stants are presented in Table II. A graph of $-\log K$ *versus* the temperature shows that the values of the ionization constants reach a maximum in each of the solvent mixtures, as well as in water, at about 20°; this is shown in Fig. 2.

Values of the standard free energy, heat content, heat capacity and entropy of the ionization process may be calculated by means of the equations

$$\Delta F_i^0 = A' + D'T + C'T^2$$
$$\Delta H_i^0 = A' - C'T^2$$
$$\Delta C_{pi}^0 = -2C'T$$
$$\Delta S_i^0 = D' - 2C'T$$

where A', C' and D' are 2.3026 R times A, C, and D, respectively.

A graph of $-\log K$ *versus* the reciprocal of the dielectric constant was made to test the validity of the Born[7] equation. The curve obtained differed only slightly from a straight line over the range of dielectric constants involved. The values obtained for the ionization constant of propionic acid in methyl and ethyl alcohol–water solutions by Patterson and Felsing[4] and in dioxane–water solutions by Harned and Dedell[8] were plotted on the same graph and were found to fall very nearly on the same line. Thus, even though the Born equation is not rigorously obeyed, it appears that the dielectric constant of the medium is more important than the nature of the added organic solvent in determining the extent of ionization of this weak acid.

(7) Born, *Z. Physik*, **1**, 45 (1920).

Summary

1. The ionization constants of propionic acid in 5, 10 and 20 weight per cent. isopropyl alcohol solutions have been determined from 0 to 40° by the use of cells without liquid junction.

2. Equations are presented which express the ionization constants as functions of the temperature. From these, the values of the standard thermodynamic quantities may be calculated.

(8) Harned and Dedell, This Journal, **63**, 3308 (1941).

AUSTIN, TEXAS RECEIVED MAY 27, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

A Photoelectronic Counter for Colloidal Particles[1]

BY FRANK T. GUCKER, JR.,[2] CHESTER T. O'KONSKI,[2] HUGH B. PICKARD[3] AND JAMES N. PITTS, JR.[4]

During the Second World War, gas mask filters were developed to such a high state of efficiency that they passed only a small fraction of the most penetrating aerosols (about 0.3 micron (μ) diameter). Recently we have described[5] an electronic photometer, designed as a smoke penetrometer for the comparisons of concentrations of very dilute aerosols, with a limit of sensitivity of 10^{-9} g./liter. If somewhat coarser test smokes are used, the penetration might be of the order of a few particles per minute, which would be beyond the limit of accuracy of this or any apparatus measuring steady illumination, since the scattered light would come in pulses. In the summer of 1944 we undertook the development of an instrument which would count individual particles and give rapid quantitative tests of the best filters.

A dioctyl phthalate (DOP) smoke of about 0.8 μ diameter was chosen for the first experiments. Preliminary tests with this smoke in our photoelectric smoke penetrometer showed that the detectable limit of sensitivity corresponded to the light from only ten smoke particles, hence the counting of individual particles of this size did not seem impossible. The change from right-angle light scattering to the more intense forward-angle scattering, and the development of a stable high-gain pulse amplifier seemed a logical line of attack. By June 1945 we had developed a photoelectronic apparatus, with an electrical background of 1 count per minute or less, which would count individual DOP particles down to 0.6 μ diameter. We are describing the apparatus here since, in addition to serving as a supersensitive smoke-filter penetrometer, it can be adapted to many other uses in colloidal chemistry, bacteriology, biology and industry.

Apparatus

The apparatus consists of three parts: (1) a cell in which a stream of the very dilute smoke, passing through an intense light beam, scatters flashes of light forward upon a photosensitive cell, (2) a stable pulse amplifier with a maximum voltage gain of about 300,000, and (3) a thyratron trigger circuit which actuates a mechanical counter. The smoke cell and amplifier are mounted on a chassis base, 7.6 × 25.4 × 35.6 cm. (3 × 10 ×

(1) This paper is based chiefly upon work done for the Office of Scientific Research and Development under Contract OEMsr-282 with Northwestern University. The later development of the instrument was carried out for the Army Service Forces under Contracts WA-18-064-CWS-137 and -160 with Northwestern University. This paper was presented before the Division of Physical and Inorganic Chemistry at the 111th meeting of the American Chemical Society, in Atlantic City, N. J., April, 1947.

(2) Present address: Department of Chemistry, Indiana University, Bloomington, Indiana.

(3) Present address: Department of Chemistry, University of Maryland, College Park, Md.

(4) Present address: Department of Chemistry, University of California at Los Angeles.

(5) F. T. Gucker, Jr., Hugh B. Pickard, and Chester T. O'Konski, This Journal, **69**, 429 (1947), and F. T. Gucker, Jr., *Electronics*, **20**, 107 (1947).

