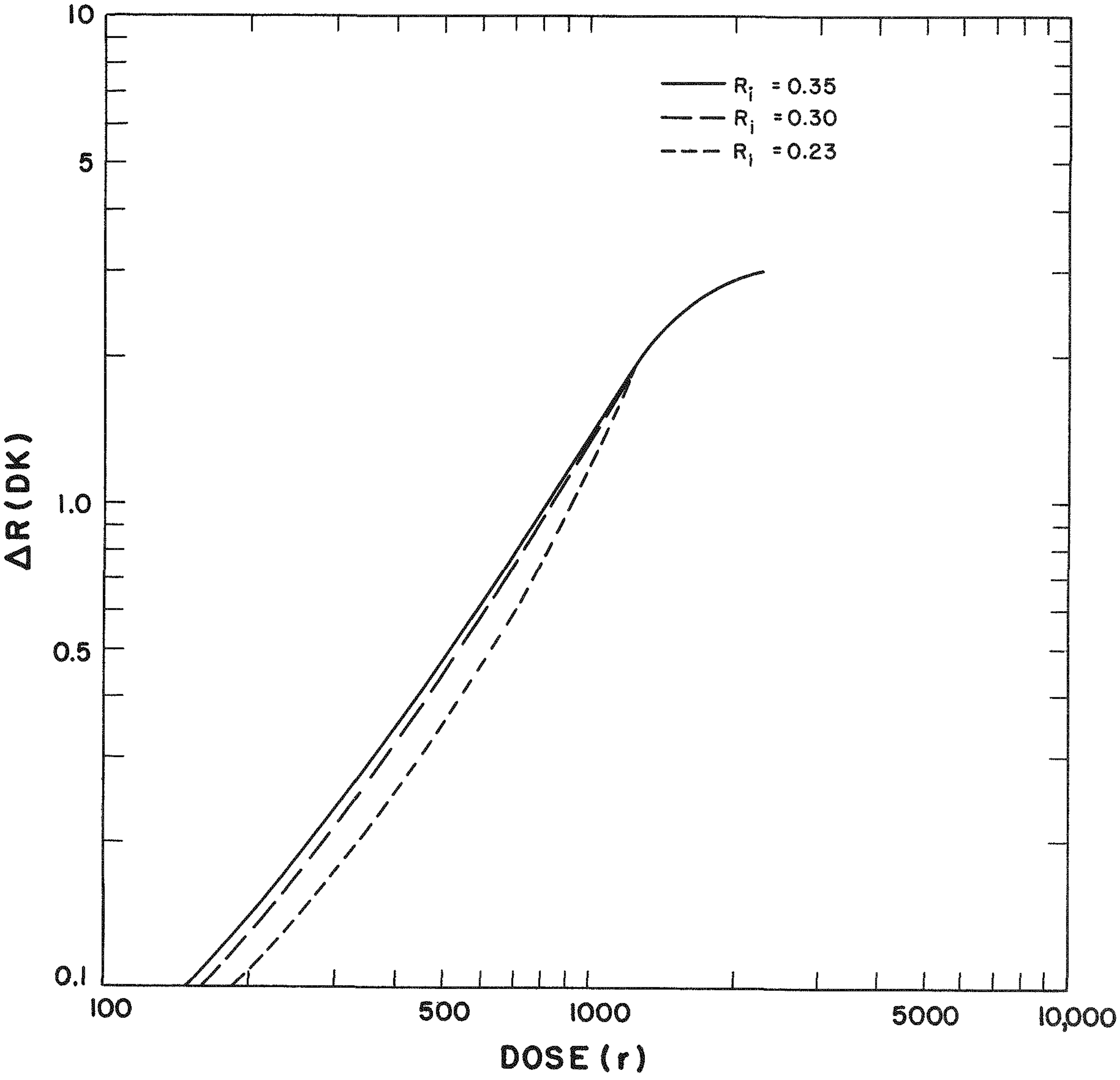

Fig. 1b. Representative response curves.

for greatest accuracy all the dosimeters should have very nearly the same R_i value (within ~ 0.05). In order to make full use of a batch of dosimeters, apparently several calibration curves are needed, based on various groups of R_i (a rather uneconomical procedure). Figure 1a indicates that log R_f versus dose tends to plot as a straight line until the indicator approaches saturation. Such relationships can be employed to "synthesize" response curves for various R_i and can be applied with some degree of confidence after sufficient experience has been gained.

An alternative procedure is to adjust the lower R_i upward, i.e., after a calibration curve on a given batch of dosimeters has been obtained, it can be used to calculate the dose required (approximately) to put dosimeters of low R into the desired R_i. It is quite simple and often worth while in practice to make these calculations (generally with the aid of a plot such as Fig. 1a) and form several groups of dosimeters which are exposed simultaneously at appropriate distances from a source. This procedure is particularly useful with the highly sensitive PR, one-phase dosimeters with which considerable variations in R_i are initially obtained. With dosimeter types containing a few tenths per cent of buffer, practically all the R_i values are the same and only a single calibration curve is necessary.

Since the absorption maxima of these indicators occur in the visible range, color changes observed visually by comparison with a set of buffered standards can be employed as a less precise evaluation method (2). The transmittances (T_A and T_B) can be determined on any spectrophotometer having sufficient sensitivity and reproducibility; many present-day instruments can meet these requirements. A Beckman DK-1 recording spectrophotometer was available for these studies and was found to be very satisfactory. In the two-phase dosimeters the layer of indicator solution is only a few millimeters high. A cuvette-shaped holder is used in which the ampuls fit snugly, and the spectrophotometer light beam passes through the indicator solution by means of a hole ($\sim$0.08 in. in diameter drilled in the holder). At the bottom of the holder a screw adjustment is present for positioning the height of the ampul so that the light beam passes through the layer of indicator solution unobstructed by either interface. This adjustment is made for each individual two-phase dosimeter; there is sufficient variation in filling and ampul dimensions that the height of the upper surface of the solution is not constant. With one-phase dosimeters the positioning screw is maintained at a single, reproducible position. A water blank is used in the reference beam in a similar holder. The need for the height-adjustment mechanism required drilling a hole in the base of the sample compartment, a modification which has not impaired the use of the instrument for other purposes.

The dosimeters are centrifuged before reading in order to form a sharp phase separation and to eliminate bubbles. The ampuls are wiped clean with a soft cloth and positioned in the holder in a reproducible manner both as to rotation and height. Owing to variations in the ampuls, the apparent T_A and T_B for identical solutions may vary; however, the ratio (T_B/T_A) remains quite constant. Approximately a minute is required to read each one-phase dosimeter and slightly longer for each two-phase dosimeter (individual height adjustment). Reproducibility of R is routinely about ±0.01.

The spectral ratios are recorded on individual dosimeter file cards, which also serve for recording data obtained later (e.g., exposure conditions, dose, R_f, and ΔR).

It has been possible also to use a filter photometer which obviates, or at least greatly decreases, the need for a more elaborate spectrophotometer. A filter photometer-type reader is also more amenable to field use. Two types of readers have been constructed.(o) In the first model, the

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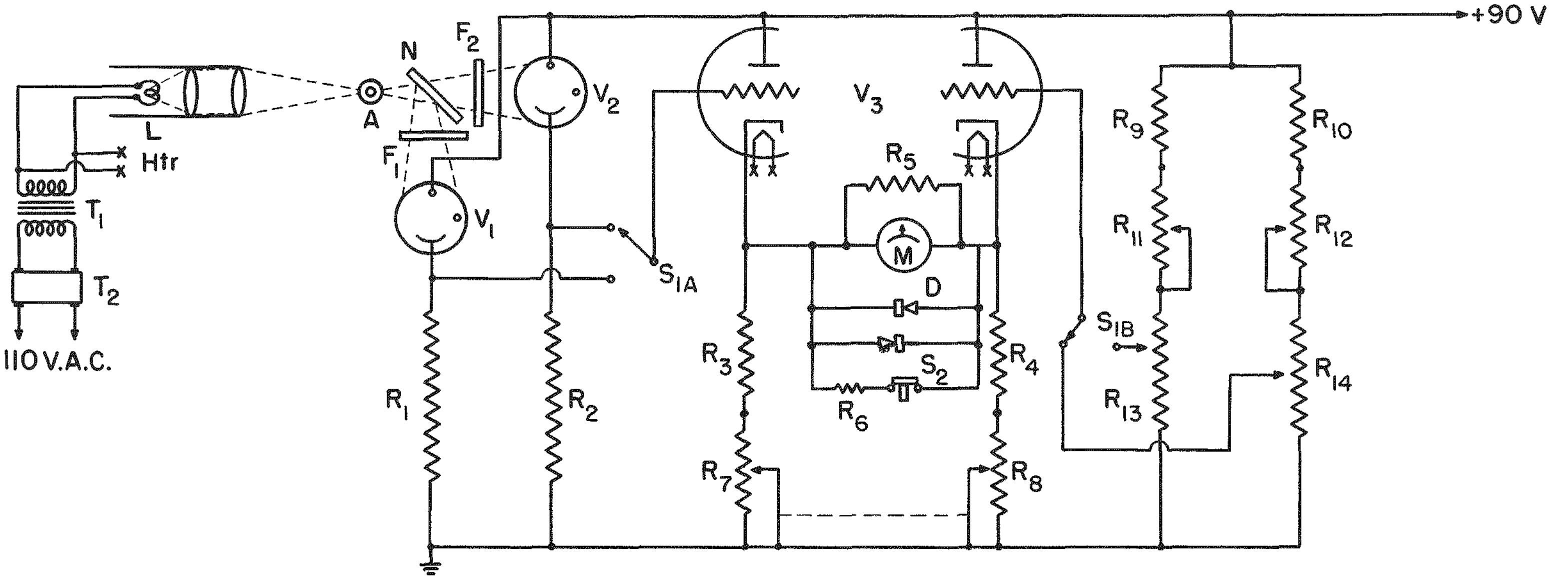
(o) The electronic circuit is based on suggestions by R. H. Müller and R. D. Hiebert. We are particularly indebted to J. H. Larkins and L. J. Carr for much of the design and for construction of the apparatus.

