The observed mobility ranges for the chief electrophoretic components of plasma and its fractions, as studied under conditions standard for control of large-scale fractionation, fall into two classes: (1) components poor in lipoids, whose characteristic mobilities appear independent of conditions of fractionation, degree of purity and usual conditions and duration of storage; (2) components rich in lipoid whose characteristic mobilities vary with these factors, generally toward increasing negativity, thus yielding overlaps of mobility range with components of the first class.

The small variations of apparent electrophoretic distributions of normal human plasma pools under standard analytical conditions is indicated in a series of analyses carried out over a period of years in potassium phosphate at pH 7.7 and sodium diethylbarbiturate at pH 8.6. Comparisons with apparent distributions in other buffers less useful for fractionation control are given.

Specific refractive index increments of electrophoretically separated albumin and γ-globulin have been found to approach with increasing electrophoretic homogeneity the increments for these components as separated chemically.

Conversion factors (based on refractive index increments in terms of weight of dried protein) have been computed for the chief electrophoretic components in plasma and the major fractions. When applied, together with corrections based on nitrogen factor differences and on deviations of apparent distributions from true relative concentrations in mixture studies, in revision of schlieren data for a second approximation of the distribution of components in plasma and fractions, the internal consistency of the results has proved little better than when unrevised apparent distributions obtained under standard conditions are used. Two factors appear chiefly responsible: uncertainties in diagram resolutions of components comprising molecular species of considerable mobility spread, together with changes of apparent distributions resulting from slight mobility changes with processing.

The principal value of the electrophoretic method in the control of fractionation has been its use in quantitative first approximation: (a) for revealing gross differences of apparent distributions with variation in conditions of fraction separation, and (b) as a rapid empirical control of uniformity of successive separations under constant conditions.

Specialized indications for the use of corrected electrophoretic diagrams in clinical and biological investigation are given.

BOSTON, MASS.   RECEIVED AUGUST 26, 1946

A Photoelectric Instrument for Comparing the Concentrations of Very Dilute Aerosols, and Measuring Low Light Intensities[1]

BY FRANK T. GUCKER, JR., HUGH B. PICKARD[2] AND CHESTER T. O'KONSKI

A study of aerosols and their filtration requires a rapid and sensitive method of measuring aerosol concentration. Under usual working conditions, the most penetrating aerosols, liquids of 0.3 micron (μ) diameter, are used at about 100 micrograms (γ) per liter. Coarser particles impinge upon the filter fibers because they cannot follow the sharply-bending flow lines, while finer particles diffuse to the fibers more rapidly because of their Brownian movement. Smokes much over 100 γ per liter coagulate rapidly and tend to clog the filter. Direct weighing or chemical methods require excessively long test periods. However, the optical effect of smokes, first noted by Michael Faraday,[3] and studied by John Tyndall,[4] yields a rapid and sensitive measure of the concentration of a colloidal system. Richard C. Tolman and Elmer B. Vliet,[5] described a Tyndall-meter employing visual measurement of the light scattered at right angles to the Tyndall beam. They showed that this light is proportional to the concentration of ammonium chloride smoke, from 1000 to 5 γ per liter, the lowest concentration they studied.

Recently, Victor K. LaMer and David Sinclair, working under the National Defense Research Committee at Columbia University, developed an elegant apparatus for observing the light scattered at small forward angles, which is much more intense for particles of 0.3 μ diameter than that scattered at right angles. Dr. Sinclair[6] states that he could detect the light from a dioctyl phthalate (DOP) smoke at 0.001 γ per liter. However, at this concentration the field of view contains so

(3) M. Faraday, Proc. Roy. Soc. (London), 6, 356 (1857).
(4) J. Tyndall, Phil. Mag., [4] 37, 384 (1869).
(5) R. C. Tolman and E. B. Vliet, THIS JOURNAL, 41, 297 (1919).
(6) Private communication.

few particles that it is not uniform, and the measurements are difficult even for a skilled and experienced operator.

Another instrument designed for the measurement of smoke-filter penetration, developed by B. Vonnegut and D. W. Beaumont of the CWS Development Laboratory at Massachusetts Institute of Technology (M.I.T.), employed small forward-angle scattering in each of two identical smoke cells, one containing raw smoke, and the other filtered smoke. A photometric cube brought the light from the two cells into a single field of vision, adjusted to uniformity by means of an optical gradient calibrated directly in per cent. penetration, and additional optical filters of 0.1, 0.01 and 0.001 transmission. The instrument has the advantage of ruggedness, simplicity and portability, but visual comparisons are tedious and quite inaccurate. Under optimum conditions individual readings vary by as much as 10% and a series of readings is required for 5% accuracy. The limit of sensitivity of the instrument which we tested was about 0.05%, chiefly due to stray light in the effluent smoke cell, which could not be reduced below that value.

The difficulties of visual comparison can be avoided by using a photoelectric cell and suitable electronic circuits. In 1937, A. S. G. Hill[7] developed such an apparatus to measure the efficiency of commercial smoke respirators. A beam of light, traversing a 50-cm. smoke cell, was focused on a photocell. The photocurrent was amplified by a thermionic vacuum tube with a conventional null-type balanced plate circuit, containing a calibrated resistor and a galvanometer with a sensitivity of 1500 mm. per μ amp. The scattering and absorption of the carbon test smoke, consisting of particles with an average diameter of 0.16 μ, at a concentration of 25 γ per liter, reduced the light on the photocell by about 9%, and the resulting change of plate current was balanced by a change in the plate resistor. The small absorption of the filtered smoke was read directly from the linear galvanometer deflection, sensitive to 0.02% penetration, or 0.005 γ per liter.

In February and March, 1942, the Physics Division of the Kimberly–Clark Corporation developed for the CWS a tester for sheets of smoke-filter paper. It consisted of two smoke cells with identical optical systems operating from a single automobile headlight bulb. In each the scattered light was viewed at right angles by an RCA type-931 photomultiplier tube, the output of which could be applied to a microammeter. The gain of the photomultipliers was adjusted to give equal readings with raw smoke in both cells, and the stray light and leakage currents were balanced electrically with filtered air in both cells. When raw smoke was passed through one cell and filtered smoke through the other, the output cur-

rents were measured and their ratio gave the penetration. The instrument worked well in the region of 10 to 100%, for which it was designed, but did not give reliable results below 0.5% penetration.