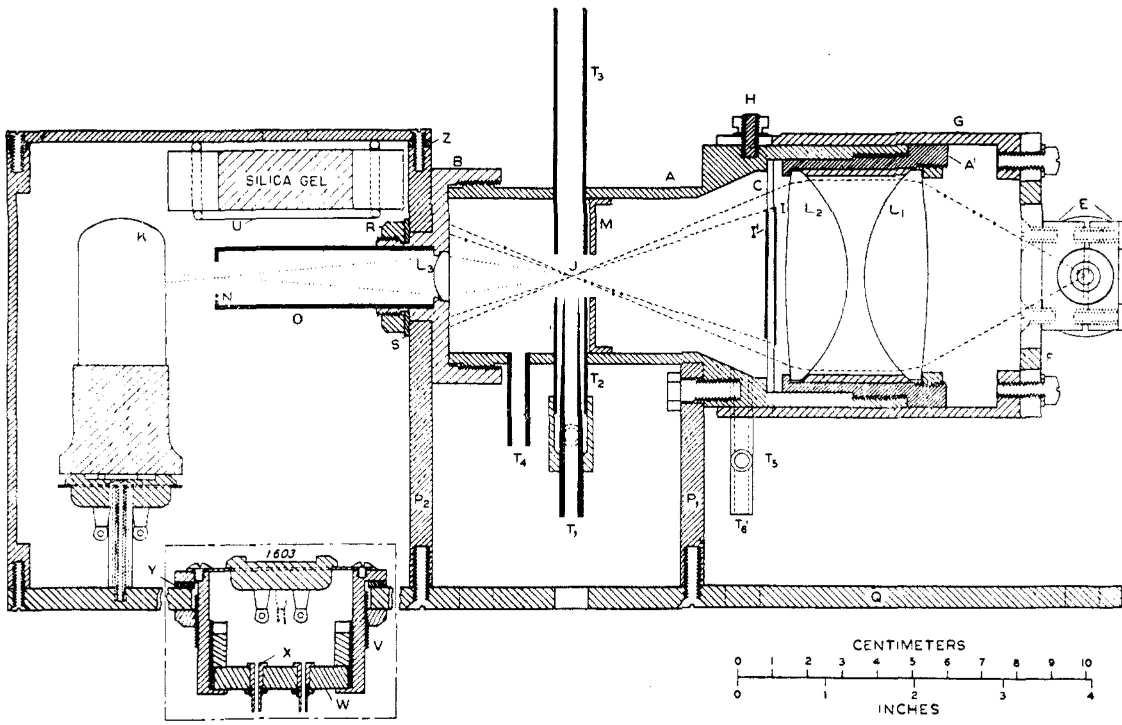

Fig. 1.—Smoke cell unit.

14 in.). A cabinet, 30.5 × 50.8 × 30.5 cm. (12 × 20 × 12 in.), houses the power supply and the time-recorder circuit, which may be used to record automatically the time for 100 counts. The two units are connected by a 4-conductor shielded cable with shielded locking-type microphone connectors on the rear of the chassis bases.

The Smoke Cell Unit.—This unit, made of brass with most joints silver-soldered, is shown in Fig. 1.

Vibrations in the optical system may cause variations in the background illumination which give spurious counts. To reduce these background counts, the optical system was made rigid and the whole unit was mounted on a heavy base plate Q. This was bolted to the chassis, but insulated from mechanical vibrations by a piece of 6-mm. felt under each end, and felt washers and rubber sleeves around each of the 4 bolts.

The smoke cell A is closed at the left end by a carefully machined cap B. The right end is closed with a glass plate C cemented in place with glyptal (glycerol–phthalic anhydride polymer). The projecting sleeve A′ is threaded to hold the mount for the 2 aspheric condensing lenses, L_1, L_2, each with a diameter of 6.4 cm. and a focal length of about 5.7 cm. The 6-v., 50-c. p. automobile headlight bulb D is mounted rigidly in the split block, E, which connects its outer terminal to ground. A flexible lead soldered to the central lamp terminal is connected to one pole of a large 6-volt storage battery, the other pole of which is grounded. Two screws passing through vertical slots in the plate F fasten it to the cylinder G which fits closely over A′ and is slotted at the left end for the stud and knurled nut H which fastens it in place. The bulb D is focused by rotation and horizontal adjustment in E, vertical motion of F, and longitudinal motion of G.

The optical system is similar to that devised in 1941 by LaMer and Sinclair[5] for their study of smokes, carried out under the National Defense Research Committee at Columbia University. A conical shadow is cut from the converging light beam by a disk of black paper, I, 3.9 cm. in diameter cemented to the outer face of the glass plate C. The light beam, outlined by the dashed lines, gives dark-field illumination of a space about 4 mm. in diameter at J.

The flow system in the cell is specially designed so that each particle must pass through the light beam with no chance for recirculation. The smoke stream, entering through the smaller of two concentric tubes, T_1, machined to a knife edge at the top, is surrounded by a streaming sheath of air flowing from T_2 at the same linear rate of 200 cm. per second. Visual tests with concentrated smoke showed that the stream from T_1 to the exit tube T_3 is well defined and uniformly smaller in cross-section than the intensely illuminated focal region J. Each smoke particle is illuminated for about 0.003 sec., and throws a flash of light into the conical shadow to the left of J. Most of this light, outlined by the dotted lines, is collected by the plano-convex lens L_3, of about 25 mm. focal length, sealed into B with glyptal cement. This scattered light, falling on the photosensitive cell K, produces an electrical impulse for each particle. The diaphragm M, placed as near the smoke tubes as possible, shields the lens L_3 from most of the light which might be scattered from the surface of the plate C or lens L_2. The disk of black paper I′ cuts down the stray light reflected from the surface of C, and the tube O and diaphragm N also help to limit the stray light reaching the cell K. The inside surfaces of the lens mount, smoke cell, and tube O, and the baffles M and N are painted with dull black optical lacquer.

The vents T_4 and T_5, connected together with rubber tubing, and to the filtered air line through the bottom of T_6, can be used to flush the whole cell before use.

To insure rigidity of the optical system, the right end of the smoke cell is fastened to plate P_1 with three cap screws, one shown in Fig. 1. P_1 is bolted to the bed plate Q, the top of which was ground flat. The other end of the cell is fastened with the hexagonal nut R and washer S to plate P_2, forming one end of a rectangular box desiccated by a small can of silica gel, held in place by a spring clamp U. This box contains the photosensitive tube, input resistors and condensers, and type-1603 tube which serves as the first amplifier. This tube is covered with a standard shield, painted black on the inside to prevent the light of the heater from reaching the cell K. The socket for this tube is mounted on a brass plug V, holding a bakelite disk W fitted with 4 hollow brass prongs X through which the leads pass to the voltage supply and the next amplifier tube. A drop of solder seals the end of each prong, gaskets S, Y, Z are coated with "Seal-Tite" cement, and the other seams are closed with glyptal cement. A soft rubber bulb from an Orsat gas-analysis apparatus, connected to the box and partly inflated when the lid is screwed down on the gasket Z, reduces a tendency to "breathing" of humid air when the temperature of the box changes.

The desiccated box assures performance of the amplifier in a very humid atmosphere. The first model of our instrument functions satisfactorily without desiccation in our air-conditioned laboratory. The cell K is surrounded by a light-tight cylindrical case, with a tube projecting from the side to match O, to which it is connected by a movable section of tubing telescoping over the outside.

The Photosensitive Cell.—In seeking a cell with the necessary high sensitivity and high signal-to-noise ratio we tried several RCA type-931 electron-multiplier phototubes in the first model of this instrument. The 931 tube, operated at high gain with 112 volts per stage, was followed by an audio-frequency amplifier having a maximum gain of 10,000, and a thyratron with adjustable grid bias. In order to obtain counts with the smoke particles, the negative grid bias had to be reduced to a point where the background was several counts per minute. With the best 931 tube available, oscilloscope observations showed that the pulses from 0.8 μ DOP particles were only about 50% above the amplitude of these background pulses, and many particles were missed. The setting of the grid bias was extremely critical, since a small decrease gave many background counts, and a small increase cut off more particle counts. The success of the arrangement was doubtful.