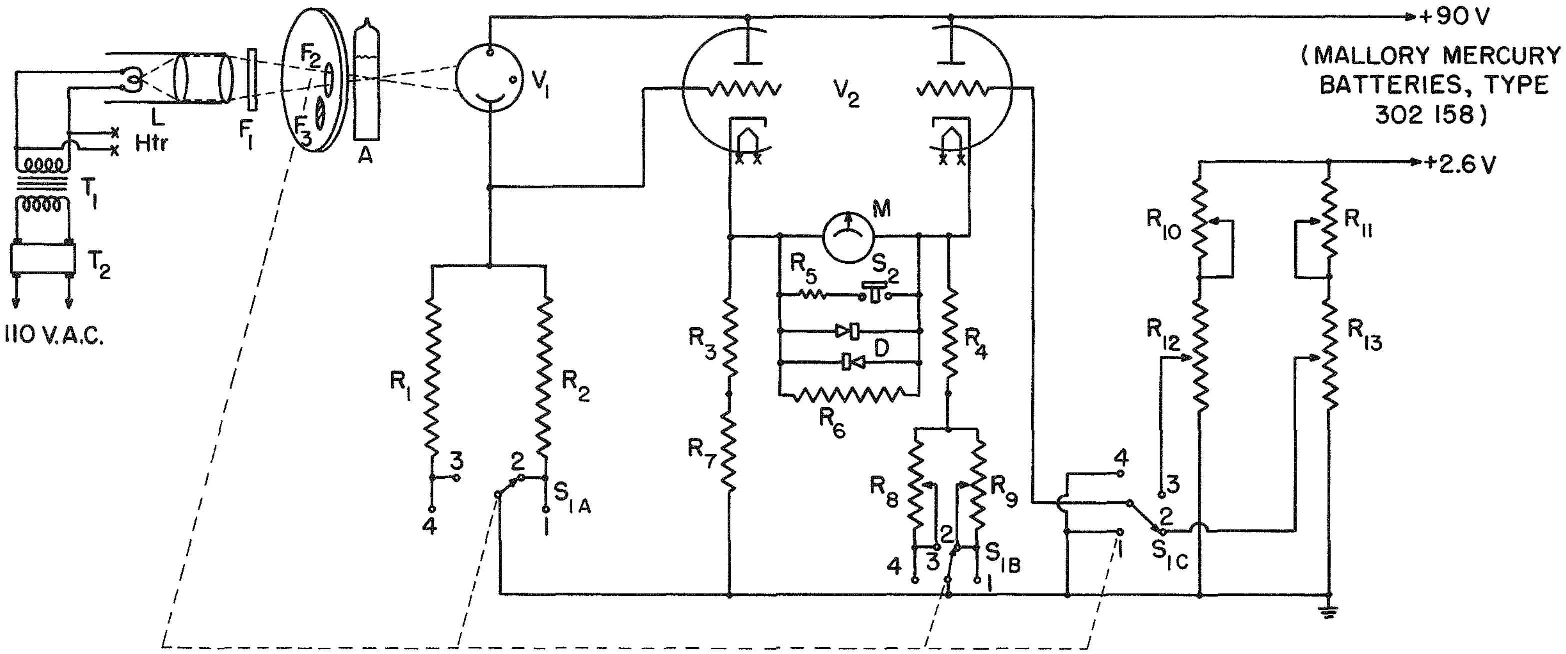
beam emerging from the ampul (contained in the same holder used with the DK) is split by a half-silvered mirror. The beams then pass separately through filters and onto two phototubes. Two detectors were employed in hope that a simple electronic circuit might be devised which could read with good precision the ratios of the photocurrents, and thus R, directly. This problem is still under consideration; however, it is felt that such a modification must not sacrifice precision and must be kept simple to warrant saving a small fraction of the total time required to prepare a dosimeter.

The circuit used (Fig. 2) treats the two circuits (for reading T_A and T_B) separately, as is done in the second model built (Fig. 3). In this reader, the light beam is filtered before passing through the ampul. The ampul is held by a spring clip into a V-shaped compartment on the circumference of a rotating drum; the drum is rotated 90° to move the ampul from loading position into the light beam. A single photocell is used; the rotating filter assembly and electronic circuits are mechanically coupled and switched simultaneously. Two Helipots for reading T_B and T_A are used, both for convenience and for allowing the readings to be quickly rechecked to determine whether drifting has occurred while the settings were being made. The filters chosen are the most satisfactory



A	Ampul
D	1N140 Diodes
F_1	Filter, λ_{max} 430 mμ, Corning 3389 and 5113
F_2	Filter, λ_{max} 555 mμ, Corning 3484 and 4303
L	Microscope Lamp, Spencer, Universal
M	Meter, Null Indicator, Marion Elec. Inst. Co. H-52
N	Mirror, half-silvered
R_1, R_2	10M
R_3, R_4	4.7K, BOC
R_5	1K, BOC
R_6	100 ohms, BOC
R_7, R_8	1K Dual (zero adjust)
R_9, R_{10}	100K (adjusted to requirements)
R_{11}, R_{12}	50K, carbon (100% adjust)
R_{13}, R_{14}	2K, 10-turn Helipots
S_1	Rotary, shorting
S_2	Pushbutton (normally closed)
T_1	6.3 v., 5 a.
T_2	Sola Constant Voltage Transformer, 1 a.
V_1, V_2	929
V_3	5814A

Fig. 2. Diagram of dosimeter reader, Model I.



A	Ampul
D	1N140 Diodes
F_1	Heat Filter, Corning 4600
F_2	Filter, λ_{max} 430 mμ, Corning 3389 and 5113
F_3	Filter, λ_{max} 555 mμ, Corning 3484 and 4303
L	Microscope Lamp, Spencer, Universal
M	Meter, Null Indicator, Marion Elec. Inst. Co. H-52
R_1, R_2	3M (adjusted to requirements)
R_3, R_4	4.7K, BOC
R_5	100 ohms, BOC
R_6, R_7	1K, BOC
R_8, R_9	2K (zero adjust)
R_{10}, R_{11}	100K, carbon (100% adjust)
R_{12}, R_{13}	300K, 10-turn Helipots
S_1	Rotary, shorting (ganged with rotating filter carriage) (Positions 1 and 4 for checking and setting R_8 and R_9)
S_2	Lever, center normally closed
T_1	6.3 v., 5 a., Filament Transformer
T_2	Raytheon Voltage Stabilizer, 1 a.
V_1	929
V_2	5814A

Fig. 3. Diagram of dosimeter reader, Model II.

of those readily available. Several modifications which would probably improve such a reader are obvious.

These readers are now used for all routine measurements. The precision is as good as with the DK, and the time required for a determination is less. The single-detector model is preferred, principally because less chance for operator error is incorporated into the design. The two-detector model requires making final balance for T_B and T_A at a definite time (about 20 to 30 seconds) after positioning a dosimeter, since R changes as the temperature of the ampul increases owing to heating by the unfiltered light source. (Nevertheless, reproducibility is excellent.) Variations in light intensity of the source are minor and slow relative to reading time, or else are transients which can be easily recognized. Owing to the broad spectral bands inherent in filter photometry, T_B, T_A, and R are not the true values as obtained by spectrophotometry; ΔR values, however, are practically the same. Additional considerations are discussed in a later section.

The length of time that elapses between exposure and reading makes little difference with the one-phase dosimeters. With two-phase systems it is important, and the dosimeters should be read at some definite time following exposure. About a day is required for all the acid to be released:

readings have usually been made at 5 hours following exposure, at which time ΔR has almost reached its maximum value. After 1 hour, ΔR has reached about two-thirds of the 5-hour value.

Sensitivity to light is apparent with the low-dose two-phase systems. Significant ΔR is produced if nonbuffered two-phase dosimeters are exposed to room light (fluorescent) for several hours or to outside daylight (not direct sunlight) for a few minutes. This is not of serious consequence, however, since the dosimeters are not affected by making repeated readings if they are kept covered (black cloth, cupboard, etc.) as much as possible. Shelf life of both types is excellent (many months or possibly years) except for the nonbuffered two-phase dosimeters. The lower range dosimeters, however, should be read (R_i determined) as close to time of exposure as practical owing to possible nonsystematic changes caused by leaching of alkali from the tip or other causes. Dosimeters which have drifted abnormally (in either direction) should not be trusted.

With high doses the indicator may bleach. Moderate bleaching merely becomes part of the calibration curve; severe bleaching, however, leads to very peculiar results. Serious damage to the indicator can be prevented (at least to 2×10^6 r) by the inclusion of thiourea. Thus, high-range, one-phase dosimeters are preferably prepared by using this chain-reaction retarder to extend the range rather than by using buffer alone.

Another factor affecting colorimetric evaluation is the discoloration (browning) of the glass caused by high doses of radiation. Moderate browning becomes part of the calibration curve; in severe cases the ampul may be opened and the solution transferred (shaken, centrifuged, siphoned, pipetted, etc.) into another ampul or tube for reading.

When the range of colorimetric evaluation is exceeded, recourse is made to titration methods. Titration is, of course, applicable at any time but is inconvenient compared with photometry. Titration is accomplished, after the solution has been transferred to a suitable container, by the use of standard sodium hydroxide solution (10^{-3}, 10^{-2}, or 10^{-1} *N* as appropriate) which contains the same concentration of indicator as the dosimeters. The end point is determined by visual comparison with solution from a nonexposed dosimeter in a similar container. The end-point determination is rather tedious; small pH electrodes can also be used. An even more convenient way of treating dosimeters with which the colorimetric range has been exceeded is to add definite amounts of standard base (containing indicator) until the color can obviously be read photometrically. The dose is calculated as the sum of the doses indicated by the colorimetric calibration curve plus the dose equivalent to the amount of base added. Equivalent amounts of data are required for calibration in all cases. Total doses much greater than 10^6 r have not been used in these studies; colorimetric performance was still satisfactory in this region.

A Co^{60} source(p) was generally used for calibration. Typical calibration curves were shown in Figs. 1a and 1b, and the composition of dosimeters for various ranges was given in Tables I and II.

The one-phase dosimeters give the same response with X rays(q) as with Co^{60} gamma rays, and their response under various shielding conditions (Lucite, lead, etc.) is the same as a Victoreen chamber similarly shielded. The two-phase system, however, is energy dependent at these X-ray energies. With no shielding, the response is approximately twice as great as produced by the same dose of Co^{60} gamma

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(p) This source (about 120 curies), housed in a large, wooden building to minimize radiation scattering, was calibrated with Victoreen Co^{60} thimble chambers which had been checked by the National Bureau of Standards.

(q) A Thoraeus II filter was used with 250-kvp X rays, which provided an effective energy of 200 kev.

rays. By shielding with 0.5 mm of lead, the response is reduced such that the indicated air dose is apparently correct. This is misleading, however, since the two-phase and the one-phase dosimeters cannot produce the same result under these conditions. Either system can be calibrated for a given set of conditions; the one-phase dosimeters should be chosen if possible when low energies are involved. The point at which the two-phase dosimeters become energy independent is not yet known, but must lie above 200 kev. Both systems are energy independent toward gamma radiation from Co^{60} (1.1 and 1.3 Mev), the Los Alamos Water Boiler (4 Mev), and the Godiva II critical assembly (4).