At about the same time that the Kimberly–Clark penetrometer was developed, a more sensitive instrument was evolved independently in Professor LaMer's laboratory. Dr. Seymore Hochberg built a balanced photoelectric smoke-filter penetrometer, based upon the same forward-angle scattering smoke cell used by LaMer and Sinclair.

The tremendous improvement in gas-mask smoke filters during the Second World War required the development of a compact and simple apparatus which would measure smoke concentrations of 0.01 γ per liter or less, in a fraction of a minute. The present article describes the development of a photoelectric apparatus which can be used to measure, within a few per cent., the relative concentrations of liquid smokes of DOP, of about 0.3 micron diameter, with a sensitivity of 0.001 γ per liter. This corresponds to a quantity of visible light of about 0.005 microlumen. This photoelectric method could be applied to colloidal systems dispersed in liquids and to many other problems which involve measurement of small quantities of light.

Design Considerations

The Smoke Cell.—Aerosol concentrations may be measured either by the reduction in intensity of the transmitted light or by the relative intensity of the scattered light. The first arrangement involves the measurement of rather large light intensities with extreme precision, in order to detect very small changes with reasonable accuracy. Thus Hill's apparatus, described in the preceding section, required a constancy of 0.002% in the light source and optical system, to allow readings to 0.005 γ per liter, or 0.02% of his test smoke. Although the amount of scattered light which can be collected in any practical optical system is only a small fraction of the total reduction of the transmitted beam, it can be measured more directly. The light source requires no elaborate precautions to assure constancy, the photometric system can be simplified, the smoke cell made much smaller and the whole system more compact and rugged.

In an instrument designed for measuring scattered light, the angle of observation next must be chosen. Using a tungsten source at a color temperature of 2870°K., a phototube with a type S-4 surface (such as the RCA 929 tube) has its greatest sensitivity at a wave length of 0.5 μ. Calculations for light of this wave length,[8] privately com-

(7) A. S. G. Hill, J. Sci. Inst., **14**, 296 (1937).

(8) Taken from the tabulations of H. Engelhard and H. Friess, Kolloid-Z., **81**, 129 (1937), based on the theory of Gustav Mie, Ann. Physik, **25**, 377 (1908), for light scattered from dielectric spheres. In the autumn of 1940, LaMer and Sinclair brought Mie's work to the attention of the aerosol group of the National Defense Research

municated by Major Robert Van Tuyle, of the CWS Development Laboratory, M.I.T., show (cf. Fig. 1) that the light scattered at 20° is about ten times as intense as that scattered at 90° by a DOP smoke of 0.3 μ diameter. However, the choice of the angle of observation depends also on the magnitude and constancy of the stray light in the system. If the limit of sensitivity in measuring the most dilute smokes is to be 0.001% of the concentration of the raw smoke, the stray light must be kept below 0.033% of the raw-smoke light, provided that the light source is constant to 3%. A series of preliminary experiments showed that we could reduce background light to a substantially lower fraction of the total smoke-scattered light in the right-angle scattering cell, and that adjustment was simpler and less critical than for the forward-scattering cell.
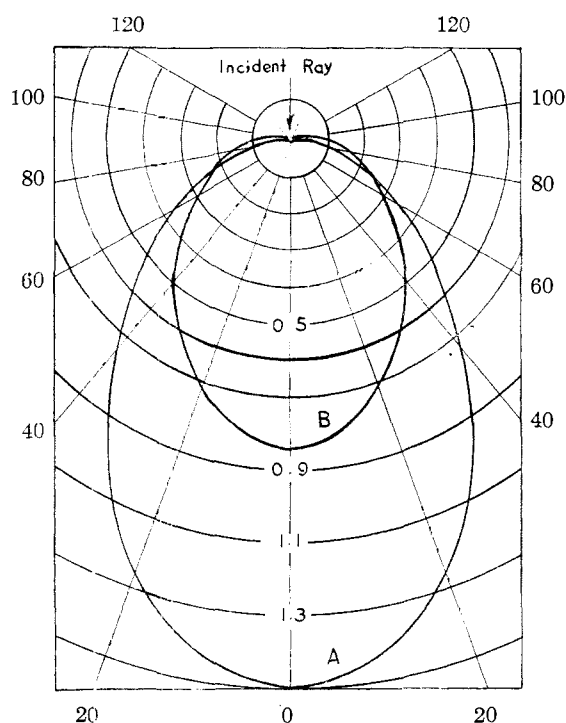

Fig. 1.—Intensity vs. scattering angle for a DOP particle of 0.30 micron diameter, for light of wave lengths 0.45 micron (Curve A) and 0.55 micron (Curve B).

The Photometric System.—The vacuum phototube was chosen for its extreme stability, reproduceability, and linear response. If electrical leakage currents are reduced sufficiently, and very high resistors are used in the phototube circuit, the resulting e.m.f. may be balanced potentiometrically, using a single-stage DC amplifier. Figure 2 shows a simplified diagram of the circuit of the instrument. Because of the linear

response of the phototube, the potentiometer can be calibrated directly in terms of scattered light intensities or smoke concentrations. The range of the instrument is extended to very low smoke concentrations by using higher resistances in the phototube circuit, always keeping the potentiometer in its optimum range of operation. The instrument is made direct-reading over the entire range by means of suitable circuits and adjustments discussed below.
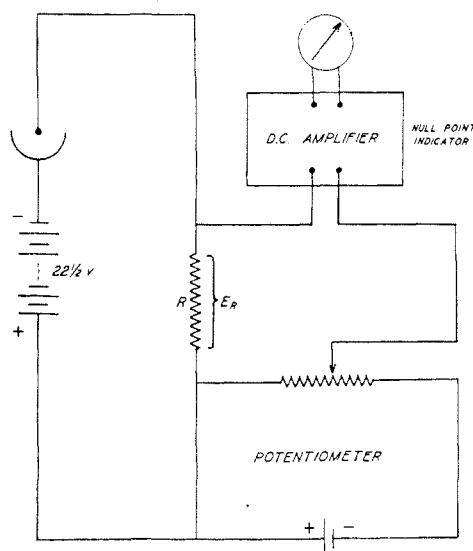

Fig. 2.—Simplified diagram of the penetrometer circuit.

Apparatus

The whole apparatus is housed in a metal cabinet 12 × 20 inches and 12 inches high, with the switches, potentiometer and other electrical controls mounted directly on the front panel. Manifolds on the side carry connections to the inlet and outlet tubes of the smoke cell, from three pairs of metal gas cocks. One cock in each pair is connected to waste, and the other to the raw smoke, filtered smoke, and filtered air lines, respectively. The cocks in a pair are coupled to turn together. In the "on" position they make a connection through the smoke cell; in the "off" position they make connection with a by-pass tube soldered between them. Thus the cell can be connected as desired by the turning of two handles.