Fortunately, at this time the photoconductive "thalofide" cell, with a special thallous sulfide surface, developed by Dr. R. J. Cashman[6] and associates in the Department of Physics at Northwestern University, was made available to us by Division 16 of the NDRC. Preliminary tests indicated a more favorable signal-to-noise ratio for the thalofide cell, which was then incorporated into the instrument. The signal-to-noise ratio was increased to 2 or 3 and the unit became more stable.

The first thalofide cells used in the instrument were especially chosen with a low dark resistance to match the 2.5-megohm input impedance of the amplifier. Later tests of the input circuit showed that the resistance of the cell most frequently used was only 1.5 megohms in the dark, and dropped to 0.6 megohm under the background illumination in the smoke cell. Later we tried two thalofide cells with dark resistances of 7 and 40 megohms and corresponding resistances of 5 and 18 megohms, respectively, under background illumination. The signal-to-noise ratio did not change appreciably, but the values of both signal and noise increased substantially so that only about one-half the amplification was required for comparable operation. Therefore, the higher-resistance units are preferable although the circuit impedances are not balanced.

In first comparing the photomultiplier and thalofide cells, we found that the 931-tube photocurrent due to background light was ten times that due to a DOP particle of 0.8 μ diameter while the ratio was about 800 to 1 in the thalofide cell, probably due to stray light of long wave length to which this cell is more sensitive. However, the background noise of the thalofide cell was independent of background illumination up to these levels, while that of the photomultiplier was a function of background illumination.

More recently we have tested both type-931 and type-931-A photomultipliers operated at considerably reduced gain, with 30 to 50 volts per stage supplied by a very well regulated variable high-voltage supply. The photomultiplier was followed by the amplifier described below, set at a gain of about 200,000. We reduced the background light by introducing the disk of optical black paper I′ (Fig. 1) and lining the tube O with optical paper. With this arrangement the signal-

(6) R. J. Cashman (a) OSRD Report No. 5997 "Development of Stable Thallous Sulfide Photoconductive Cells for Detection of Near Infra-red Radiation." (b) Abstract in *J. Opt. Soc. Am.*, **36**, 356A (1946). (c) More detailed article in Proc. of the National Electronics Conference, **2**, 171 (1946).

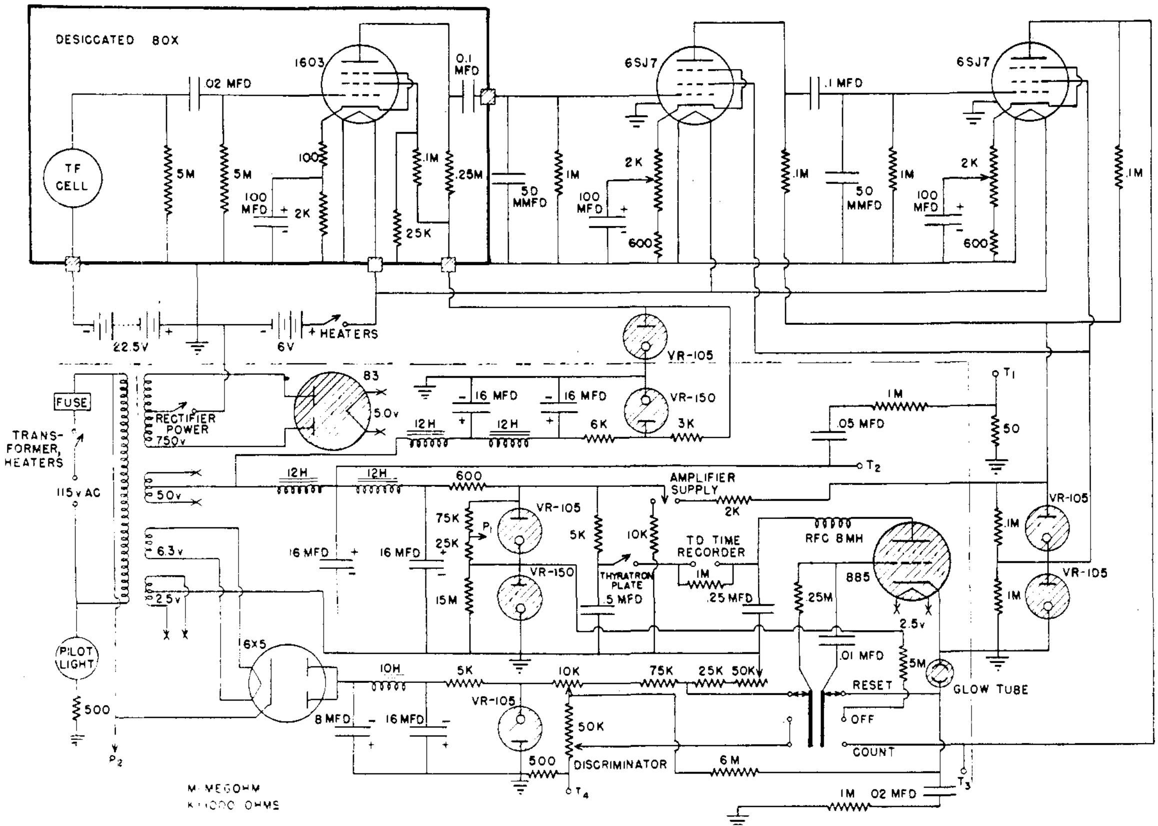

Fig. 2.—Photoelectronic counter circuit.

to-noise ratio was increased to about 2, so that the photomultiplier system proved comparable with the thalofide, as shown in the section describing comparative tests.