The responses of these dosimeter systems to neutrons will be the subject of a report to be published in the near future; however, a few qualitative observations follow. Both the one-phase and two-phase dosimeters are very sensitive to thermal neutrons. Therefore, lithium shielding is used when necessary. The two-phase system may have a response of several per cent to fast neutrons. The one-phase dosimeters produce about one-third as much acid from 1 rad of fast neutrons (fission spectrum, Godiva II critical assembly) as is produced by 1 rad of gamma radiation.(r)

(r) The discrepancy between this value and the value of 0.50 found by Sigoloff (2) has not yet been resolved.

Preliminary experiments with monoenergetic neutrons indicate that the one-phase system may not be energy independent toward fast neutrons. Dose-rate dependence has been observed for both systems at 10^8 rads per second, which results in the measured dose being approximately 9 per cent low. High doses of mixed radiation, which cause browning of the glass ampul, necessitate transfer of the solution to another container for reading, since the amount of discoloration produced by neutrons is different from that produced by gamma rays.

CHAPTER 4

EFFECTS OF INDIVIDUAL COMPONENTS

4.1 Indicators and Photometric Considerations

Examples of several types of dosimeters designed to cover various dose ranges were given in Tables I and II. The sensitivity of both one-phase and two-phase dosimeters can be varied in several ways. One component which is common to both systems is the indicator solution. The two indicators which have been used in this study are chlorpenol red (CPR, dichlorophenolsulfonphthalein) and phenol red (PR, phenolsulfonphthalein). These indicators have absorption maxima which are well separated with respect to wave length, have good visual characteristics, and cover satisfactory ranges of pH with good sensitivity. Chlorphenol red, which has a useful pH range of about 6.2 to 5.2, has been used in all cases except for the carbon dioxide-free one-phase system. This latter type is designed to provide increased sensitivity in keeping the concentration of buffering materials (including carbon dioxide) to a minimum and by using a pH range near neutrality, for which PR (pH range about 7.6 to 6.6) is well suited. Since these indicators are organic weak acids, they themselves function as buffers; however, at the dilute concentrations employed, this effect must be small.

The concentration of indicator is important, however, with respect to the effect on the spectral ratio and the consequent slopes of the response curves (e.g., ΔR versus dose). Deciding what is the optimum concentration is somewhat arbitrary, since the effect is not nearly so evident as the effects of other variables to be discussed later. Representative data are shown in Figs. 4a, 4b, 4c, and 4d. The solutions were contained in 7-mm ampuls.

From the indicator-concentration curves it might appear that the highest concentration of indicator should be used for the greatest relative change. However, the precision of reading low transmittances is not good. For most spectrophotometric procedures, the error curve has a minimum in the region of 20 to 60 per cent transmission; the optimum for filter photometers depends on the particular instrument. The transmittance of one or the other of the two bands at the highest concentration (10^{-4} $\underline{M}$) is much less than 10 per cent over most of the range. The solutions at 5×10^{-5} $\underline{M}$

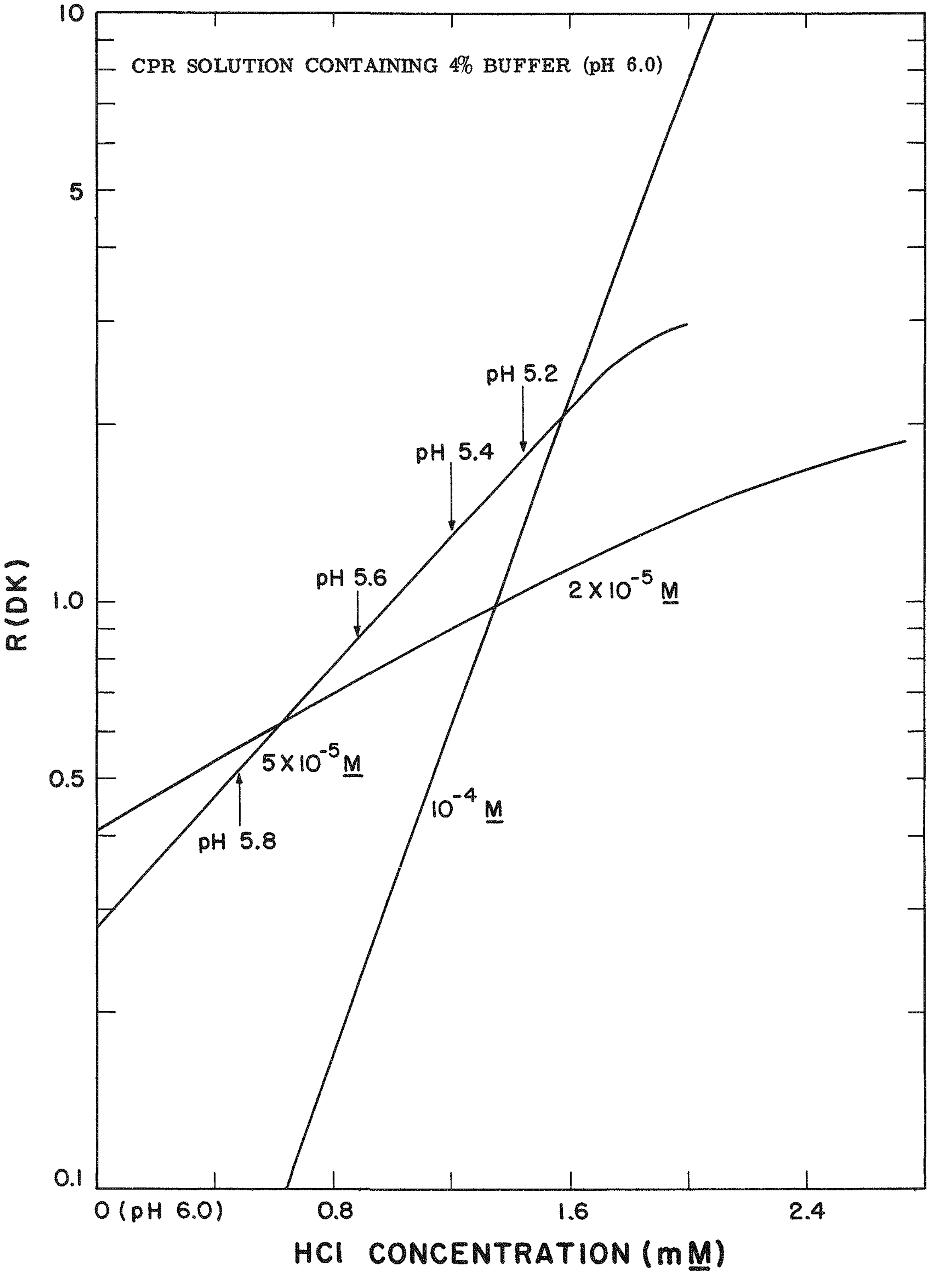

Fig. 4a. Effect of CPR indicator concentration on spectral ratio (Beckman DK-1).

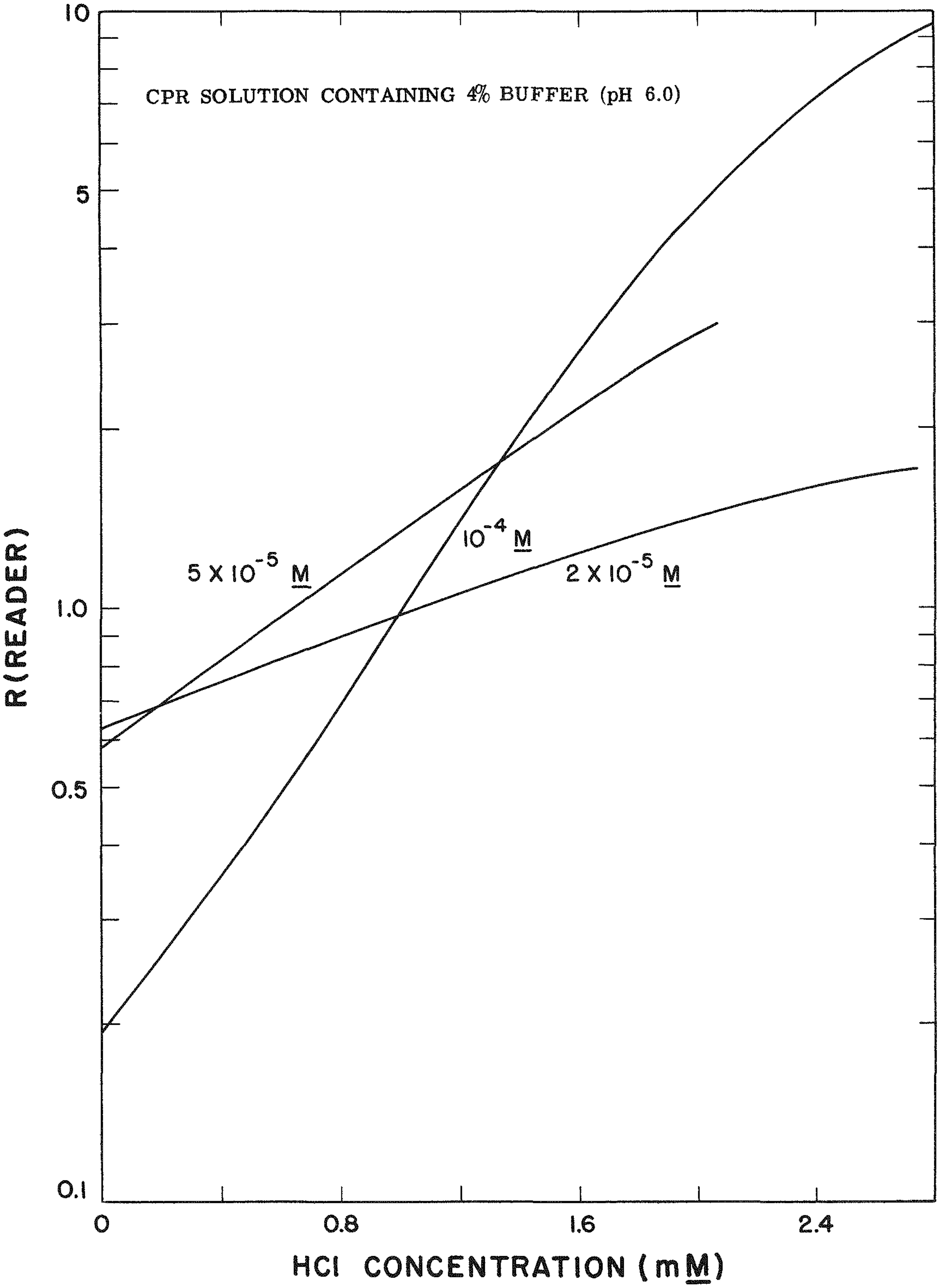

Fig. 4b. Effect of CPR indicator concentration on spectral ratio (reader).