The Optical System.—The smoke cell, shown in 2 cross-sectional views in Fig. 3, is made of thin brass tubing A, lined with optical black paper B. A short piece of smaller tubing C connects to the phototube housing by means of a telescoping fit as shown. A thin brass disk D, closing the end of C, has a 6 × 18 mm. rectangular opening over which is cemented a thin piece of microscope slide glass, E. Smoke enters the cell through F and leaves through G. The bottom of the cell is closed with a cap H made from thin tubing soldered to a stout square base plate, with 4 holes in the corners to fasten the cell in place.

A 12-mm. ring I is soldered to the cell case, so that the bottom of the cell can be sealed tight with a strip of cellulose acetate adhesive tape, T. A block of wood J, glued to the base of the cell, forms a V-shaped light trap.
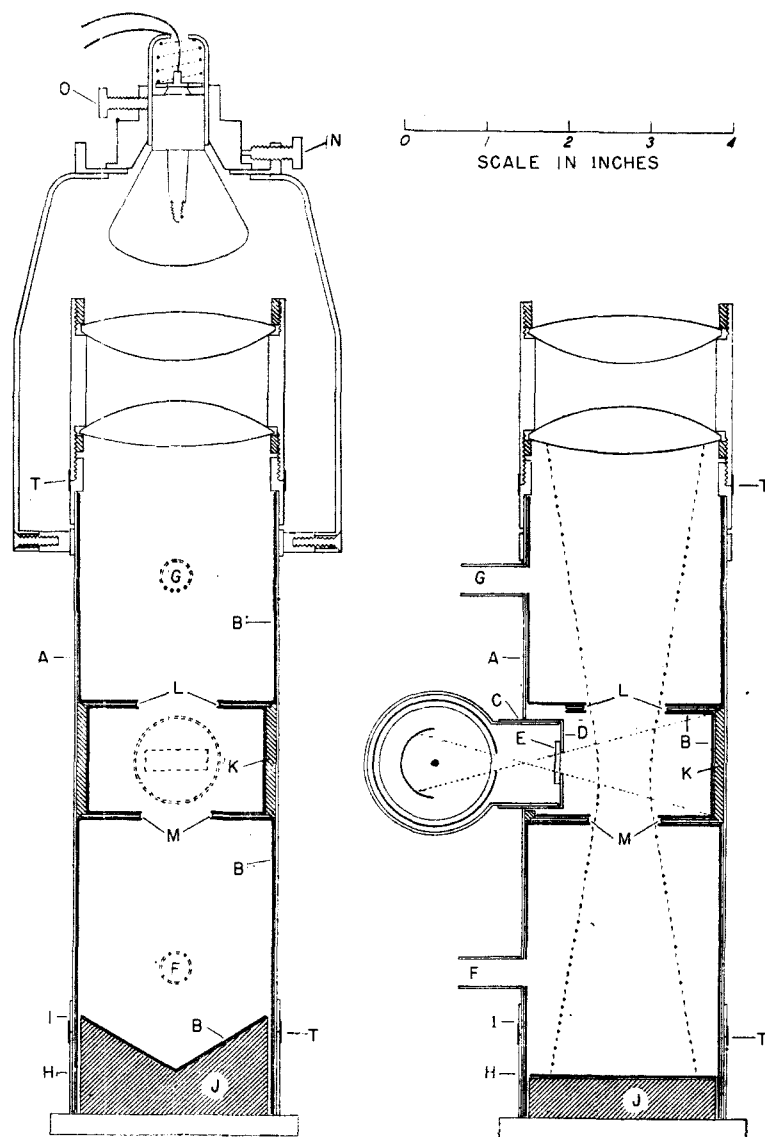

Fig. 3.—The smoke cell.

The pair of aspheric condenser lenses, each with a focal length of about 5.7 cm. and a diameter of 6.35 cm., are mounted as shown. The lower lens is sealed in place with a little glyptal (glycerol–phthalic anhydride polymer) varnish. To the top of the cell is soldered a threaded collar into which the lens mount is screwed. This joint also is made tight with tape, T. The light beam is outlined by the dashed lines.

The stray light on the phototube is reduced by the baffles L, M, soldered to the snug-fitting brass ring K. L and K are cut away enough to allow the baffles to be pushed into place from the bottom. The opening in D and a similar opening P in the black paper wrapped around the phototube (see Fig. 4) allow the phototube to "see" only the center of the cell, excluding the edges of L and M which are illuminated somewhat by scattered light. The scattered light reaching the photocell is outlined by the dotted lines.

The 6-v, 50-c.p. automobile headlight bulb may be adjusted horizontally by means of 3 knurled screws, one of which is shown as N, and may be raised or lowered to give the proper focus, then held in place by the knurled screw O. Stray light is decreased by buffing the trade mark from the end of the bulb. The total stray light is reduced to 0.03% of the raw smoke light when the cell is lined with optical black paper, and to 0.02% when the paper is coated with soot from burning camphor.

The arrangement of the type-929 phototube is shown in Fig. 4. The base is removed, and the leads are insulated with amphenol (polystyrene) sleeves. The phototube fits into a thin brass sleeve which slides in the packing gland shown at the left. The other end of this sleeve is closed by a cap carrying a small calibrating light bulb pushed through a tight rubber grommet. The cap is made fast with stopcock grease. Opposite the photosensitive surface, a short side tube, telescoping into tube C as shown in Fig. 3, also is sealed with stopcock grease.