Power Supply.—The development of a stable power supply for everything except the phototube involved considerable experimentation. The final circuit, occupying the lower lefthand section marked off by long-dashed lines in Fig. 2, was mounted on a chassis in the bottom of the cabinet housing the time-recorder circuit. The full-wave type-83 mercury-vapor rectifier supplies two filter systems. The first, consisting of a 2-section choke-input filter followed by a VR-105 and VR-150 in series, supplies the main power output of 255 volts for the thyratron plate, time-recorder circuit, and the second VR stage supplying the 6SJ7 amplifiers. The second independent filter, consisting of a 2-section choke-input filter followed by a VR-150 tube, supplies the 1603 tube through a second VR-105 stage. This arrangement adequately decouples the 1603 tube from the output of the second 6SJ7 and reduces the ripple from the rectifier.

A 6X5 tube used as a half-wave rectifier is connected directly to the 115-volt a. c. power supply. The rectified voltage is applied to a condenser-input filter, followed by a VR-150 tube connected to a circuit which regulates the negative bias on the type-885 thyratron tube. Since one side of the power line is grounded, and the amplifier chassis also is connected to a water pipe or other convenient ground, a pilot lamp is connected as shown in Fig. 2, to give a red warning light when the cord is plugged into the 115-volt receptacle with the wrong polarity.

The Photocircuit and Amplifier.—This circuit, shown above and to the right of the long-dashed lines in Fig. 2, is mounted on the chassis with the smoke-cell unit. To reduce the noise, Shallcross Akra-ohm 5-megohm wirewound resistors are used in the phototube and 1603-grid circuits. A 1603 tube is used in the first stage because of its rigid construction and low microphonics. The plate voltage is supplied by the VR-105 tube which also furnishes about 20 volts for the screen grid, through the voltage divider shown.

The second and third amplifier stages use 6SJ7 tubes, the screen grids and plates of which are supplied with 210 and 105 v., respectively, from the second VR stage connected to the main power supply. The gain of these tubes is controlled by varying the negative feedback with the 2000-ohm potentiometers in the cathode circuits. Cathode resistors provide the biasing voltages for all three stages. The 1-megohm input resistors of the 6SJ7 tubes are shunted with 50-MMFD condensers to decrease the gain at high frequencies and thus increase the stability of the amplifier. The amplification at 10,000 cycles per second is about half that at 10 to 1000. The values of the resistors and shunting condensers in the cathode circuits, and of the grid resistors and coupling condensers, were chosen to give large time constants, thus extending the amplifier range down to 10 c. p. s. with little attenuation. This allows reproduction of the low-frequency components of the non-sinusoidal pulse from the photocell and eliminates the pulse multiplication we observed with a more conventional amplifier.

In assembling the amplifier, precautions were taken to reduce pickup and positive feedback which could cause ripple, instability or oscillations. The phototube and 1603-type amplifier are effectively shielded by the desiccated brass box, as shown in Fig. 2. The grid leads of the other tubes are short and surrounded by woven shields, securely grounded to the chassis. The bottom of the amplifier chassis is covered with a piece of sheet iron.

Amplifier Test Circuit.—The 120-cycle ripple across the first condenser of the main power supply is picked up by means of the 0.05 MFD condenser and fed through a voltage divider to the binding post T_1 in Fig. 2. The ripple voltage e is measured with a calibrated oscilloscope connected between T_2 and ground. The test voltage is then fed into the grid of the 1603 tube, and the output voltage E for various settings of the gain controls is measured by means of an oscilloscope connected between T_3 and ground. Knowing the input resistance R of the oscilloscope and the output impedance (10^5 ohms) of the circuit, the voltage amplification factor A is given by the equation

$$A = 2 \times 10^4(1 + (10^5/R))\ E/e$$

A setting of the gain controls giving an over-all amplification of 200,000 is satisfactory for operation of the apparatus.

Thyratron "Trigger" Circuit.—A type-885 thyratron tube is used with a self-quenching plate circuit[7] consisting of an 8 MH radio-frequency choke and a 0.25 MFD condenser. The grid bias is obtained from the VR-105 tube, through a circuit arrangement to compensate for variations in individual tubes of both types. The ratio r of the 5K and 500-ohm resistors is measured potentiometrically within 1%. A potentiometer is then connected from T_4 to ground, set at a value of $(100/r)$ v., and balanced by adjusting the 10-K resistor. The voltage drop across the whole 50-K *discriminator* potentiometer is then 100 v., and its dial reads directly in volts. The *discriminator* knob is removed and the shaft rotated until the tube fires. The knob is then replaced, pointing to 0, so that any subsequent setting gives directly, within 1 v., the voltage of the minimum pulse required to fire the tube. The rest of the circuit associated with the *count-reset* switch will be discussed under the next section.

The Time-Recorder Circuit.—This circuit, shown in Fig. 3, is arranged to measure simultaneously the duration of an experiment and the number of counts. The type S-10 timer, built by the Standard Electric Time Co. of Springfield, Massachusetts, operates from a synchronous motor, through a clutch accurate to 0.01 sec. The type-73511 impulse counter, made by the Central Scientific Co., indicates impulses up to 100, and then closes an auxiliary switch S which may be used to actuate a 5-place magnetic counter operated from the 115-v. a. c. line. The impulse counters eventually become worn and inaccurate, hence two are used to give a continuous comparison of their behavior. Since most of our tests involved a relatively small number of counts, we developed the *time-recorder* circuit to measure automatically the time for 100 counts. This arrangement gives in each experiment the same probable error of $0.67/100^{1/2}$ or 6.7%.

The *automatic-manual* switch is a 4-gang 2-position non-shorting-type rotary switch, shown in Fig. 3 as the 4-pole double-throw switch S_1. Momentarily depressing the *start* button operates the leaf switches L_1 and L_2, the function of which is explained below, and then turns on S_2, starting the timer and connecting the thyratron output to the counter. S_2 consists of 2 type-BZ-RLX microswitches, made by the Micro Switch Corp., Freeport, Illinois, mounted on a 10,000-ohm No. A23307 microswitch relay made by C. P. Clare &