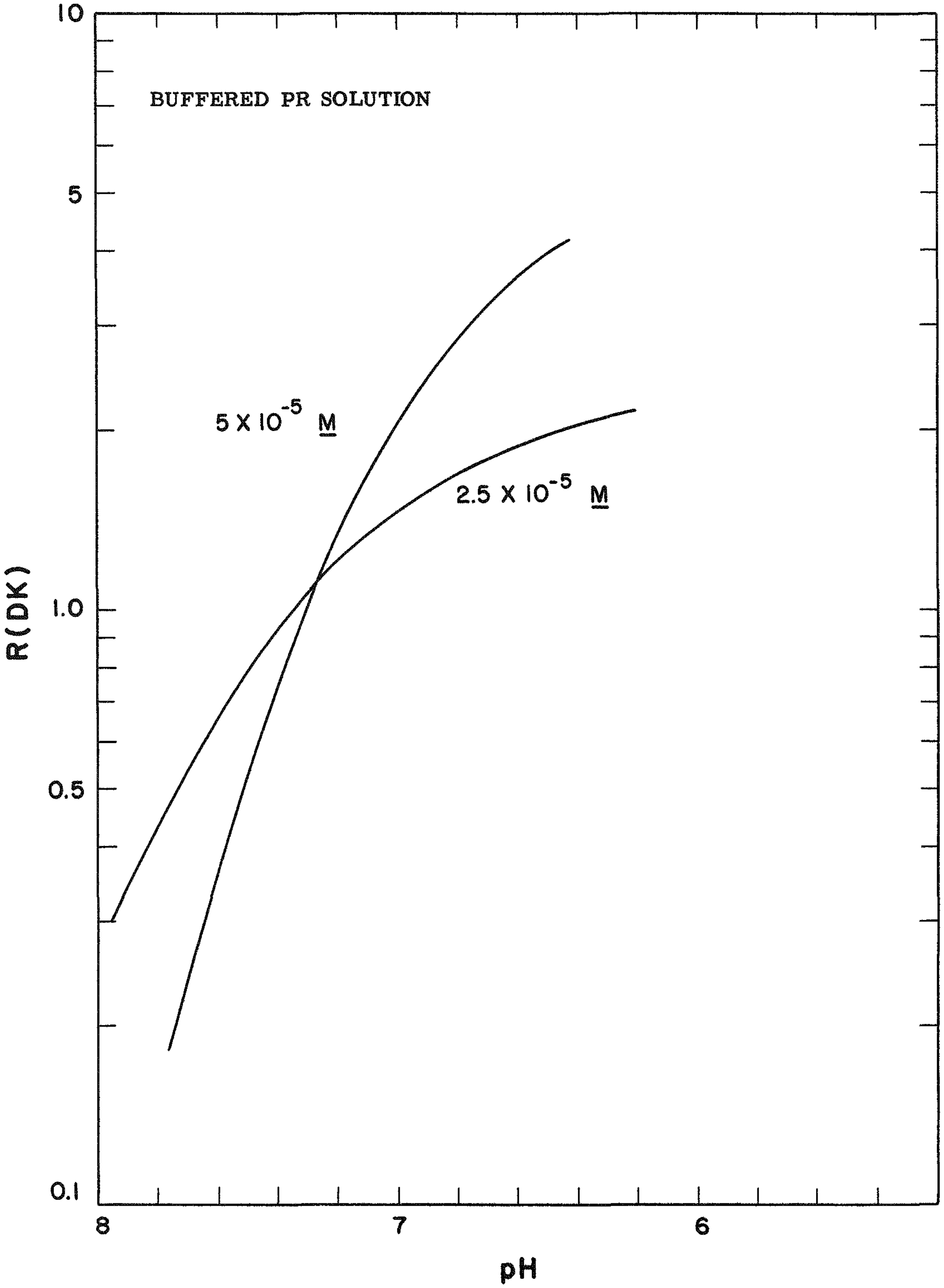

Fig. 4c. Effect of PR indicator concentration on spectral ratio (Beckman DK-1).

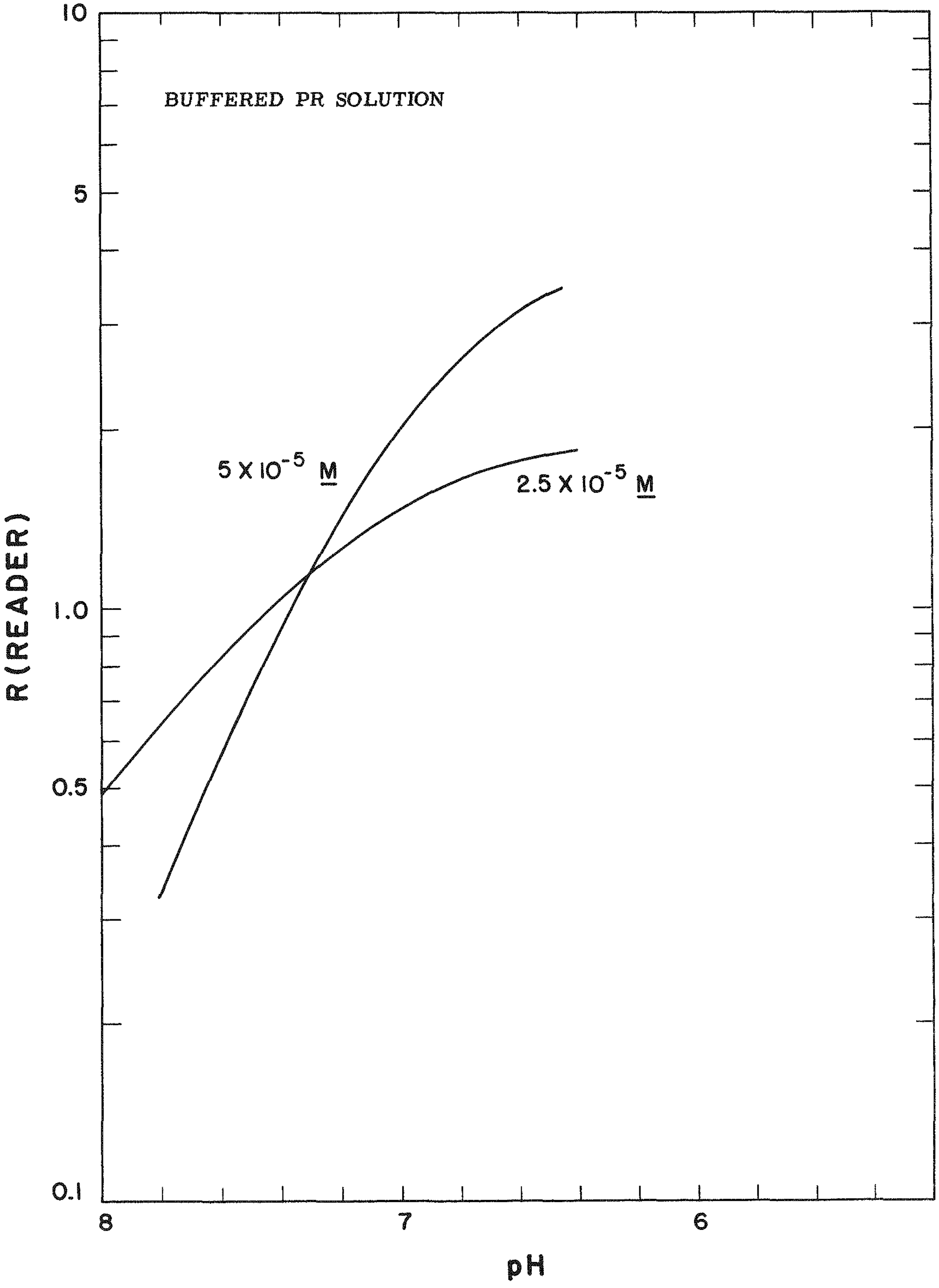

Fig. 4d. Effect of PR indicator concentration on spectral ratio (reader).

transmit in the 20 to 60 per cent range. At the lowest concentration, 2 x 10^{-5} M, transmittances are in the 30 to 70 per cent range (not too high for accuracy, but sensitivity is not so great). If a filter photometer is used, the effect of concentration of indicator on sensitivity should be evaluated for the particular type of instrument (the Beer-Lambert law is not strictly applicable). The curves in Figs. 4a, 4b, 4c, and 4d also afford comparison of data from the DK and from the reader.

The sensitivity is dependent on R_i, as illustrated for small differences in Figs. 1a and 1b. Generally, with CPR indicator the starting pH is approximately 5.9; for greater sensitivity (greater $\Delta R/r$), a lower initial pH can be used. For the low-dose two-phase dosimeter (Table II), the starting pH was about 5.4. This, of course, shortens the range. Conversely, longer range can be obtained with decreased sensitivity at the lower doses by using smaller R_i.

Variations in R and consequently ΔR, caused by differences in ampul diameters, are not serious; comparisons of buffered indicator solutions at various R in ampuls varying from 7.0 to 7.4 mm in diameter indicated only a small effect well within the experimental error of dose determination. Ampuls might advantageously be grouped according to size if better positioning in the reader carriage results.

4.2 Buffer

The photometric range of any type of dosimeter can be extended by buffering the aqueous indicator solution. Although the addition of a retarder (see Sec. 4.3) effectively decreases the response, buffer is advantageous (particularly with medium-range dosimeters). One benefit from buffer, which in practice becomes quite important, is masking the effects, such as acid produced in sealing.

An almost linear relationship exists (over the range investigated) between buffer concentration and the amount of acid required to produce a given change in the spectral ratio. In Fig. 5a, buffer concentration is expressed as per cent of MacIlvaine's pH 6.0 buffer and the effect on sensitivity in terms of the quantity of acid necessary to change the spectral ratio (reader) from 0.5 to 1.0. The same data are plotted in a different manner in Fig. 5b. The sensitivity is expressed relative to a nonbuffered solution. For example, sensitivity is reduced to 10 per cent by the addition of 0.8 per cent buffer, or alternatively the range is extended by a factor of 10. It should be noted that the range for titrimetric evaluation is not affected by buffer.

