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NATIONAL BUREAU OF STANDARDS REPORT

4923

FIRE EXTINGUISHMENT BY MEANS OF DRY POWDER

by

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U. S. DEPARTMENT OF COMMERCE
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FIRE EXTINGUISHMENT BY MEANS OF DRY POWDER¹

ABSTRACT

The theory that dry chemical extinguishment results from the release of carbon dioxide has been disproved by successful use of inert powders. Optical measurements of the effect of dry chemical in shielding the fuel from the radiant energy of the flame indicate that in full scale fires, most of the energy can be blocked. The minimum powder concentration required has been measured. On a small fire this concentration was of the order of 10^{-4} gm/cm³. Although the effectiveness of dry chemical may be largely attributable to the interruption of combustion chain-reactions, these results indicate that radiation shielding is a significant factor.

1. Introduction

A common type of commercial fire extinguisher is charged with dry powder which is expelled by the discharge of compressed gas. The powder, known in the trade as "dry chemical", is finely-ground sodium bicarbonate with small amounts of additives to improve its flow properties. Numerous experiments have demonstrated the effectiveness of such extinguishers in fighting flammable-liquid fires. In a series of tests to determine the relative effectiveness of various types of small portable devices, commercially available four and five pound dry-chemical extinguishers proved equal to 10 pound carbon dioxide extinguishers on flammable liquid fires of ten different conformations. The Factory Mutual Laboratories consider dry-chemical extinguishers about twice as effective as carbon dioxide extinguishers of equal weight capacity on the basis of the relative areas of gasoline spill fires for which these devices are considered adequate protection (1)².

¹This paper was originally presented at the Sixth International Symposium on Combustion in August 1956.

²Numbers in parenthesis indicate references given at the end of the paper.

Although dry sodium bicarbonate has been used in one manner or another since the beginning of this century, or before, the prototype of our modern dry chemical did not appear until 1928, when D. J. Block applied for a patent on a dry chemical composed of sodium bicarbonate with enough magnesium stearate added to keep the powder free flowing(2). About 1943 it was found that the effectiveness of the extinguishers was somewhat improved by the use of more finely powdered material. Fire-fighters generally believed that the sodium bicarbonate decomposed when heated and liberated enough carbon dioxide to extinguish the fire. This belief seems to have been the basis upon which the dry-powder method of extinguishment was developed.

As plausible as the carbon dioxide theory seemed, it was not very satisfactory when considered quantitatively. On this basis, how could five pounds of sodium bicarbonate be as effective as 10 pounds of pure carbon dioxide? If it were completely decomposed, the sodium bicarbonate would liberate about 26 percent of its weight as carbon dioxide. Samples of dry chemical were collected after an actual extinguishment and were quantitatively analyzed. According to this analysis less than 15 percent of the bicarbonate had decomposed, therefore less than four percent by weight of the powder was liberated as carbon dioxide. It appears that the carbon dioxide theory which motivated the development of the dry chemical extinguisher does not account for a large part of the extinguishing action.

The ultimate objective of the investigation of which this work was a part was to determine the mechanism of dry chemical extinguishment.

2. Mechanisms of Extinguishment

A brief consideration of the general nature of flammable-liquid fires suggests some possible mechanisms. Once the vapors are ignited, the flame provides heat to vaporize more fuel. The rising vapors are heated by the energy liberated in the reaction zone until they are hot enough to react and produce more heat. The reactions occurring in hydrocarbon flames are not well known but spectral studies and other experiments indicate that they are complex branched-chain type reactions involving short-lived free radicals which carry the impetus of the reaction to succeeding links in the chain (3). In a continuous cycle, the flame heats the fuel and the heated fuel and oxygen feed the flame. Any mechanism which interrupts this cycle extinguishes the flame.

There are a number of conceivable physical mechanisms of extinguishment of flammable-liquid fires, including the following:

1. Throttling. The influx of fuel is stopped.
2. Cooling. So much heat is removed that combustion ceases.
3. Blowing-out. The velocity of the gaseous fuel or air exceeds the velocity of the combustion wave and the combustion wave recedes, finally disappearing as a result of other mechanisms.
4. Smothering. The influx of air or oxygen is stopped.
5. Diluting. Inert gas is mixed with the atmosphere.
6. Shielding. Material is interposed between the flame and the fuel to prevent the transfer of energy by radiation.

Chemical mechanisms of extinguishment include the following:

1. Chain-breaking. Material is introduced into the flame so that potentially reactive particles encountering this material will not propagate the reaction chain.
2. Preferential oxidation. A material with a strong tendency to unite with oxygen is introduced into the flame so that the available oxygen combines with the extinguishing agent rather than the fuel.