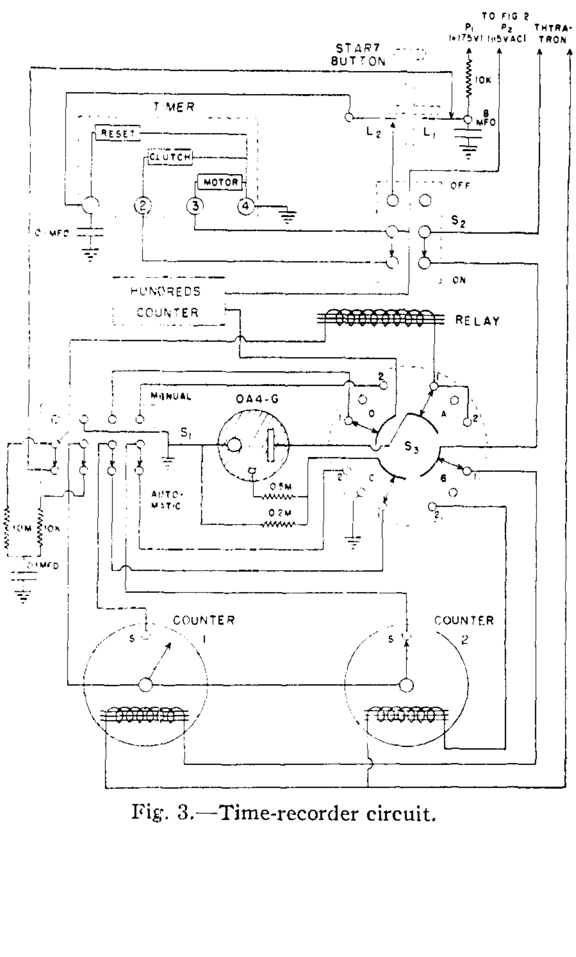

Fig. 3.—Time-recorder circuit.

(7) J. R. Dunning, *Rev. Sci. Inst.*, **5**, 387 (1934).

Co., Chicago, Illinois. In the starting position, the switch S in the counter is closed, and the 0.1-MFD condenser is charged to +175 v. through the 10-megohm resistor. When 100 counts are recorded, S is closed, discharging the condenser through the 0.2-megohm resistor. This momentarily swings the starter anode positive and fires the OA4-G tube. The anode current operates the relay which opens the microswitches, stopping the timer and disconnecting the counter. The timer records the time for 100 counts. As the *start* button is pressed for the next experiment, L_1 first is opened to extinguish the OA4-G tube, then L_2 is closed to reset the timer, and finally S_2 is turned on, opening the timer reset circuit and starting the timer and counter. The 0.1-megohm resistor across the leads to the time recorder (Fig. 2) prevents a spurious count when S_2 first is closed and the 0.25-MFD condenser becomes charged.

The 4-circuit 3-position shorting-type selector switch S_3 is connected with the *off* position in the center. The center contact of section C is grounded to discharge the 0.1-MFD condenser and prevent firing the OA4-G tube when the switch is turned to position 1 or 2. The 10-K resistor limits the discharge current and protects the contacts of S.

When S_1 is turned for *manual* operation the *hundreds counter* circuit is connected to section D of S_3, and the common recorder-switch lead is grounded. The auxiliary *hundreds counter* is actuated each time S is closed. The experiment is started as before by means of the *start* button and run for any desired length of time. By switching to *automatic*, the timer may be stopped at any even hundred counts.

When the counting rate is too slow to justify waiting for 100 counts, the time for a given number is noted, and the counter is brought to the 100 mark by throwing the 2-pole 3-position lever-type switch of Fig. 2 to the *reset* position. This connects the thyratron grid to a small relaxation oscillator consisting of the 0.25-watt neon glow tube, 6-megohm resistor, 0.02-MFD condenser and 1-megohm resistor, shown in Fig. 2. This circuit sends about 15 pulses per second to the grid of the thyratron tube, rapidly bringing the counter to the 100 mark. The proper thyratron grid bias is obtained by adjusting the grounded 50-K resistor to a position which gives satisfactory reset operation. If the resistance is too high, the thyratron will not fire; if too low, the grid will not regain control after each pulse.

The counter may be stopped at any time by turning the lever switch from *count* to *off*. The connection between the *off* contact and the VR-150 tube maintains a charge on the 0.01-MFD condenser and prevents a spurious impulse when the switch is turned to the *count* position.

Smoke Generators.—Preliminary experiments were made with dioctyl phthalate (DOP) smokes made with a generator of the type developed by LaMer and Sinclair.[8] The uniformity and size of the smoke was judged by illuminating it with a beam of parallel light and observing the spectra scattered at different angles to the incident beam. The observations were made through a polaroid disk arranged to pass light with the electric vector perpendicular to the plane of observation, defined by the incident beam and the line of sight. Clear spectra are only obtained with homogeneous smokes, and the number of orders observed is practically equal to the radius of the smoke particles, in tenth-microns. Our smokes were 3 or 4 order, *i. e.*, 0.3 or 0.4 μ in radius. This method of determining particle size, based on an interpretation of Gustav Mie's theory of light scattering,[9] was developed by LaMer and Sinclair[10] in their work for the NDRC.

When we found that our apparatus counted DOP smokes as small as 0.3 μ radius, we then carried out some experiments with a smoke of spores of *Bacillus globigii* (BG), set up with an apparatus furnished by the group with which we coöperated at Camp Detrick. The aqueous suspension of the spores at 1 to 200 $\times$ 10^8 per ml. was sprayed through a nebulizer[11] into a mixing chamber where it was mixed with a stream of dry air as shown in Fig. 4 to give an aerosol of dry spores. Tests at Camp Detrick showed that practically all the resulting particles contained only single spores. The spores are ellipsoidal, with a major axis averaging about 1.2 μ and a minor axis of about 0.8 μ as shown by electron photomicrographs. The aerosol could be made up to 10^7 spores per liter, or about 5μg./liter, but the usual test smoke contained about 10^6 spores (0.5 μg) per liter. Although care was taken to purify the original aqueous suspension, it was found to contain appreciable foreign particles from the nutrient medium.

The smoke generator and flow line were arranged to furnish smoke to the counter at a pressure slightly above atmospheric. If the smoke is sucked through the cell, special care must be taken to seal all joints and all connections perfectly, since a small percentage of room air will give a very high background count. Unfiltered laboratory air passed through the cell may contain far more than 1000 particles per liter. This number cannot be readily counted with the instrument.

Experimental Methods

Adjustment of the Smoke Cell.—The 50-c. p. lamp is clamped with the V-shaped filament in the plane of the optical axis. The cell is removed from its base, swept out with air, and adjusted in the dark room.

Air at 3 liters per minute (l. p. m.) is passed

(8) Unpublished report, 1941.