The buffer does not affect the radiation sensitivity of one-phase dosimeters, i.e., the amount of acid produced per rad. The same type of curves as in Figs. 5a and 5b could

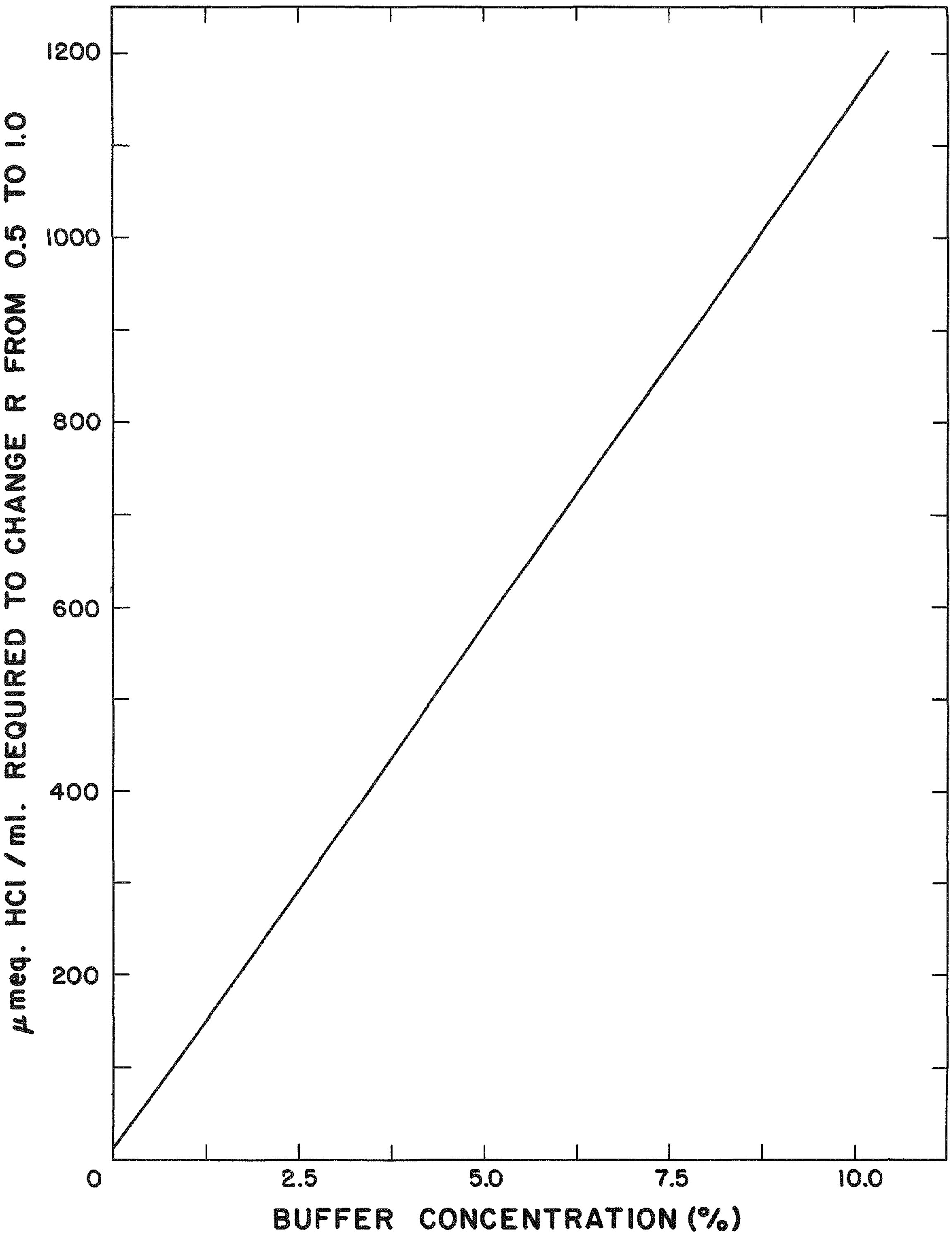

Fig. 5a. Effect of buffer concentration on sensitivity.

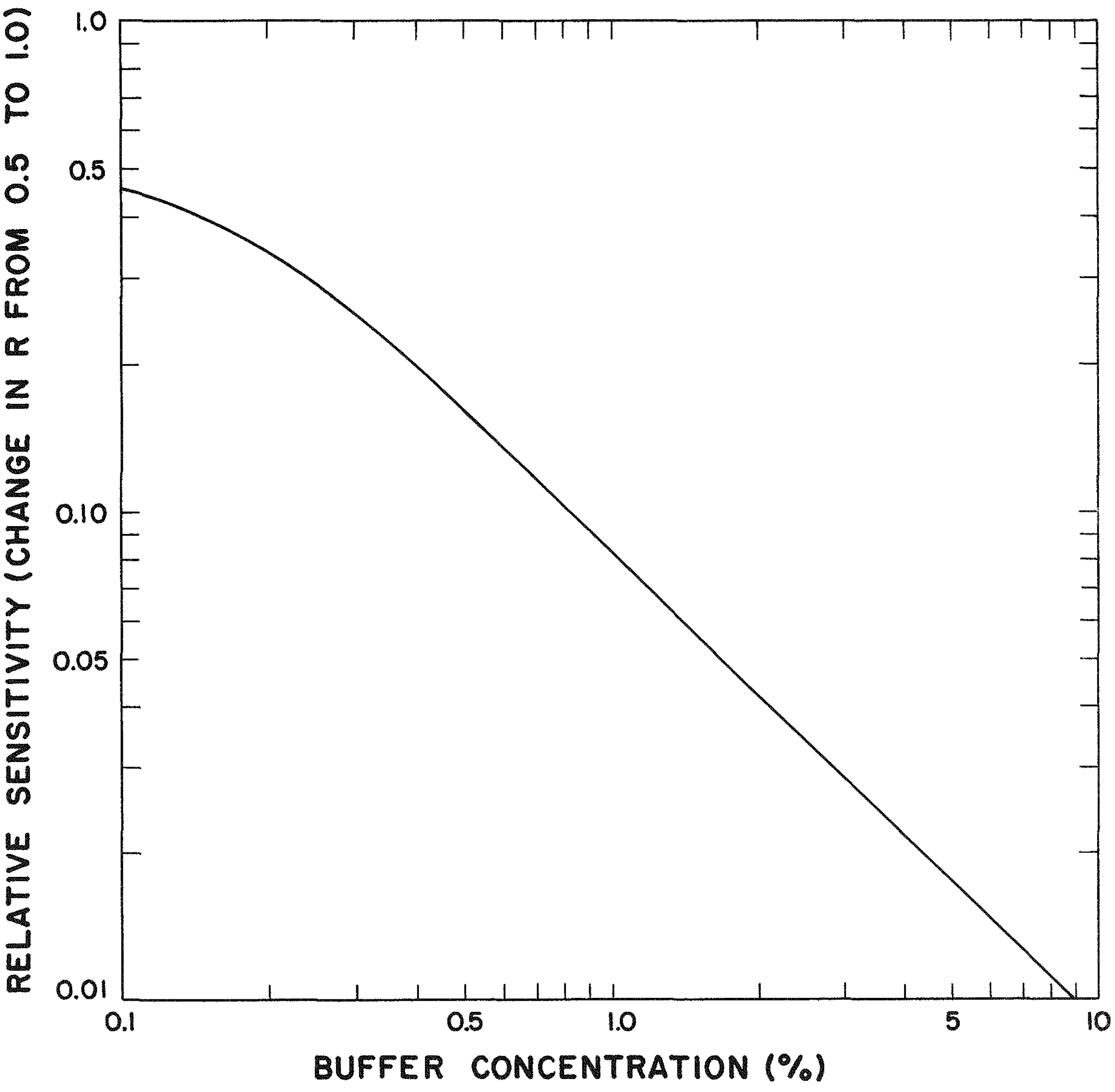

Fig. 5b. Effect of buffer concentration on sensitivity.

have been obtained by using radiation to produce the acid instead of adding it directly as hydrochloric acid. This has been verified experimentally for a number of points. An additional effect of buffer on high-range two-phase systems has been noted, i.e., a greater decrease in sensitivity is found than can be attributed to buffering action alone. This has not been further investigated.

4.3 Chain-Reaction Retarders

By the addition of a solute which interferes with and effectively terminates the chain-propagation step in the acid-producing reaction initiated by radiation, the sensitivity of the system is reduced.

With one-phase dosimeters, thiourea has been found to be a convenient water-soluble retarder. Figure 6a shows the effect of thiourea concentration on the relative dose required to change the spectral ratio (reader) from arbitrarily 0.6 to 0.8. The same data are plotted in a different manner in Fig. 6b. Thiourea concentrations greater than 0.4 per cent (0.053 M) were not investigated. The radiation yield of acid $[G(H^+)]$ has been reduced from 25 with no thiourea to less than 2 with 0.4 per cent thiourea. In the PR carbon dioxide-free system, 0.005 per cent resorcinol was tried in one instance and the sensitivity was reduced by a factor of about 5.

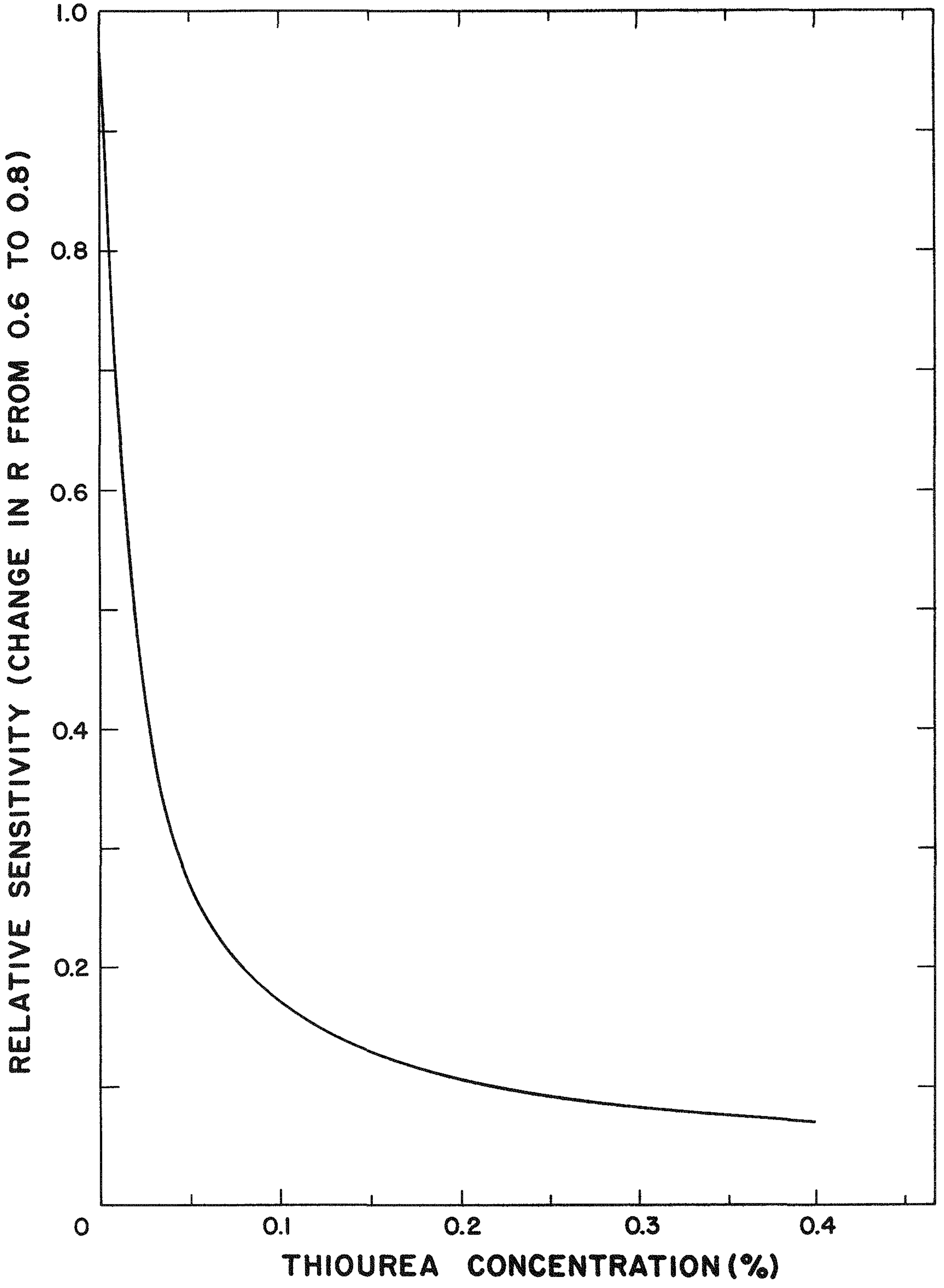

Fig. 6a. Effect of thiourea concentration on sensitivity.