It is quite likely that this list of mechanisms is incomplete, but it will serve as a basis for the present discussion.

3. Preliminary Experiments With Various Powders

In view of the many conceivable mechanisms, it was felt that the more likely ones should be determined by a comparison of the effectiveness of a variety of powders in extinguishing gasoline fires. Powders were selected on the basis of their physical properties. The fineness ranged from 85 percent through 200 mesh to over 85 percent through 400 mesh. Three tests were performed on each powder, under actual fire-fighting conditions. The fuel, 5/8 gallon of leaded gasoline, was placed on a slightly indented 4 x 4-ft concrete surface, ignited and allowed to burn five seconds before the extinguisher was discharged into the fire. An effort was made to keep the discharge operation uniform for various powders, the extinguisher being aimed at the base of the flames and advanced slowly while sweeping from side to side. The extinguisher was a commercial "stored-pressure" device of 2.5 lb capacity, pressurized with dry nitrogen at 350 psi gage. The powder charge weighed 2 to 2.5 lbs, depending on the bulk density of the powder. The average discharge rate ranged from 0.4 to 0.5 lb/sec for the various powders.

Extinguishment efficiency was based on the average time rate of extinguishment or extent to which flames were suppressed, as evaluated by two observers. The most effective powders were rated +3, the least effective -3 and the others were rated between these values in algebraic order. Positive numbers were used if the fire was extinguished, negative numbers if not. The most easily dispersed powders were rated A, the least C, on the basis of visual observation during use. Table 1 lists the various powders, some of their properties, and their extinguishment efficiencies. In the table, the powders are listed in order of apparent effectiveness based on efficiency and dispersibility.

To determine whether or not the discharge was merely blowing the fire out, an extinguisher charged with dry nitrogen at a pressure of 450 psi gage was tried. The gas discharge fanned the flames and increased the intensity of the fire. This result shows that the flame is not merely blown out by the discharge of a dry chemical extinguisher, and also indicates that the mechanism by which such devices operate is neither smothering nor diluting, for these mechanisms should be provided as well or even better by the inert gas.

It is noted that immediately after extinguishment the fire could be reignited, indicating that the powder was not forming a film on the gasoline and throttling the fire.

The effectiveness of borax and silica proves that the release of carbon dioxide is not the principal mechanism of extinguishment by means of dry powder. The results shown in table 1 seem to indicate that the combination of fine particle size and good dispersibility is an important requirement for extinguishment by means of dry powder. The salts of the alkali metals were more effective than other types of materials tested.

Among the materials tested, there was no observable correlation between the effectiveness of powders and their heat capacities. The amount of energy required to heat one gram of each material from 18°C to 300°C was calculated and is shown in table 1. Heat of reaction was included where decomposition or dehydration would occur. With the materials listed in order of effectiveness, there is no apparent order among the heat capacities. It must be noted that mechanisms involving the heating of particles are not necessarily ruled out by this observation alone, since heat transfer phenomena are not governed only by heat capacity. Nonetheless, heat transfer theory shows that heat transfer from gases to fine particles is very efficient, due to the high surface to mass ratio involved.

The results of these preliminary experiments indicated that the mechanisms of throttling, cooling, blowing-out, smothering, and diluting are of minor importance if operative at all. Since the preferential oxidation theory was inapplicable to the best dry powders tested, the original list of mechanisms under consideration was reduced to two principal mechanisms, shielding and chain-breaking. These mechanisms would depend upon the projected or other area of material in a cloud and therefore would require fine particle size and good dispersibility, in accord with the results of these experiments. There is a considerable amount of corroborating evidence for these conclusions, based upon combustion experiments not simulating fire-fighting conditions (4, 5, 6, 7, 8).

4. Optical Properties of Dry Chemical

In order to determine the possibilities of the shielding hypothesis, measurements were made of some optical properties of commercial dry chemical dispersed in the air. Measurements were made to determine how much of the incident radiant energy would be transmitted undeviated through a cloud of powder and how much would be deflected through various angles. It was felt that, with the aid of the theory of scattering, the deflection measurements might reveal information concerning the relative magnitudes of the effective particle diameters and the wavelength of the bulk of the radiant energy.