(9) G. Mie, *Ann. Physik*, **25**, 377 (1908).

(10) Unpublished report, 1941. V. K. LaMer and Irving Johnson, THIS JOURNAL, **67**, 2055 (1945), "Observations on the Angular Scattering of Light by Sulfur Sols."

(11) Made by the Vapo-Nefrin Co., Upper Darby, Pa.

through T_2 (Fig. 1), while 4 l. p. m. is drawn out through T_3. Thus 1 l. p. m. is drawn through T_1, which may be connected through a piece of rubber tubing to a flask filled with cigaret smoke. An image of the illuminated smoke stream at J is thrown upon a thin sheet of paper fastened over the end of the diaphragm support O. The bulb is adjusted to form a uniform image of the smoke stream, white in the middle and somewhat red around the outside, in the center of the shadow of the diaphragm N. After adjusting the lamp, the tube O is removed and the cell viewed through the lens L_3. Some background illumination will be seen, but there should be no bright regions. A bright ring around the edge of the black disk I indicates that its size should be increased. This disk should be just large enough to cut off all illumination of the cell K by the direct beam.

Arrangement of Apparatus.—The electrical circuits are connected as shown in Figs. 2 and 3, with all switches turned off. First the *transformer, heaters* switch is closed, turning on the transformer and heaters of the rectifiers and the thyratron. After about fifteen seconds, when the filament of the 83-tube has warmed up, the *rectifier-power* switch can be closed. Then the battery is connected to the 50-c. p. light, and the *heaters* and *amplifier supply* switches are turned on. The 10-K resistor across the *off* position of this last switch prevents the overloading of the first bank of VR tubes whenever the amplifier unit is disconnected.

In making measurements with the counter, the smoke is introduced at 1 l. p. m., measured by difference to avoid using a flow meter in the smoke line. The rate of flow of the air sheath is set at 3 l. p. m., and the smoke adjusted to bring the effluent flow to 4 l. p. m. Both are measured on calibrated flow meters.

Before use, the cell is flushed out with carefully filtered air at 3 l. p. m. until the dust count has fallen to 1 per minute or less. The complete removal of dust in the air sheath is necessary when measuring background counts in the instrument. We found that 2 sheets of the best grade service-canister filter paper, or 2 complete pleated filters fastened into a canister were satisfactory, *after air had been passed through them at 3 l. p. m. for several hours, or preferably overnight.*

Oscilloscope Tests.—If the background exceeds 1 count per minute, an oscilloscope is connected across the output of the amplifier, with the thyratron circuit turned off. Careful shielding and removal of a. c. appliances will reduce the 60-cycle ripple to a few volts with the random background fluctuations appearing as a heavy "hash" superposed upon it. The background noise level can be evaluated by covering the screen with a horizontal strip of paper, and raising this until the number of pips per minute appearing above it is reduced satisfactorily. The voltage corresponding to the height of the strip is read from the calibration curve of the oscilloscope. We found a normal background level of less than 1 count in ten seconds above 10 volts, at an amplification of 200,000. These pulses are separated from the particle counts by proper setting of the *discriminator*.

The appearance of the high-frequency electrical background pulses is very different from the particle pulse of about 0.003 sec. duration, and this helps distinguish electrical background from dust particles. When a thalofide cell is used, turning off the 50-c. p. light only changes the oscilloscope pattern appreciably if the pulses are from dust counts or a defective cell.

Tests of the Counter with Thalofide Cell

Two questions arose in connection with the functioning of the instrument: (1) Will it give a true indication of the particulate concentration of the very dilute aerosols of the type encountered in filter testing? (2) What is the practical range of the instrument in its present form, *i. e.*, without a scaling circuit or rate meter?

The first question is hard to answer unequivocally, in the absence of a proved standard of comparison. Obviously particles below a certain size will be missed because of the rapid decrease of light scattering with size. However, if every particle in a very dilute aerosol is safely above the critical size, and if the whole cross section of the smoke stream at J is illuminated with equal intensity, no particle should escape the counter. To determine whether or not any of the spores in the BG test smoke failed to register in the counter, comparisons were made at Camp Detrick between the counts with our apparatus and the number of viable spores collected on a cotton impinger, determined by the number of colonies grown on agar plates incubated twenty-four hours. In these early experiments, we obtained counts exceeding the number of viable spores, thus suggesting the presence of additional particles presumably including some non-viable spores, and also extraneous matter. This hypothesis was later confirmed by studies of electron microphotographs. Later experiments showed less counts than viable spores, and indicated that a certain fraction of the particles do not register on the counter.

Since the counter and the biological tests measure different quantities, filter tests with either system must be made self-consistent. Counts from the raw smoke were above the range of our instrument, hence we reduced them to a known fraction by passing the smoke through a filter of measured transmission, or a smoke-dilution apparatus.

Two methods were used to determine the upper limit of the present counter, both depending on comparisons with the photoelectric penetrometer[6] previously developed.

The first method employed a constant filter pad of low penetration. The influent smoke was reduced by an initial filter to a point where it gave a reading on the penetrometer which could be measured with an accuracy of 5 or 10%. The filter pad was chosen to give an effluent smoke of 10–20 counts per minute in the counter. In a series of tests, the influent concentration was increased in steps, by changing the initial filter, and measured by the penetrometer current, C in $\mu\mu$-amp. (10^{-12} amp.), while the effluent particulate concentration c was measured with the counter. The ratio (C/c) is plotted against counting rate c, and extrapolated to 0, where $(C/c)_0$ represents the limiting ratio at a very low counting rate. As the counting rate increases (C/c) increases and the value of $(C/c)/(C/c)_0$ is the count-rate factor necessary for the counter at the corresponding rate. With DOP smokes this method checked satisfactorily with the second method described below, but with BG smoke it was unreliable, due probably to clogging of the filter at the higher influent concentrations. Later, however, we developed a smoke-dilution apparatus which obviated this difficulty.

The second method, which gave consistent results with both smokes, employs a variable filter pad, made of individual sheets the penetrations of which are measured at higher concentrations with the smoke penetrometer, and a dilute influent smoke, of constant concentration, checked with the penetrometer. The experimental arrangement is shown schematically in Fig. 4. Counts are made on the effluent smoke from the pads. Counts per minute (equal to counts per liter) c_2 divided by the fractional penetration P measured with the penetrometer, should give a constant value of the influent counts, $c_1 = c_2/P$. Actually c_1 calculated in this way decreases with counting rate c_2, due to missing of counts at high rates. Extrapolation of calculated values of c_1 to low counting rates gives a value which can be used to determine the count-rate factor as before.