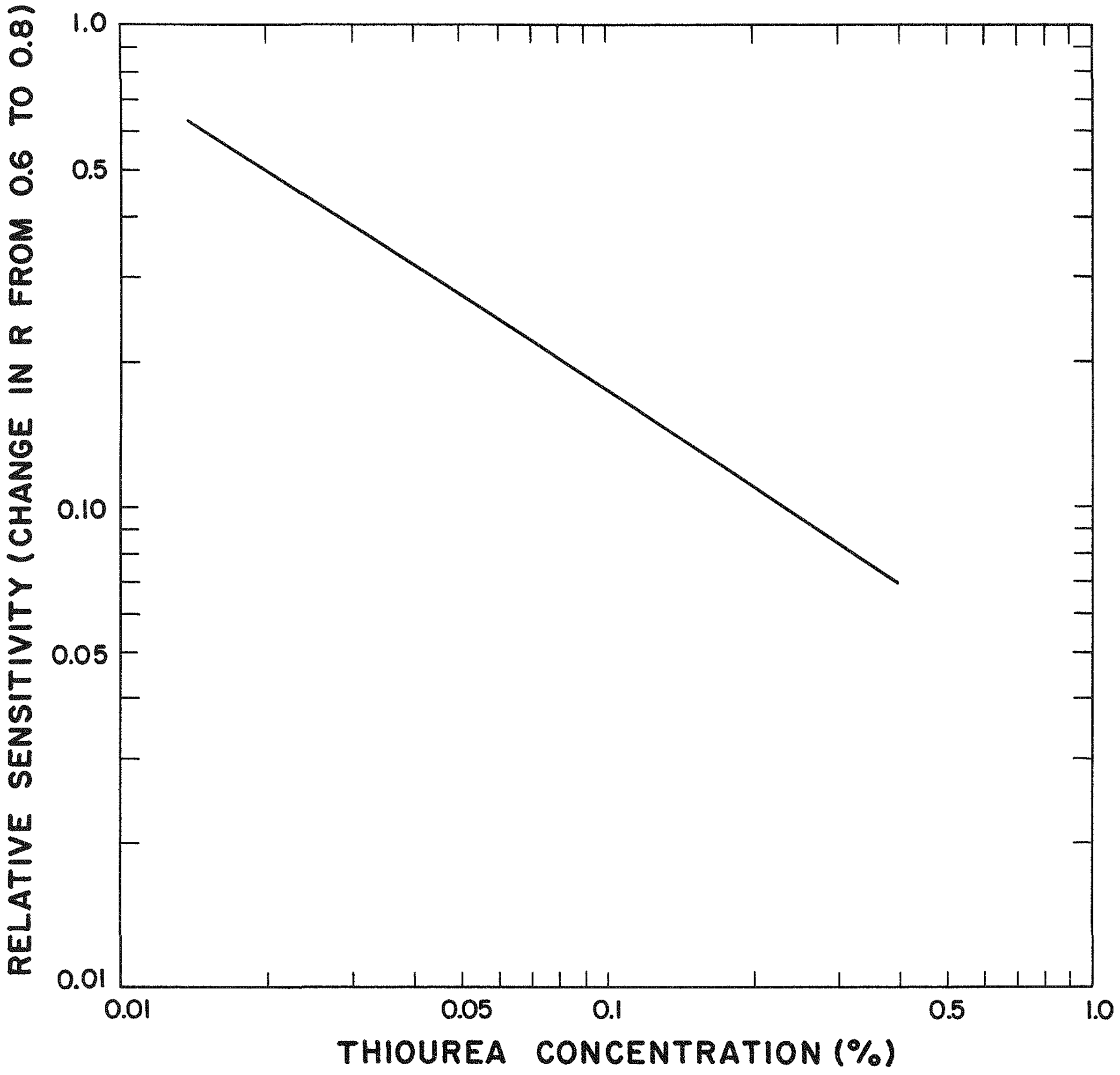

Fig. 6b. Effect of thiourea concentration on sensitivity.

In addition to decreasing the acid yield, thiourea also decreases the radiation yield of other products (e.g., oxidizing agents). At high doses decomposition of the indicator (as evidenced by bleaching or a pale blue-violet color) has been noted when thiourea was not present. Such effects make photometric evaluation impossible eventually. Thiourea has been successfully used to prevent bleaching of the indicator solution at doses of greater than 10^6 r.

In the two-phase systems, the radiation-induced reaction of interest occurs in the lower tetrachloroethylene phase; the upper aqueous phase merely serves as an indicator of this reaction. 2,6-Di-tert-butyl-p-cresol (DBC), which is insoluble in water, is dissolved in the tetrachloroethylene (T_4CE) as a chain-reaction retarder. This addition is necessary to make the system reproducible, dose-rate independent, and relatively stable to heat and light (2). The effect of DBC concentration was examined briefly. For T_4CE containing 0.2 per cent Ionol, $G(H^+) \cong 17$. Very little effect on sensitivity was noted using concentrations of 0.005, 0.01, 0.05, 0.1, 0.2, 0.5, and 1.0 per cent. The lowest concentrations afforded slightly more sensitivity with more scatter in the data. The two highest concentrations appeared equivalent and decreased the sensitivity to about three-fourths of that for 0.2 per cent concentration. The effects on dose-rate dependence and thermal and light stability were not further investigated.

Bleaching of the indicator can be encountered also with the two-phase systems at high doses. The addition of 0.2 per cent thiourea to the indicator solution (thiourea is insoluble in T_4CE) readily overcomes this difficulty, at least to doses of 2×10^6 r. Thiourea does not affect the sensitivity of the system, i.e., it exhibits no noticeable buffering action on the indicator solution nor does it affect the acid yield from the lower phase. Thiourea also suppresses acid formation, if any, in the upper phase caused by proton recoils from fast-neutron interactions with water. "One-phase dosimeters" were prepared from T_4CE-saturated water. The response was found to be one-sixth as great as the analogous T_3CE (conventional one-phase) dosimeters. For example, a dose of about 20,000 r is required to produce a ΔR of 0.1 in nonbuffered upper phase, which contains 0.2 per cent thiourea. This represents approximately 0.1 per cent of the yield from the lower phase.

4.4 Trichloroethylene Concentration

The equilibrium concentration of T_3CE in water was found, by the Fujiwara pyridine-alkali method (5), to be 0.7 mg/ml. This concentration is essentially independent of temperature from 25 to 40°; it is greater by almost a factor of 2 at 10°. The rate of saturation of water with excess T_3CE appears to be quite rapid, as a few hours (probably less) are sufficient.

Surprisingly, the radiation sensitivity is the same within experimental error for dosimeters prepared from solutions completely saturated, 75 per cent saturated, and 50 per cent saturated with T_3CE. This is fortunate, since it practically eliminates concern over time and temperature of saturation.

4.5 Ratio of Phase Volumes

This is probably the simplest way to effect rather limited changes in the dose range of two-phase dosimeters. The sensitivity is directly proportional to the ratio of the volume of lower phase to the volume of upper phase. For example, a 4:1 ratio is four times as sensitive as a 1:1 ratio.

CHAPTER 5

CONCLUSION

Satisfactory preparation of these types of chemical dosimeters is largely a matter of perfecting techniques. The effects on sensitivity produced by varying the components can be predicted so that dosimeters covering particular dose ranges can be readily prepared. For measurements of dose from gamma (only) sources, the one-phase system is preferred, particularly if low-energy radiation is present. In a mixed-radiation field, the fast-neutron insensitivity of the two-phase system makes it valuable for measurement of dose from the gamma component. Both systems offer good shelf life, dose-rate independence, stability toward heat and light, and availability in mass-produced quantities.

Investigations in progress or planned for the near future at this Laboratory include:

1. determination of the response of both systems to

thermal neutrons, degraded fission neutrons, and monoenergetic fast neutrons;

2. evaluation of chemical dosimeters for use in depth-dose studies;

3. trials of similar modified systems to obtain increased sensitivity, particularly for fast neutrons;

4. fundamental investigation into the radiation chemistry involved in these systems.