Since commercial dry-chemical extinguishers discharge powder at a rate which is initially very high, and which decreases very rapidly, they were not considered suitable for use in controlled optical experiments. It was found that commercial dry chemical would remain on a fixed 100 mesh sieve but would flow if the sieve were vibrated. This fact made it possible to dispense a stream of powder which could be irradiated and observed under controlled conditions. The powder was placed in a light metal cylinder 12 cm in height and 5 cm in diameter, open at the top and bottom, resting on the center of a round 100 mesh sieve 20 cm in diameter. An electric vibrator was used and the rate of powder discharge was controlled by adjusting the voltage on the vibrator. To avoid interference from particles floating around in the air, a vacuum cleaner was used to remove the powder as it fell. The vacuum cleaner was equipped with a conical attachment 20 cm in diameter placed 20 cm below the dispensing sieve. At this distance, the exhaust system had no apparent effect on the free fall of the powder in the first 8 cm of fall. The diameter of the falling powder stream contracted from 5.0 cm at the sieve to 4.0 cm at 2.5 cm below the sieve and remained fairly constant for an additional 5 cm. On the basis of previous estimates of the discharge rate

employed in fire-fighting, the powder was discharged so that its flow rate was $0.012 \text{ gm/sec-cm}^2$ in the region under observation.

Measurements were made using radiant energy in the visible region of the spectrum and in the infrared. For the visible region, the optical system consisted of a 100 watt incandescent lamp, projection lenses, a photovoltaic cell, and a recording potentiometer. The photocell was mounted so that it could view the powder stream from various angles. The lamp and photocell combination gave an effective spectral distribution similar to the relative visibility curve for the normal human eye but shifted about 0.05 micron toward the long wavelengths.

Previous investigations had shown that the spectral distribution of the energy emitted by hydrocarbon diffusion flames is similar to that of a black body at 1470°K , having a maximum in the infrared at a wavelength of about 2 microns (9). To approximate this distribution, an electrically powered hot-wire source was operated at 1200°K and gave a spectral distribution with a maximum around 2.4 microns. A radiation pyrometer was used as a detector.

Measurements were made of the fraction of the incident energy which was transmitted directly and the fraction deflected through angles from 30° to 150° at 15° intervals. The observed relative intensities of the deflected energy are shown in figure 1. It was found that 85 percent of the visible light and 81 percent of the infrared energy were transmitted directly through the 4.0 cm stream. There was much more energy deflected at forward angles than at backward angles and the observed relative intensity of deflected energy (within the angular range covered) was two to five times as great in the infrared as it was in the visible. This would be expected if the particle diameters were greater than the effective wavelength of the infrared source. An independent analysis of the particle diameter distribution with a Roller Analyzer (an elutriation type separator) indicated three percent by weight less than 10 microns, 14 percent from 10 to 20 microns, 38 percent from 20 to 40 microns, and 45 percent above 40 microns.

In a gasoline spill-fire on an area four feet square, flames often rise six to eight feet in the air. The powder cloud used in extinguishing such fires would have a depth of the order of 45 cm. If the concentration were the same as that of the powder stream in these experiments and Bouguer's exponential law of transmission may be assumed,

it appears that less than 10 percent of the energy radiated in the direction of the gasoline would be transmitted by the powder cloud. It would seem that this effect should make a substantial contribution toward the extinguishment of the fire.

If the shielding effect is a substantial part of the mechanism, and the size distribution of particles in the dispersion is that indicated above, one would predict on the basis of optical principles that powders having a larger part by weight in smaller particles would be more effective if the small particles were discrete in the dispersed state. The preliminary experiments seem to show such a trend for the range of particle sizes used.

5. Transmittance Measurements During Extinguishment

The uncertainties involved in interpreting laboratory data in terms of fire-fighting conditions made it desirable to simulate actual conditions. For this reason, a group of measurements was made of the effect of dry chemical on the radiant energy from a flame during actual extinguishment. The objective was to determine how much of the energy radiated toward the fuel was transmitted by the dry chemical cloud. The adverse conditions at the surface of the fuel made it impractical to place a detector there, so a burner was constructed with a window in the bottom. The burner was a thin steel cylinder 10 cm in diameter and 6 cm deep, open at the top. The window in the bottom was made of clear fused quartz.

The powder was placed in a cylinder 8 cm in diameter and 45 cm in height with a compressed air inlet at the bottom and a nozzle at the top (figure 2). The 1 x 10 mm nozzle opening discharged a stream having a cross section of greater width than height. To avoid the transient flow conditions produced when the compressed air was turned on or off, the extinguisher was allowed to discharge continuously. Except when it was desired to apply powder to the flame, the powder stream was caught by a funnel connected to a vacuum dust collector. The funnel could be pulled aside for a given time interval, by means of a solenoid and an electronic timer. This arrangement provided short bursts of powder with a nearly constant flow rate during the discharge.