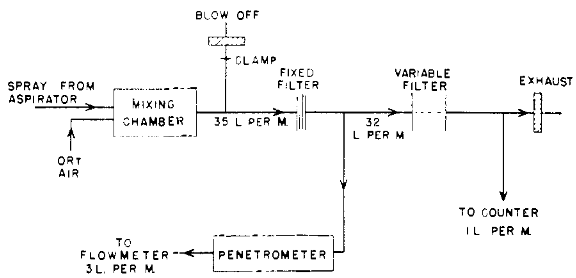

Fig. 4.—Flow line for testing counter.

Figure 5 shows the results obtained by Sgt. A. Cohen and Cpl. W. Voelker at Camp Detrick. The values of c_1 calculated from counting rates up to 500 per minute were averaged, since they showed no systematic trend. This average, divided by c_1 at each rate, gives the count-rate factor shown in Fig. 5. Counts up to 1000 per minute can be made with no factor, and the practical range of the counter is about 3 to 1200 counts per minute. With an inlet concentration of 10^8 per liter, and a background count less than 1 per minute, the range of the instrument is about 3 to 1200 micro per cent. By decreasing the influent concentration with filters of known penetrations, measurements may be extended to any desired filter, but the counter is less convenient than the penetrometer for measurements in the range where the latter can be used.

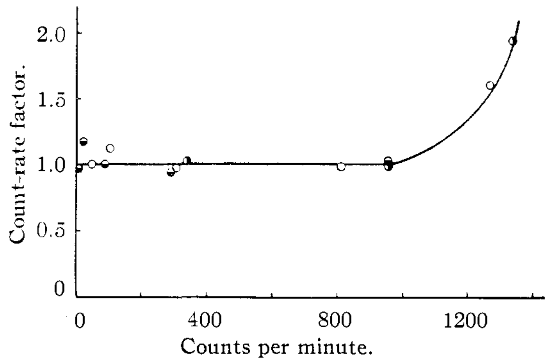

Fig. 5.—Count-rate curve for BG smoke, showing results obtained by Sgt. A. Cohen and Cpl. W. Voelker on three consecutive days: O, run 1; ◑, run 2; ◒, run 3.

Comparative Tests with Thalofide and Photomultiplier Tubes

In the summer of 1946, a counter using a thalofide cell was built in our Laboratory by Mr. Leo E. Farr for the use of Dr. Ronald M. Ferry of the Harvard Medical School. At that time we were experimenting with 931-A tubes in our apparatus, and we made a careful series of tests to compare the behavior of the two instruments and to obtain the count-rate curves, using the smoke penetrometer readings calibrated in terms of spore concentrations. The BG generator was operated with a constant pressure of 6 lb. per sq. in. on the atomizer, and a constant flow of 25 l. p. m. of mixing air, giving a total flow of 30 l. p. m. A suspension of BG obtained from Camp Detrick had been found there to contain 4×10^9 viable spores per ml. Portions of this were diluted with water to give relative concentrations $^1/_{16}$, $^1/_8$, $^1/_4$, $^1/_2$ and $^3/_4$ of the original suspension. It was thus possible to produce raw smokes in which the relative concentrations of viable spores, and presumably of other particulate matter, varied over a considerable range, while the relative humidity, which might affect the scattering power of the particles, remained constant.

A sample of the raw smoke was passed through our penetrometer, in which the photocurrent was measured 10 times or more, at about one-minute intervals over the time required to atomize a measured quantity of suspension. Another portion of the raw smoke passed through a quantitative 3-stage diluting system designed to avoid the selective removal of different-sized particles in a filter. Tests of the stages individually showed that the diluting system reduced a smoke to 0.030%

of its original concentration. Samples of the diluted smoke were passed through the two counters, in which the counting rates were measured about 10 times for each suspension. Both counters were operated with gains adjusted to about 3 counts per minute background, and with discriminators set about 20 v. above the firing point.

From the data we calculated the ratio r between concentration s (spores per liter of aerosol) and penetrometer current C in $\mu\mu$ amp. from the equation

$$r = s/C = nS/F\overline{C}t$$

where n is the number of ml. of suspension, containing S spores/ml., atomized in t minutes, F is the total smoke flow through the generator, in l. p. m., and $\overline{C}$ is the average current. We determined $\overline{C}t$ by graphical integration under the curve of C versus t.

The results given in Table I show only random deviations from the average value of r, over a 16-fold range of smoke concentration, indicating that the penetrometer readings and dilution factor are self-consistent over this range.

TABLE I

PENETROMETER CALIBRATION IN SPORES PER LITER PER MICROMICROAMPERE

$10^{-9}S$	n	$\overline{C}t$	$r = nS/F\overline{C}T$	Deviation from $\bar{r}$, %
0.25	2.0	444	37600	+12%
.25	2.0	575	28500	−15
.5	2.0	862	38700	+15
1.0	2.0	2190	30400	− 9.5
2.0	2.0	4190	31800	− 5.4
3.0	2.0	5760	34700	+ 3.3
4.0	2.0	8080	33000	− 1.7
4.0	1.0	3960	33800	+ 0.6
Av. spores × l^{-1} × $\mu\mu$ amp.$^{-1}$, $\bar{r}$ =			33600	± 7.8

The data necessary to calculate the count-rate factor are given in the first 5 columns of Table II. The results enabled us to determine the ratio of counts to spores from the equation

$$\text{counts/spores} = c/CrD$$

D is the dilution, expressed as a fraction. Substituting the values of $D = 0.00030$, $r = 33600$

$$\text{counts/spores} = 0.099c/C$$

The average value of C/c for the thalofide counter was 0.31, while for the photomultiplier counter it was 0.21, giving a ratio of counts to viable spores of 0.32 in the first case, and 0.47 in the second. Later readjustment of the lens in the thalofide counter to focus more of the red on the cell increased the counting rate by a factor of nearly two, giving a value of about 0.6 count per viable spore.