The Amplifier Grid Circuit.— To reduce leakage currents across the insulation of the grid-circuit components, the whole circuit is enclosed in a box fitted with a lid screwed down tight on a paper gasket. It carries a desiccating cartridge of silica gel, the indicator of which is visible through a small window in the lid. The switches are operated through airtight packing glands. Seven leads to the amplifier tube socket and phototube battery are carried to the outside through brass pins in a Bakelite (phenol–formaldehyde plastic) disk, mounted in a brass ring held in the bottom of the box by means of a large nut and washer as shown. The "breathing" of humid air through minute leaks in the box is reduced by a soft rubber bulb of the type used in the Orsat gas-analysis apparatus, partly inflated when the box is closed. The desiccant rarely needs regeneration.
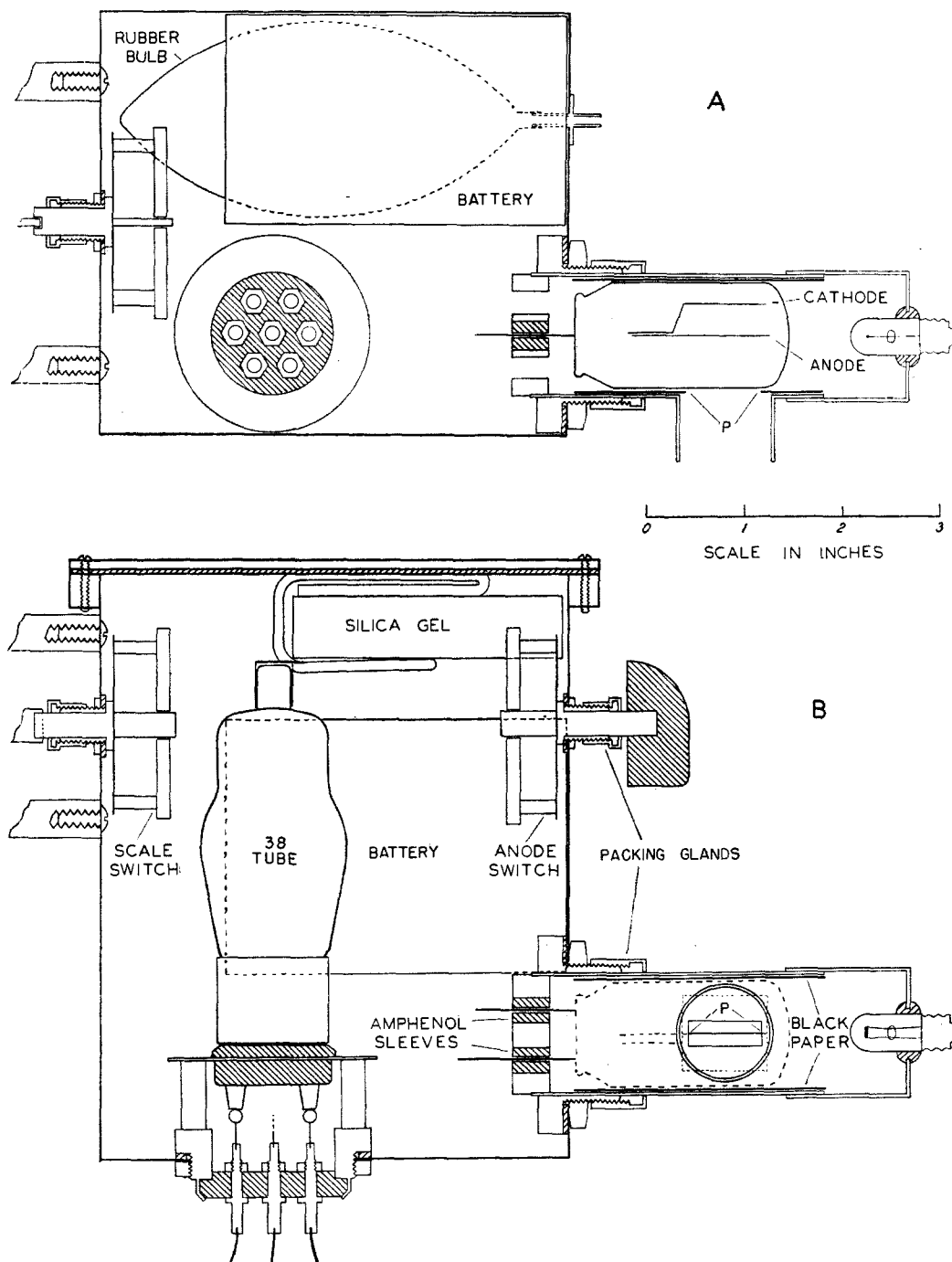
Fig. 4.—Amplifier tube box and phototube mounting: A, cross section; B, elevation.

The arrangement of the phototube and amplifier circuits is given in Fig. 5. The numbered test points are connected to the e.m.f. check circuit given in Fig. 6, which will be described later. A large 6-v. transformer, connected to a voltage-stabilizing 115-v. transformer, supplies the heater of the amplifier tube and the light for the smoke cell. Transformer and light are not shown in Fig. 5.

In measuring very small photocurrents, we must consider parasitic currents in the grid circuit.

(a) Dark current in the phototube is negligible for the 929 tube at room temperature.

(b) Leakage current of the phototube can be reduced to an insignificant value (about 10^{-12} ampere) by removing the base, desiccating the housing, and carrying leads through amphenol sleeves.
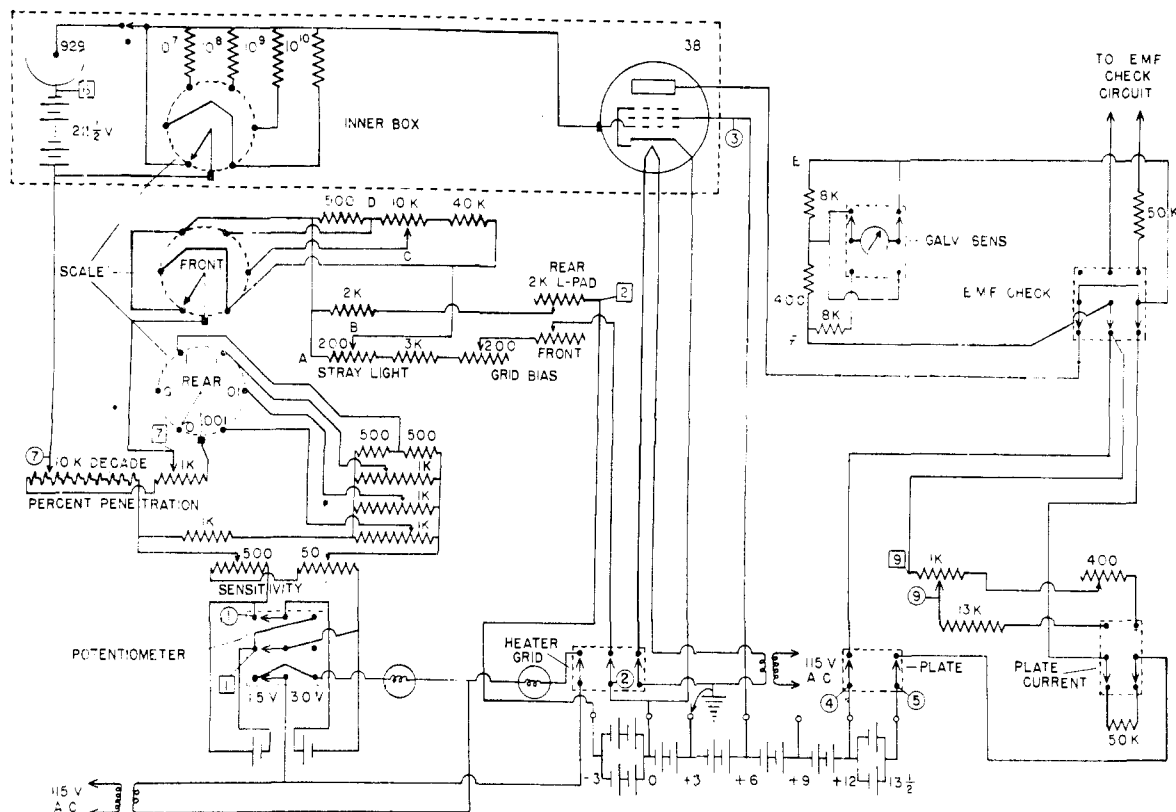
Fig. 5.—Phototube and amplifier wiring diagram—K = 1,000 ohms.