A lead sulfide infrared photoconductive cell was placed below the window to detect the energy radiated toward the fuel and another such cell was placed above and to one side of the burner to detect the energy radiated in that direction. This arrangement is shown in figure 2. In

order to limit the effect of radiation from other sources, infrared filters were used to limit the spectral sensitivity of the detectors to the wavelength region from 0.7 to 2.6 microns.

The fuel was a commercial mixture of heptanes with a boiling point range of about 88°C to 100°C. This fuel was chosen because it represents a major component of gasoline, the most common hazardous flammable liquid, but has a much more uniform burning rate in a spill-type fire. The fuel was floated on a thin layer of water to prevent overheating of the window and its mounting gaskets. The thickness of the water layer was 1.1 cm and the thickness of the fuel layer was 0.4 cm at the start of the experiment. The metal rim of the container extended about 3 cm above the fuel level. When the burner had warmed up, the flame measured about 10 cm in diameter, at its widest part, and about 40 cm in height.

In the part of the spectrum used, thin layers of water and quartz transmit nearly 100 percent at all wavelengths. A 4 mm layer of heptane transmits nearly all energy in the wavelengths from the visible spectrum to 1.6 microns with the exception of sharp absorption bands at 1.25 and 1.45 microns, and about 77 percent from 1.6 to 2.3 microns, with the exception of a narrow absorption band at 1.7 microns. Thus the spectral sensitivity of the lower detector was little different from that of the upper one. There was practically no change in these absorbing layers during the small fraction of a second involved in making a measurement. Aside from these considerations it was not necessary to take into account the transmittance and reflectance of these various layers because only relative values of the irradiance at the receiver were required for transmittance measurements.

In the usual measurement of transmittance, a radiant source of constant intensity is employed and a determination is made of the ratio of the relative amounts of energy received with and without a sample interposed between the source and receiver. In the present case, the source was a flame which decreased in intensity when the powder cloud was injected. The upper detector measured the decrease in intensity in the upward direction and it was assumed that the intensity in the downward direction changed in the same ratio. The transmittance, measured by the lower detector, was then corrected for the decrease in flame intensity.

Because the extinguishment occurred so quickly, it was necessary to record the data with a high speed automatic recorder. The recorder used was essentially a row of 2-inch cathode ray oscilloscopes that were photographed simultaneously by a 35 mm camera in which the film was exposed continuously as it moved at right angles to the deflections of the spots on the tubes. The output of a 40 cps fixed frequency oscillator was applied to one channel to provide a time scale.

The radiant intensity of the flames dropped very rapidly after the appearance of the powder. The time required to extinguish the flame averaged about 200 milliseconds as observed by means of the upper detector but only about 170 milliseconds as observed by means of the lower detector. During the time that the radiant intensity was diminishing, slight fluctuations in the intensity produced relative maxima and minima in the two radiometric records. The measurements of transmittance were made at the maxima because such corresponding points on the two curves presumably represented events which occurred simultaneously.

Thirty measurements of this kind were made with the powder concentration near the minimum value required for extinguishment. The average transmittance was found to be 53 percent. This result seems to support the belief that even in a small fire, the shielding effect of the powder may contribute materially to the extinguishing process. The cloud of powder used in these experiments had a depth of about 6 cm. In larger fires, where thicker and more concentrated clouds are used, a somewhat greater effect would be likely.

6. Concentration Measurements During Extinguishment

Quantitative considerations of the mechanism of extinguishment hinge ultimately upon knowledge of the concentration of material required for extinguishment. The relative effectiveness of different powders can be expressed quantitatively if the minimum effective concentration of each is known. The quantitative control of concentration during a series of experiments depends upon measurement of concentration. A satisfactory method of measurement should give the concentration during extinguishment. Direct sampling techniques were not employed because such methods disturb the distribution of the powder and disrupt the normal course of events during extinguishment. To avoid these difficulties, optical methods were employed to measure several related physical quantities from which the concentration was calculated.

The average weight rate of discharge for a time period of a few seconds could be obtained by direct weighing and timing, but during a small fraction of a second the weight change was too small to be differentiated from variations in the recoil of the discharging cylinder. It was found that the average rate of discharge was proportional to the average optical density of the powder stream. (This is a manifestation of Beer's Law, usually applied to the relationship of optical density and concentration in solutions.) This fact was utilized in calculating the instantaneous rate of discharge from the optical density of the powder stream measured by projecting a light beam through the stream onto a photoelectric cell and recording the response automatically.

Another such photoelectric system was placed a fixed distance downstream and when a short burst of powder was injected the elapsed time between the appearance of powder at these two points was recorded. The burner was placed below a point midway between the light beams as shown in figure 2. The data obtained were used to calculate the velocity of the stream at the burner. The average observed velocity was 43 cm/sec.