These results indicate that the present apparatus does not respond to every particle in the smoke. This fact was obscured by a numerical error in the calculations outlined above, which was not discovered until the article was in proof. At the present time (September, 1947) a small optical probe has been developed, and we have made a preliminary survey of the 4-mm. field illuminating the smoke stream at J. This field is much less uniform than it had appeared to our earlier visual observations. Probably a fraction of the particles are not illuminated strongly enough to register on the cell. We find that a concentrated arc lamp[12] and a pair of achromatic lenses give a much more uniform illumination. It is hoped that this new optical system will eliminate the counting error, and also will reduce the stray light.

Uses of the Particle Counter

Beside its use as a penetrometer to test the best filters which can be produced, the counter has a number of other applications. One of these instruments is now in use by a group at Harvard University, where its utility is being appraised in a study of bacterial aerosols. It may have wide applications in bacteriology. In testing contamination of a system where sterile conditions are desired, the dust in a trace of room air will show up instantly in the counter, whereas the accompanying bacterial contamination will not appear until hours later in the ordinary plate counts.

TABLE II

CALCULATION OF COUNT-RATE FACTORS FOR BG SMOKE IN COUNTERS USING THALOFIDE AND PHOTOMULTIPLIER CELLS

Av. C ($\mu\mu$a.)	Av. counts per liter 931-A C-1[a]	931-A C-2	Thalofide C-1	Thalofide C-2	Av. C/c 931-A C-1	931-A C-2	Thalofide C-1	Thalofide C-2	Count-rate factor[b] 931-A C-1	931-A C-2	Thalofide C-1	Thalofide C-2
23.5	110	106	69	78	0.21	0.22	0.36	0.31	1.00	1.09	1.09	1.07
42.8	204	202	147	158	.21	.21	.30	.28	1.00	0.95	0.91	0.97
94.8	449	432	293	340	.21	.22	.33	.28	1.00	1.00	1.00	.97
194	718	773	537	576	.27	.27	.36	.33	1.28	1.23	1.09	1.14
308	987	1039	711	832	.31	.30	.43	.37	1.47	1.36	1.30	1.28
377	1079	1180	852	989	.35	.32	.44	.38	1.67	1.46	1.33	1.31

[a] C-1 and C-2 refer to counters 1 and 2. [b] Based on limiting values of 0.21, 0.22, 0.33, and 0.29, respectively, for C/c obtained by averaging the results at the 3 lowest concentrations.

The first three values of C/c were found to be constant for both counters, hence the instruments are self-consistent up to about 350 counts per minute. The average of these 3 values in each column is used in calculating the count-rate factors shown in the last 4 columns.

(12) Made by the Western Union Telegraph Company.

The counter could also be adapted to liquid systems and used in making counts of suspended cells of various kinds, which could be distinguished by different settings of the *discriminator* if they differed enough in their light-scattering properties.

The 931-A tubes, with which we are now experimenting, have a much better high-frequency response than the thalofide cell. If we can refine the optical system and reduce stray light greatly, the background noise of the 931-A tube can be cut below that of the thalofide cell and the counting range extended to smaller particles. We are also working to determine the size of smoke particles individually and rapidly by means of these techniques. If uniform illumination is achieved, the size of the light pulse will characterize a spherical smoke particle. Otherwise, simultaneous determination of the pulses sent at two different angles to the light beam, or of the components of the pulse polarized perpendicular and parallel to the plane of observation, will allow a calculation of the particle size from the Mie[9] theory of scattering. A rapid method of determining particle-size distribution may answer a number of puzzling questions about the difference in the filtration of smokes which appear to have the same average particle size.

Comparison with Guyton's Particle Counter

Apparently the only other automatic particle counter comparable with the present apparatus was developed by Arthur C. Guyton[13] at Camp Detrick between June and October, 1945. The principle of operation is entirely different from ours. In his apparatus, the test smoke is forced through a fine jet at high velocity, to impinge upon a metal collector placed very close to the jet. A solid dielectric smoke particle transmits to the collector an electrical pulse of about 50 microseconds duration, the voltage of which is proportional to the square of the diameter of the particle Just how the pulse is produced is not clearly understood, but apparently it is due to static electricity generated by friction against the collector. Solid conducting particles and aqueous drops produce weak pulses. However, charging the collector increases these pulses in direct proportion to the potential applied. The original pulses are put through a 4-stage amplifier with a gain of 100,000, followed by an oscilloscope for visual observation or a thyratron circuit to operate a mechanical counter. An electrical discriminator limits the counting to particles above a chosen size, so that the apparatus serves to determine relative size distribution. Guyton's counter was not sensitive to particles less than about 2.5 μ in diameter. He stated that this limitation was due to the amplifying circuit, which he considered capable of improvement so that it would respond to particles of 1 or even 0.3 μ diameter. The simplicity of the pulse pickup in Guyton's counter should encourage further study to determine the theory of its operation and its practical limitations. Only after further study of the photoelectronic counter also will it be possible to compare the advantages and disadvantages of the two systems.

(13) A. C. Guyton, *J. Ind. Hyg. Toxicol.*, **28**, 133 (1946).

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Mr. Norman Nachtrieb for the construction of the original smoke cell unit, and to Mr. John E. Kamper for the construction of the later model, to Mr. Wendell Weber for assistance in some of the tests of the instruments, and to Mr. Elmer Engquist and Miss Betty Hengeveld for help in the preparation of the drawings.

Summary

We have described the construction and operation of a photoelectronic counter, utilizing the flashes of light scattered by colloidal particles traversing a small space under brilliant dark-field illumination. The stray background count may be made less than 1 per minute. The device was tested with uniform dioctyl phthalate aerosols of diameter down to 0.6 μ (10^{-13} g. per particle) and with aerosols of ellipsoidal spores of *Bacillus globigii* averaging about 0.8×1.2 μ (5×10^{-13} g. per particle). The practical range of the counter, without a scaling circuit, is from 3 to 1200 counts per minute. At present, a certain fraction of the particles is missed, apparently because the smoke stream is not uniformly illuminated.

Tests of respirator filters can be made with a sensitivity of $10^{-8}\%$ using concentrated aerosols of dioctyl phthalate which may contain up to 10^{10} particles per liter.

The principle of the apparatus should have wide application in colloidal chemistry, bacteriology, biology and industry.

EVANSTON, ILLINOIS RECEIVED MARCH 20, 1947