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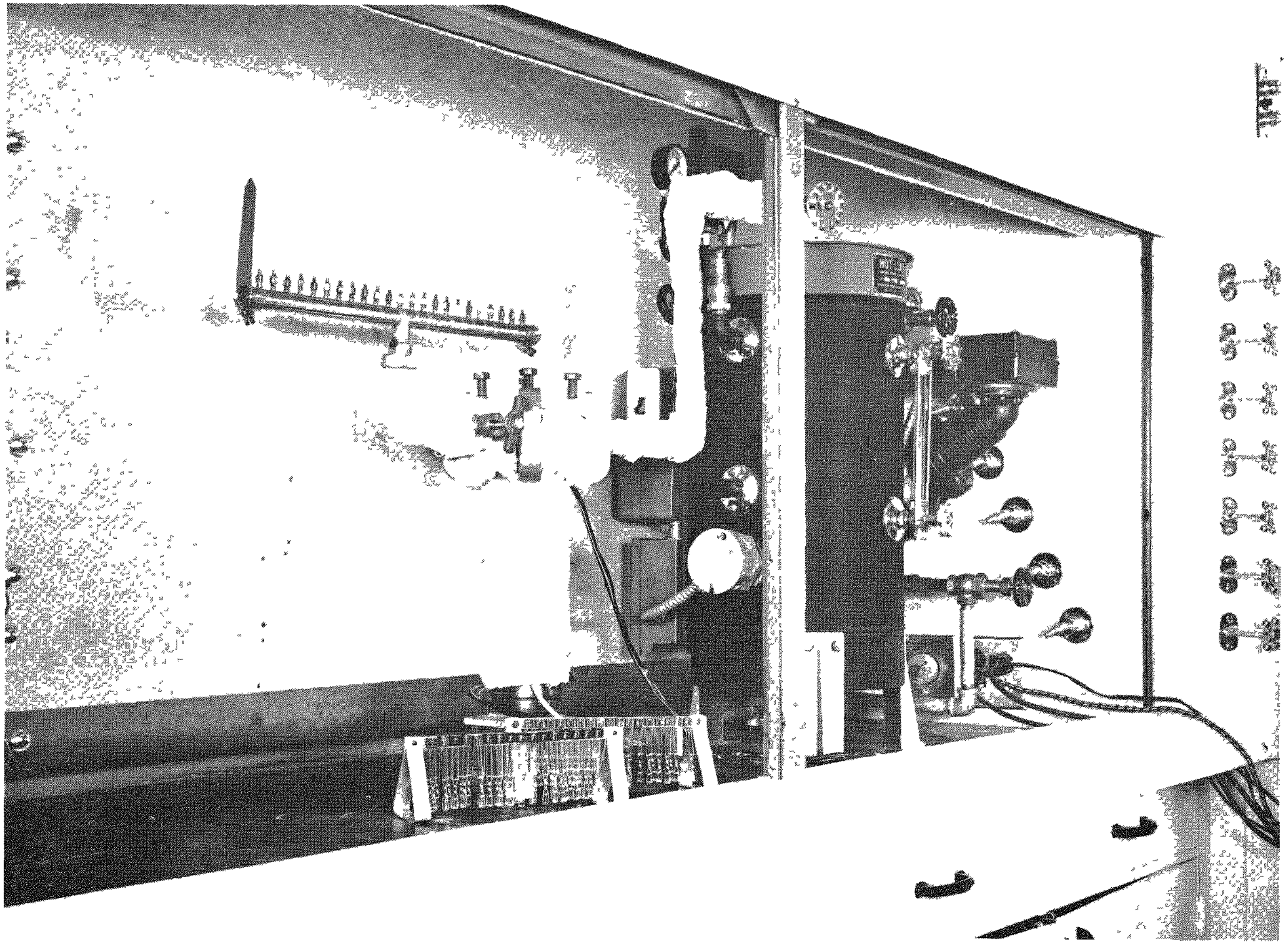
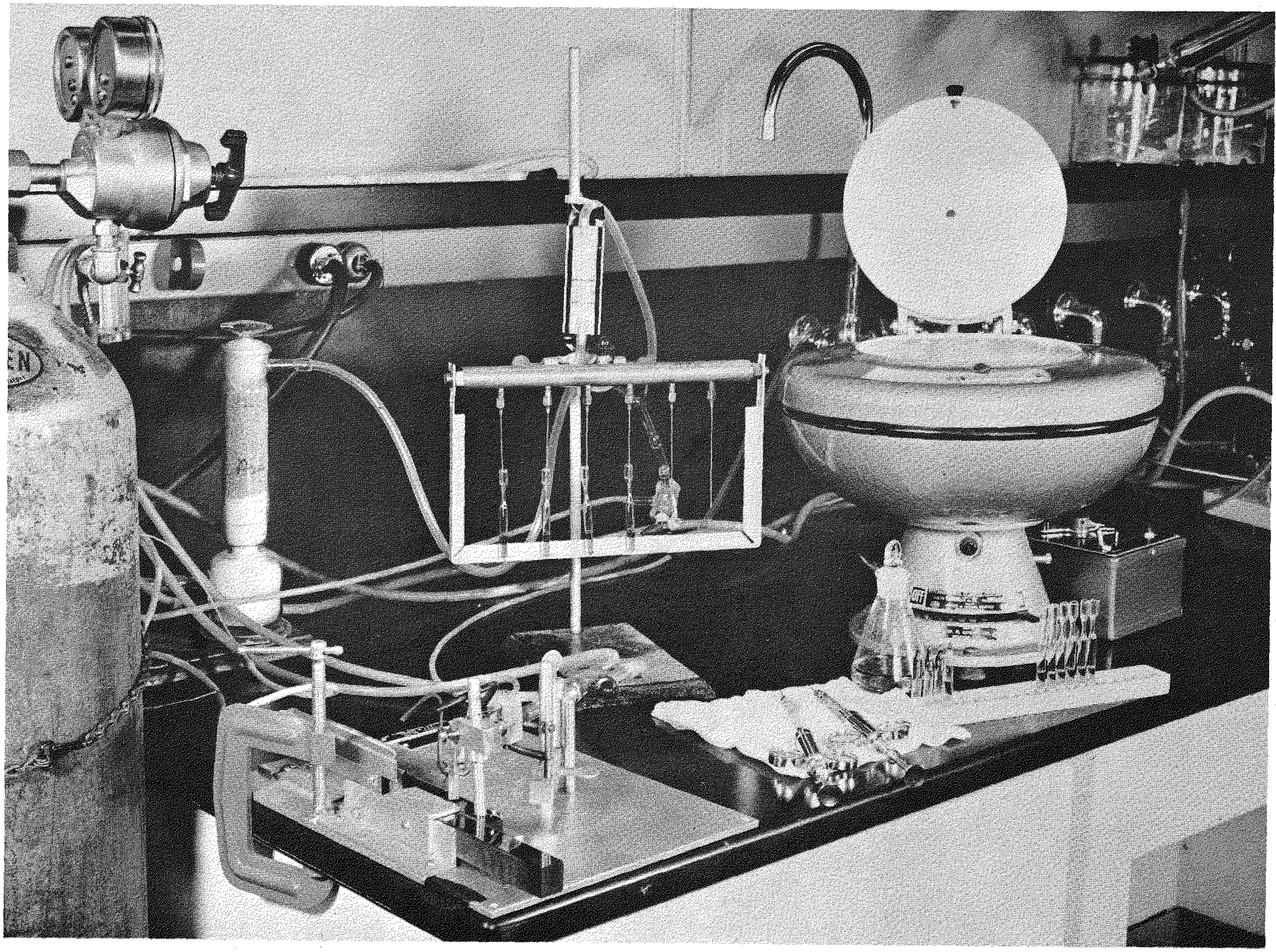
APPENDIX

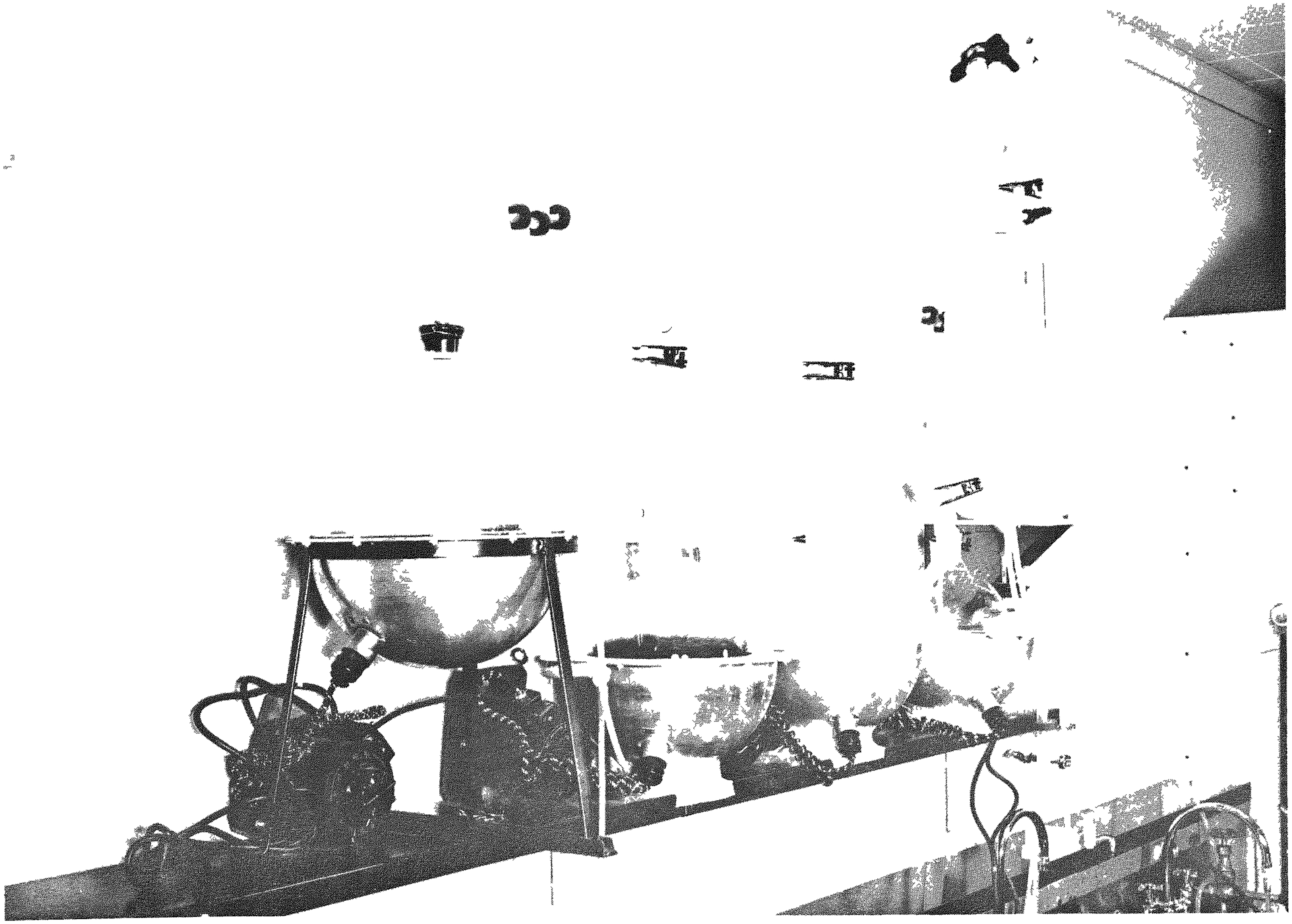
The following photographs illustrate some of the equipment and apparatus used in this study.