(c) Grid current in the amplifier tube, due to grid emission and ionic or electronic currents in the tube, may be reduced to -10^{-11} amp. or less in a suitable tube[9] by decreasing the heater voltage, keeping the maximum interelectrode potential below 15 v., the ionization potential of the residual gases, and making the grid sufficiently negative. The grid current is the same whenever the plate current is brought to a constant value in balancing the amplifier.

We found that the grid current–grid voltage curve of the 38 tube can be shifted along the current axis by changing the potential of the heater with respect to the cathode. The magnitude of this effect, probably due to internal leakage currents, varies from tube to tube. In this circuit the grid current of the tube may be made to balance part or all of the leakage and stray-light currents from the photocell, by changing the point on the battery which is connected to the grounded side of the heater.

(d) Current due to stray light scattered in the

(9) In investigating tubes, we found the 1C7-G, 1D7-G and 38 suitable for this instrument. Since the first two were discontinued during the war, we used the 38 described by E. A. Johnson and C. Neitzert, Rev. Sci. Inst., 5, 196 (1934), and E. A. Johnson and A. G. Johnson, Phys. Rev., 50, 170 (1936). About a third of the tubes we tested could be operated at grid currents of -2 to -8×10^{-12} amp. The acorn-type RCA 954 tube described by G. H. Gabus and M. L. Pool, Rev. Sci. Inst., 8, 196 (1937), for use in circuits involving resistances up to 10^{11} ohms, was hard to obtain during the war but might be useful in this instrument.

smoke cell is reduced to about 5×10^{-12} amp. by careful design.

All of these parasitic currents are compensated by means of the "stray light" potentiometer shown in Fig. 5. The proper bias first is applied to the grid of the amplifier tube. The "scale" switch is turned to 0, disconnecting the potentiometer battery, and connecting the point A directly to the grid of the tube. The potential at this point is varied by means of the L-pad and the 200-ohm resistor, so as to balance the galvanometer. Turning the "scale" switch to the C (check) position connects the 10^{10}-ohm resistor across the photocell. With filtered air in the smoke cell, the drop in potential caused by the parasitic currents is compensated by moving the "stray light" potentiometer B to the right. When the "scale" switch is turned to lower grid resistors, the compensating voltage is reduced proportionately, to preserve compensation on all scales. Initially the 10-K potentiometer is set at the midpoint, and C is adjusted to give compensation for the 10^9-ohm resistor on the 0.01 scale. Connection to D gives compensation on the 0.1 scale, while none is required on the 1 scale. The compensation is not affected by subsequent changes in the "grid bias" circuit, since the total resistance in this circuit cannot vary more than 3%.

Percentage Penetration Potentiometer and Scaling Circuits.—The potentiometer for meas-
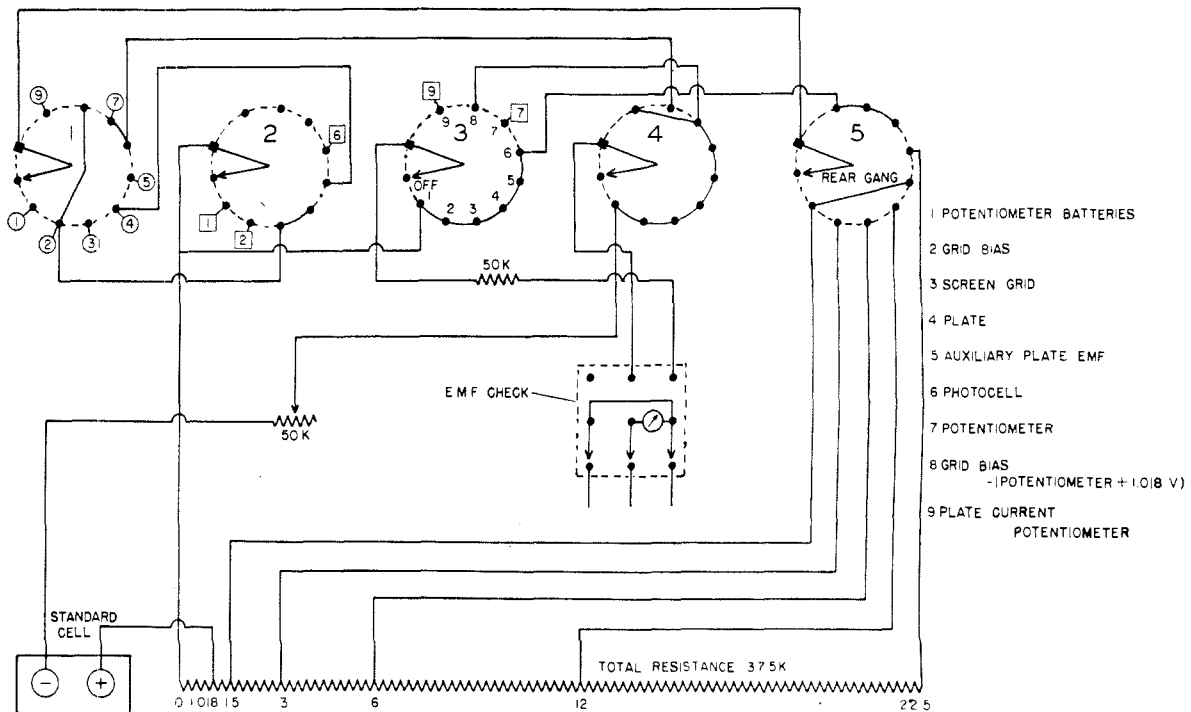
Fig. 6.—E. m. f. check circuit—Positions on 5-gang selector switch make nine connections listed at right.

uring percentage penetration consists of a 10-K decade and a 1-K slidewire. The fraction of the e. m. f. of the batteries which is applied to this potentiometer may be adjusted by means of the "sensitivity" controls, so that the 100% setting exactly balances the potential drop of the unfiltered smoke photocurrent across the 10^7-ohm resistor.