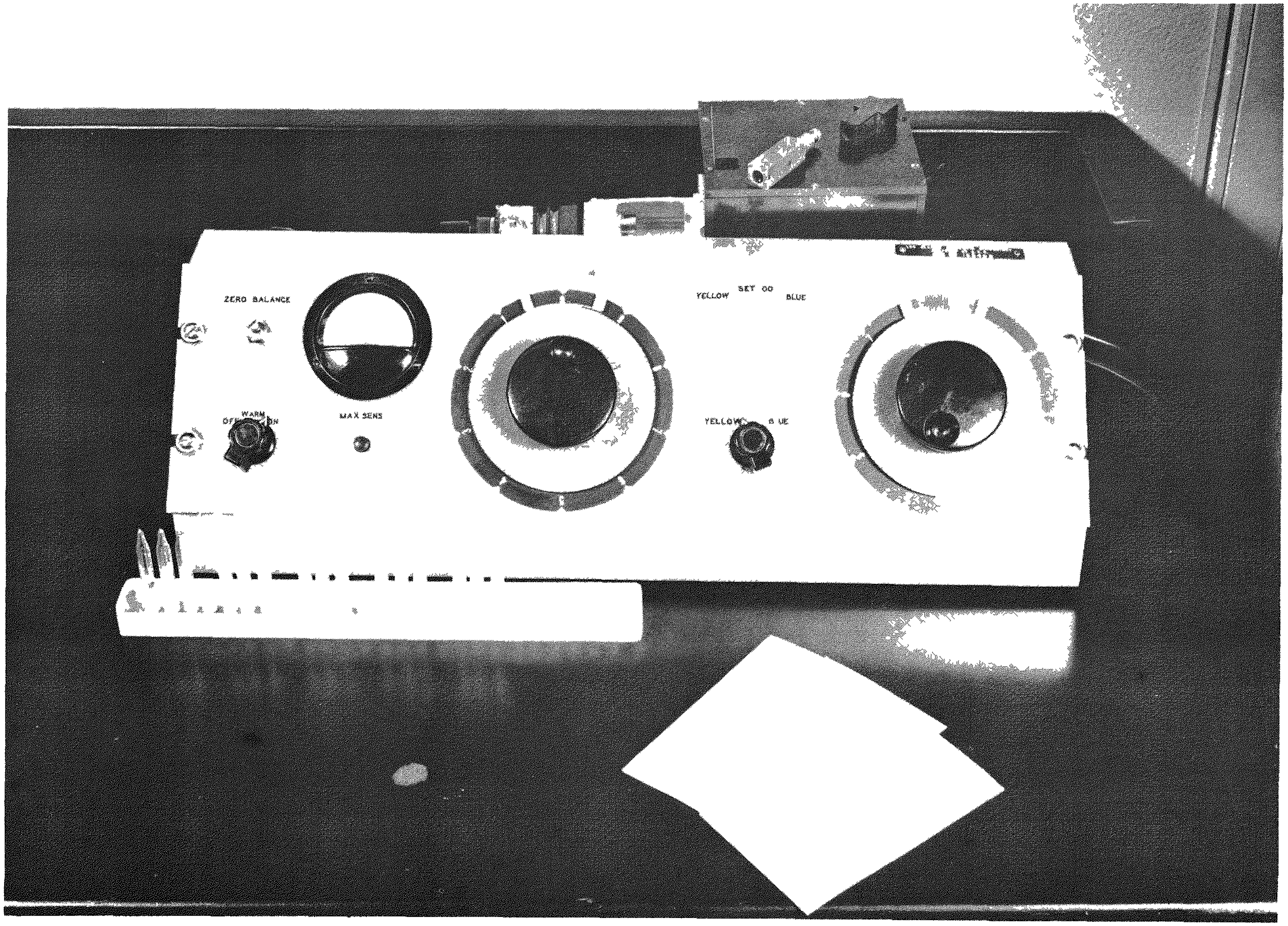
A.1 Steam-cleaning facility.



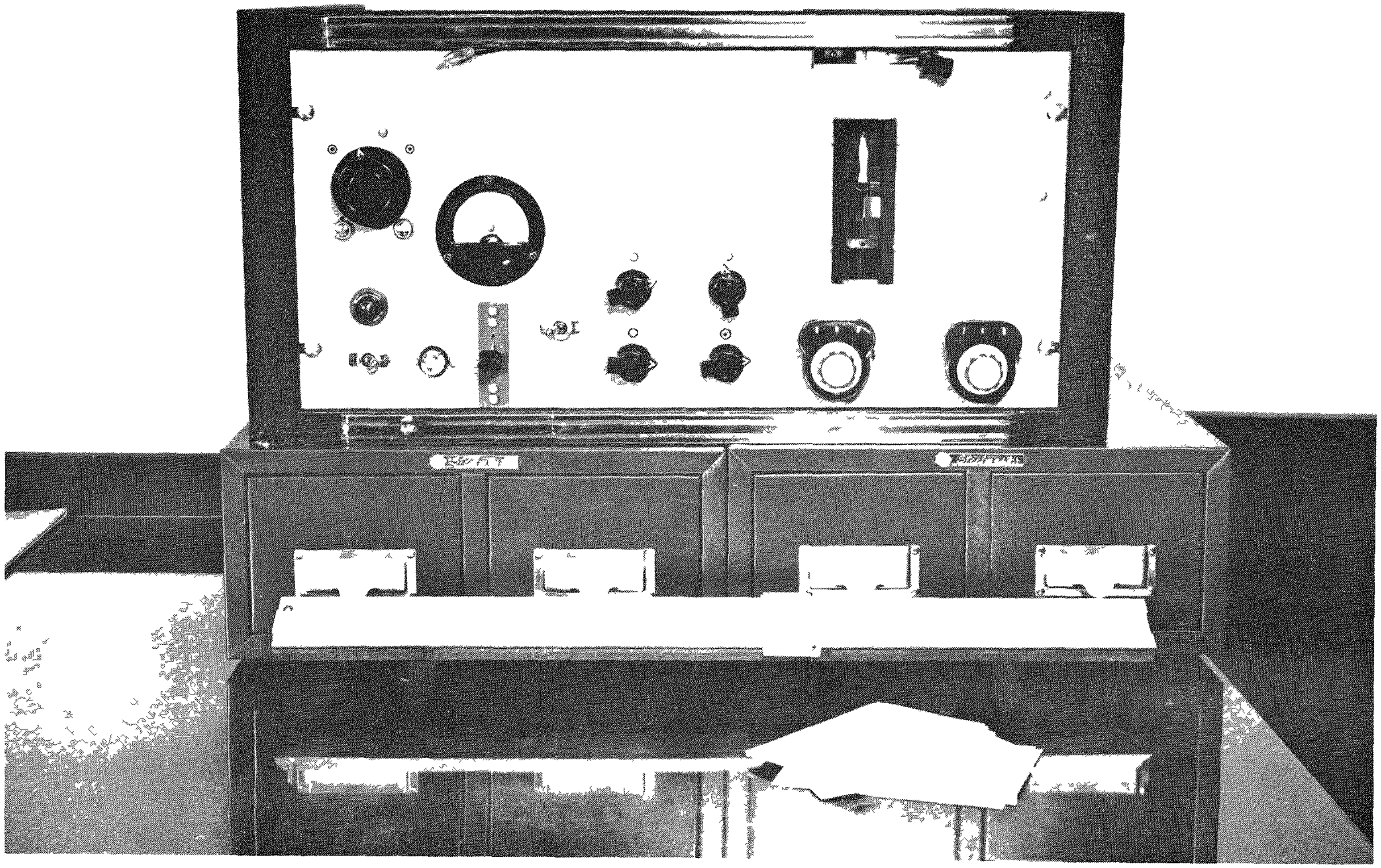
A.2 Ampul sealer and flushing manifold.



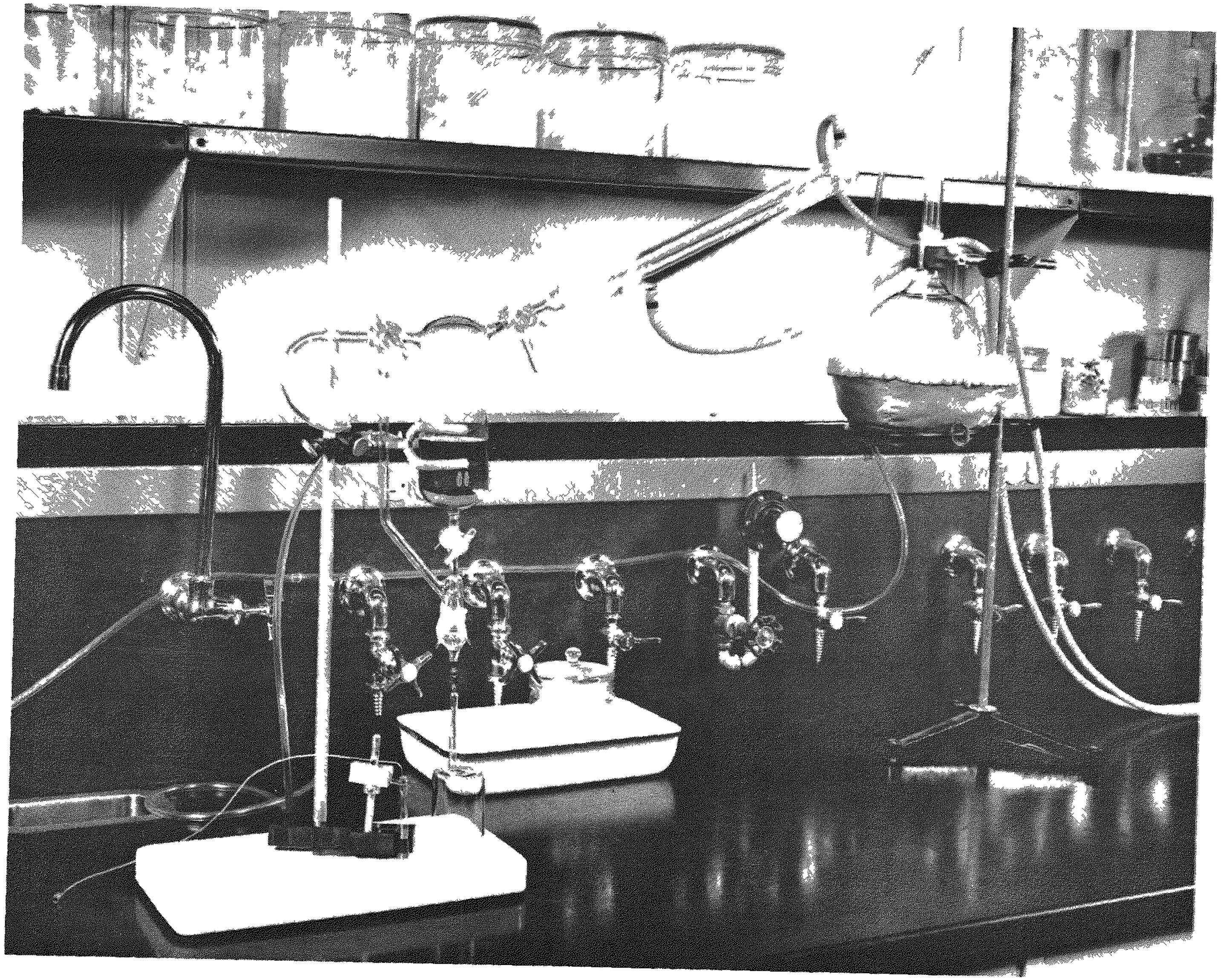
A.3 Water-distillation apparatus.



A.4 Dosimeter reader, Model I.



A.5 Dosimeter reader, Model II.



A.6 Apparatus for preparing carbon dioxide-free dosimeters.