The four metallized resistors, nominally 10^7, 10^8, 10^9, and 10^{10} ohms, respectively, are connected to a 6-position switch mounted on special ceramic insulation in the inner box, forming the third gang of the "scale" switch. The four selected high resistors may differ by as much as 10% from their nominal values, but this is compensated by the arrangement of a 1-K resistor in series with a parallel set of 1 center-tapped 1-K resistor and three 1-K potentiometers, connected to the "rear" gang. This allows an adjustment of the potentials applied to the 0.1, 0.01 and 0.001 scales within ±12.5% of that applied to the 1 scale.

The 1-K potentiometers of the scaling circuit are adjusted until the "percent penetration" readings for the same photocurrent on any two adjacent scales differ by a factor of 10. To provide a suitable steady photocurrent, filtered air is passed through the smoke cell and the flashlight bulb in the cap of the phototube housing is connected to the 6-v. transformer through a suitable resistance, not shown in any of the figures. Thus, starting on the 1 scale, the "percent penetration" dials are set at 10% and the e. m. f. due to the photocurrent is balanced with the "sensitivity"

controls. The scale switch then is turned to 0.1, the dials are set at 100%, and the amplifier is balanced by adjusting the top scale-correction potentiometer. The 1 and 0.1 scales are now self-consistent at any point. Similar adjustment of the other scale-correction potentiometers makes the four scales self-consistent.

Plate Circuit.—When the "plate" switch is turned on, the "plate current" and "e. m. f. check" switches are down as shown in Fig. 5, and the galvanometer is balanced, the potentials at E and F are equal. Since all the plate current is flowing through the 50-K plate resistor, the potential drop across it (50,000 I) must equal the potential of the last section of the plate battery (1.5–1.6 v.) and the plate current is 30–32 μ amps. at balance.

The plate-circuit galvanometer is type 2310-d, made by Leeds and Northrup Co., with a resistance of 1000 ohms, a C.D.R.X. of about 8000 ohms, and a sensitivity of 0.125 μ amp. per mm. It is mounted in a frame of $^1/_2$-inch angle brass, with the scale projecting through a hole cut in the lid of the cabinet. A D.P.D.T. push-button switch controls the galvanometer sensitivity. When the button is pushed in, the galvanometer is connected across an 8-K damping resistor, as shown in Fig. 5, to give high sensitivity. When the button is released, the switch returns to the normal position where the galvanometer sensitivity is reduced to 5% of its former value.

E. m. f.-Check Circuit.—The voltages of the batteries can be checked simply and rapidly by means of the circuit shown in Fig. 6. Wires

connect the numbered test points with the corresponding points on Fig. 5. A resistance of 37.5-K, provided with taps connected to test points 1–6 by the gang switch, acts as a voltage divider to supply 1.02 v. (nominal value) which is opposed by the voltage of the standard cell. Throwing the "e. m. f. check" switch up connects the galvanometer into this circuit, the resistance of which is adjusted by means of the 50-K resistor so that the galvanometer reads directly in percentage deviation of the battery from its nominal value. Cells which are 10% low are replaced.

Experimental Procedure

Measurement of Filter Penetrations.—The "heater-grid" switch (Fig. 5) is turned on and the 38 tube warmed up for a half hour before using the amplifier. Then the "scale" switch is set on 0, the "plate" switch turned on, and the amplifier balanced with the "grid bias" controls. After carefully filtered air is passed through the smoke cell, the "potentiometer" switch is turned to 1.5 v., the "scale" switch to C, and the parasitic currents are balanced with the "stray light" controls. This adjustment is checked every half hour.

Next, raw smoke is passed through the cell, the "scale" switch is set on 1, the "percentage penetration" dials on 100, and the amplifier is balanced with the "sensitivity" controls. When filtered smoke is passed through the cell, the "scale" switch set at the proper value and the amplifier balanced with the "percentage penetration" dials, the reading gives directly the percent penetration of smoke through the filter, if the light scattering is proportional to the smoke concentration in each case.

If the raw smoke is so concentrated that its scattered light cannot be balanced by applying 1.5 v. to the potentiometer, the switch can be turned to 3.0 v., and the stray light and sensitivity balanced as before. A DOP smoke of 0.3 μ diameter at 100 γ/liter requires a potentiometer voltage of about 0.25 v.

Measurement of Smoke Currents and Concentrations.—The potentiometer is adjusted to read in centivolts on the 1 scale, by throwing up the "e. m. f. check" switch (Fig. 6), setting the associated 5-gang switch on position 7, the "potentiometer" switch on 1.5 v., the "scale" switch on 1, and the "percent penetration" dials on 101.8, and balancing the galvanometer with the "sensitivity" controls. After changing back to the measuring circuit, the parasitic currents are compensated as before, and the amplifier is balanced with smoke in the cell. The dial setting then gives the smoke current directly in $m\mu$ amp.

The penetrometer may be calibrated directly in γ/liter of any particular smoke, if the concentration is measured (e. g., by collecting and weighing the smoke in a known volume), the "percent penetration" dials set to correspond, and the amplifier balanced with the "sensitivity" dials.

Measurement of Stray Light, Grid and Leakage Currents.—The potentiometer first is adjusted to read directly in centivolts, its dials are brought to zero and the "scale" switch set on 0.001. A closely-fitting cap is slipped over the top of the smoke cell to cut off the light, and the amplifier is balanced with the "grid bias" controls, thus compensating grid and leakage currents. Filtered air is passed through the cell, the cap is removed, and the amplifier is balanced with the potentiometer dials. The reading corresponds to the stray-light current in $\mu\mu$ amp.

To measure the amplifier grid current, which is opposite in sign to the stray-light current, the potentiometer is calibrated in centivolts, the anode switch in the phototube circuit (Fig. 5) is opened to eliminate leakage and dark currents, the "stray light" potentiometer is turned to 0, and the amplifier balanced on the 0.001 scale by means of the "grid bias" controls. The grid voltage includes

the IR drop of the grid current, which is eliminated by turning the scale switch to 1. The "percent penetration" potentiometer must be adjusted to rebalance the amplifier, and the dial reading is the negative grid current, in $\mu\mu$ amps. Grid currents should lie between 0 and -10^{-11} amp. (10% on the dial).

If the anode switch is closed and the cap put on the smoke cell, the above procedure measures the amplifier grid current plus the phototube leakage and dark currents, (about $+10^{-12}$ amp.) which are determined by difference.

Determination of Amplifier-Tube Characteristics.—The choice of a tube with a suitably low grid current and the selection of optimum operating conditions requires a knowledge of the amplifier-tube characteristics, which can be obtained as follows:

The anode switch is opened and the potentiometer calibrated in centivolts. Then the 5-gang selector switch is turned to 8, opposing the grid voltage with the sum of the standard cell and potentiometer voltages. The grid bias then can be set at any desired value between -1.02 and -2.5 v. The corresponding grid current is measured as described in the preceding section.

The "plate current" switch (Fig. 5) is turned up to put a 1-K potentiometer and 400-ohm rheostat across the 1.5 v. auxiliary plate battery. The plate current can be determined from the measured value of the 13-K resistor and the voltage from the 1-K potentiometer needed to balance the galvanometer. To make the potentiometer dial direct reading, the "e. m. f. check" switch is turned up, and the 5-gang selector switch set on 9, opposing the standard cell and the potentiometer, which must be adjusted to 1.018 v. in order to balance the galvanometer. The plate current to give this potential drop across a resistor, e. g., of 13,420 ohms, would be $1.018/13,420 = 76 \times 10^{-6}$ amp. Hence by setting the potentiometer dial at 76 and balancing the galvanometer with the 400-ohm variable resistor, the potentiometer scale will read the plate current directly from 0 to 90 μ amps., within a few per cent.

Experimental Results and Test of Validity of the Penetration Measurements

The validity of the measurement of low filter penetration by means of light-scattering cannot be checked directly by a gravimetric procedure, but a series of measurements can be tested by the well-established law of filtration: The fractional penetration of a given smoke through a filter under fixed conditions is independent of smoke concentration. If P_1 is the fractional penetration per sheet, and n is the number of similar sheets in a composite pad, the fractional penetration, P, of the pad will be P_1^n; hence a plot of P vs. n on semi-log paper will give a straight line. Two series of results obtained with one of our early meters, shown in Fig. 7, follow the filtration law over a 250-fold change in concentration.

Unless the test smoke is uniform, a comparison of light scattering will not necessarily measure filter penetration, since the light scattered per particle depends upon the radius, and selective filtration may cause a change in the size distribution. Thus a linear change of the logarithm of the penetration for a large number of sheets of paper indicates a uniform test smoke as well as a reliable penetrometer. A curve which is concave upwards indicates an inhomogeneous smoke, the larger particles of which are removed chiefly in the first few sheets of paper.

Where the test smoke is not extremely homo-

geneous, penetration readings may depend upon the angle of observation in the smoke cell, since the ratio of 90° scattering to small-angle scattering depends upon the particle size. This meter was compared with a penetrometer employing forward-angle scattering. Various filters were tested with the instruments connected in parallel to the same DOP smoke generator. The average of about 30 measurements with the two instruments differed by only 4%. The maximum differences between any of the measurements on the same filter were less than 20%. The larger differences might easily be attributed to selective filtration, hence within the range of possible experimental variations, the instruments can be said to agree quite well.

A series of tests of different filter materials using several photoelectric meters was carried out at the CWS Development Laboratory, the results of which were communicated privately by Major Van Tuyle. The penetrometers used were (1) a standard meter used in production-line testing, which employs right-angle scattering, (2) a laboratory tester designed for forward-angle scattering (10–20°), (3) the present instrument. The tests showed agreement of (1) and (3) within 10%. The results with (2) showed about the same correlation for canisters wrapped with fiberglass but in tests involving asbestos papers there were deviations from the results of the other meters which were sometimes as great as 65%.

To determine whether these discrepancies were due to the difference in scattering angle, (2) was modified to use right-angle scattering. Subsequent penetration measurements were consistently higher than those obtained at the forward angle. The increase was about 50% for fiberglass and somewhat over 100% for various asbestos-bearing papers. This discrepancy may be due to selective filtration of a somewhat inhomogeneous smoke, for if the average particle size were reduced by filtration, right-angle scattering, which is increasingly less effective than forward-angle scattering as the particle radius increases, would lead to higher measured penetrations.

The fact that there was closer correlation between measurements employing the two types of scattering in the first-mentioned tests might be attributed to a more homogeneous smoke.

Applications to Other Problems

The instrument here described is applicable to many other measurements in addition to that of smoke-filter penetration. It could be used to check the completeness of combustion in steam plants by measuring the amount of dust in the flue gas, and to check loss of the "fluid catalyst" used in oil cracking, by measuring the amount in the exit gas from the regenerating units. It would be applicable to the measurement of dust and smoke contamination in the atmosphere and to the testing of filtered air in any chemical and
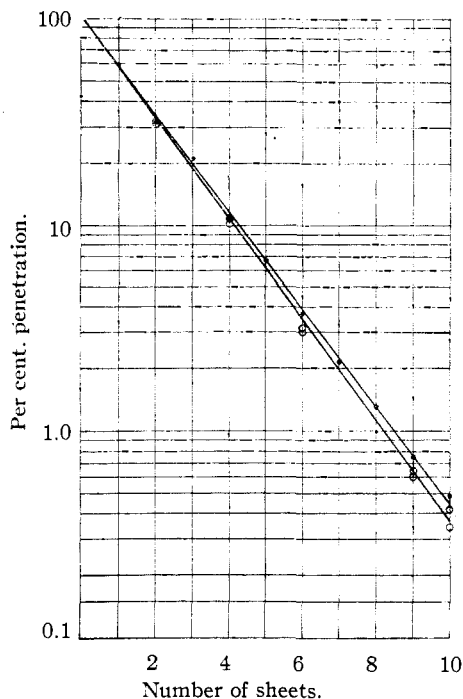

Fig. 7.—Test of validity of penetration measurements.

biological manufacturing processes where bacterial or dust contamination must be prevented. By substituting for the smoke cell a cell designed for liquid systems, the instrument could be used to study the concentrations of liquid colloidal systems, as an extremely sensitive nephelometer. The use of phototubes with different spectral response characteristics, suitable light filters, and polaroid disks would allow a convenient measurement of many optical properties of aerosols, suspensoids or emulsoids. Finally, the sensitive photometric circuit would be applicable to a study of intensities of spectral lines, fluorescence, and Raman spectra.

Summary

This article describes the design, construction, and operation of a sensitive photoelectric instrument which was developed primarily for measuring smoke penetrations through efficient gas mask filters. The instrument measures the photocurrents produced by the light scattered at right angles from smokes which are intensely illuminated in a suitable smoke cell. A vacuum-type phototube views the scattered light, and photocurrents are measured potentiometrically using a balanced DC amplifier as a null-point indicator. The stray-light and leakage currents are balanced electrically. A new scaling circuit compensates for the deviations of the high resistors (10^7 to 10^{10} ohms) from their nominal values, and allows a direct comparison of photocurrents within a few per cent. and hence a direct reading of filter penetrations. The sensitivity of the instrument is 10^{-9} g./liter of a dioctyl phthalate smoke of 0.3

micron diameter, or 5×10^{-9} lumen. The unit is small, rugged, and self-contained, incorporating suitable circuits for checking the operation of the vacuum tube, the condition of the phototube and the smoke cell, the scaling circuits and the batteries.

Penetration measurements with this instrument are self-consistent, and agree well with those obtained with instruments developed elsewhere during the last four years. The instrument can be calibrated to measure smoke concentrations. It is applicable to a wide range of uses in colloidal chemistry and photometry.

Absorption Isotherm for Determination of Barium in Quantities as Low as 10^{-10} Gram Atom

BY M. H. KURBATOV AND J. D. KURBATOV

Introduction

There is an excellent method for the determination of small quantities of radioactive atoms using coincident counting technique.[1] However, the determination of *stable* nuclei in such small quantities as those formed during activation processes and accompanying radioactive nuclei is not known. Specifically, the determination of stable isotopes in quantities below one microgram is the object of the present work.

Quantities of the divalent ions of barium, strontium, and some others, which lie beyond the range of usual analytical methods are readily adsorbed from solution by hydrous oxides in amounts varying with concentration of divalent ions. So it is plausible to suggest using the adsorption isotherm as a means of determining unknown quantities, with the limitation that the reference isotherm for a given ion should be obtained with a slope which is not unity for only then is the fraction adsorbed a measure of concentration.

Various hydrous oxides which may be prepared in solutions and maintained without change in adsorptive surface area during experiments, can be offered as adsorbents.

Since some information was previously obtained on adsorption of barium (mainly in conventional quantities) on hydrous ferric oxide, this combination of adsorbate and adsorbent was chosen for study at very low concentrations.[2]

Experimental

Chemisorption of quantities of less than one microgram is relatively easily measured using radioactive tracers. Thus the proposed method is dependent, first, on the existence of radioactive isotopes of divalent elements with appropriate half-life and radiation intensity, and second on preparation of a tracer of high specific activity so that the weight of an isotope added as a tracer, is negligible compared to the amount of inactive ion being traced. Therefore a parent material differing in atomic number from the tracer element is the more advantageous for such a study.

The radioactive isotope, Ba^{133}, of half-life 38.8 hours was selected as tracer. It was separated without carrier after deuteron bombardment of spectroscopically pure cesium chloride. The target chemistry is described elsewhere.[2] The purified Ba^{133} in the form of chloride was diluted with $0.01 \ N$ hydrochloric acid 1×10^4 times and one ml. of tracer was used per experiment. Since the bombarded cesium chloride cannot contain more than 1×10^{-6} g. of barium, the one ml. of tracer can have no more than 1×10^{-10} g. of common barium. On the other hand, the quantity of radioactive Ba^{133} per experiment was less than 1×10^{-12} g., since it produced on an average 2,000 counts with a counter efficiency of about 16%.

The data described later were obtained with a high rate counter·having an electronic recorder which allows reading the number of discharges on neon lamps instead of a dial recorder. Consequently the fluctuation and correction due to the dead interval of the dial recorder was eliminated.[3]

The resolving time of the Geiger–Mueller counter used did not exceed 1×10^{-4} sec. Therefore variations in the experimental data due to the resolving time of the counter was less than 1% cent in the range of activities measured.[4]

In addition, the counter data given in the following tables are mean values obtained from decay curves for each individual sample. Thus the final figures presented are averages corrected against fluctuations.

The chemisorption procedure consists in first establishing a reference isotherm with known concentrations of barium under a given set of conditions and then carrying out the adsorption of an unknown quantity under identical conditions, determining the fraction adsorbed and using it to read the unknown value from the isotherm.

The reference isotherm is established as follows:
(a) A series of barium chloride solutions of known concentrations, (from 10^{-6} to 10^{-11} g. atoms per ml.) is made up by repeated dilution with hydrochloric acid, usually $0.01 \ N$ and not less than $0.001 \ N$, of an analyzed solution of barium chloride. (b) A tracer solution is made in dilute hydrochloric acid $0.01–0.001 \ N$, so that one ml. of solution contains adequate activity for accurate measurement of a portion of the solution after absorption and after several days of disintegration. (c) A ferric chloride solution of known concentration (usually 1×10^{-5} g. atom of iron per ml. of solution) is freshly prepared in dilute hydrochloric acid such that one or two ml. of this solution contain the amount of iron to be used in each adsorption experiment.

It has been shown that even extremely dilute solutions of barium in $0.01 \ N$ hydrochloric acid, in new glass vessels, maintain experimentally constant molarity for the duration of an experiment. Freshly redistilled water checked by pH was used for the experiments.

(1) L. G. Elliott and M. Deutsch, *Phys. Rev.*, **64**, 321 (1943).

(2) J. D. Kurbatov, J. L. Kulp and Edward Mack, THIS JOURNAL, **67**, 1923 (1945); other references in this paper.

(3) L. I. Schiff, *Phys. Rev.*, **50**, 88 (1936).

(4) J. D. Kurbatov and H. B. Mann, *ibid.*, **68**, 40 (1945); J. D. Kurbatov and G. K. Groetzinger, *ibid.*, **69**, 253 (1945).