A photoelectric system such as those described was used to scan the stream horizontally and vertically at the burner position to determine the distribution of the powder in the stream. The distribution determined in this way appeared to be nearly uniform over an area approximating an ellipse and to drop rapidly to zero outside this region. From the plotted density, an estimate was obtained of the lengths of the axes of an ellipse which would encompass all of the powder if it were uniformly distributed. This ellipse had axes of 6 and 10 cm, giving an area of 47 cm².

The measured values of weight rate R , velocity v , and cross sectional area A were used to calculate the concentration of powder c by means of the equation $c = R/vA$. All of these measurements, except the area scanning were recorded simultaneously with the transmittance measurements during extinguishment by the use of six channels on the oscillograph. It was found that when the concentration exceeded 2.8×10^{-4} gm/cm³ the flame was always extinguished but when the concentration fell below 0.7×10^{-4} gm/cm³ the flame was not extinguished. At concentrations between these values, both successes and failures were recorded. These values may be applicable to this flame only but the order of magnitude is established for theoretical considerations. The technique described here was the only practical method of concentration measure-

ment found which met the conditions imposed by the nature of the experiments.

7. Conclusions

The theory of extinguishment involving the evolution of carbon dioxide is not satisfactory because powders that do not release carbon dioxide are effective agents. The combination of fineness and dispersibility of powders appears to have some correlation with their effectiveness. Salts of alkali metals appear to be particularly effective. The evidence indicates that the mechanism of dry-powder extinguishment is not principally that of excluding oxygen, diluting the atmosphere, cutting off the fuel supply, or blowing out the fire. A minimum concentration of the order of 10^{-4} gm/cm³ of commercial dry chemical is required to extinguish small fires involving heptane under the conditions of the experiments. In the light of prevailing theories of combustion and flame propagation, it appears that dry-powder extinguishment may be largely attributable to the interruption of chain-reactions in the combustion process. The rapidity of the action, the apparent dependence of effectiveness on fineness, and the small concentration required, as determined in these experiments, seem to support this view. However, it appears that a full account of the mechanism of dry-powder extinguishment of flammable-liquid fires must also include the factor of radiation shielding.

8. References

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The Properties and Effectiveness of Various

No.	Powder ¹	Special Characteristics
1	Potassium bicarbonate with 2% zinc stearate	Decomposes on heating, fine particles
2	Dry chemical (contains 95+% sodium bicarbonate)	Decomposes on heating, free flowing
3	Borax with 2% zinc stearate	High heat capacity, loses water on heating
4	Sodium carbonate ⁴	High interior surface area
5	70% sodium carbonate 30% magnesium carbonate	Better flow than magnesium carbonate
6	50% sodium carbonate 50% Portland cement; dried at 120C	
7	60% silicon dioxide 40% sodium carbonate; heated at 280C, 3 hr	Better flow than silicon dioxide
8	30% silicon dioxide 70% sodium carbonate	Better flow than silicon dioxide
9	Sodium carbonate (derived from untreated sodium bicarbonate)	
10	Sodium bicarbonate dried at 120C	Poor dispersibility
11	Silica with 2% zinc stearate ⁵	Inert, hard & irregular surface
12	Borax with 2% zinc stearate	Coarse particles
13	Gypsum plaster ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)	Loses water on heating
14	Portland cement dried at 120C	Dark gray color
15	Talc	Soft surface
16	Fire clay	Light gray color, low heat conductivity
17	Sodium bicarbonate, not dried	Poor dispersibility

¹Powders were either technical or commercial grade.

²ASTM Standard Specification for Sieves for Testing Purposes, E11-39.

³Includes sensible heat and heat of reaction where applicable (cal/gm).

⁴All sodium carbonate except as noted was derived from commercial dry

⁵Improved performance was obtained in a later test when discharge

Powders for Fire Extinguishment

No.	Sieve Mesh ² (passing 85%)	Estimated ³ Heat Capacity (18C-300C)	Dispersi- bility	Effi- ciency
1	270 est.	238	A	3+
2	325	259	A	3
3	270 est.	463	A	3
4	325	79	A	2
5	325	72	A	2
6	325	68	B	2
7	400 est.	67	B	2
8	325	74	B	2
9	170 est.	79	A	2
10	200	259	B	1
11	400 est.	60	B	1
12	170 est.	463	A	-2
13	400 est.	61	B	-2
14	325	58	C	-2
15	Impalpable	66	C	-2
16	200	63	A	-3
17	200	259	C	-3

chemical, decomposed by heating.
pressure was increased about 25 percent.

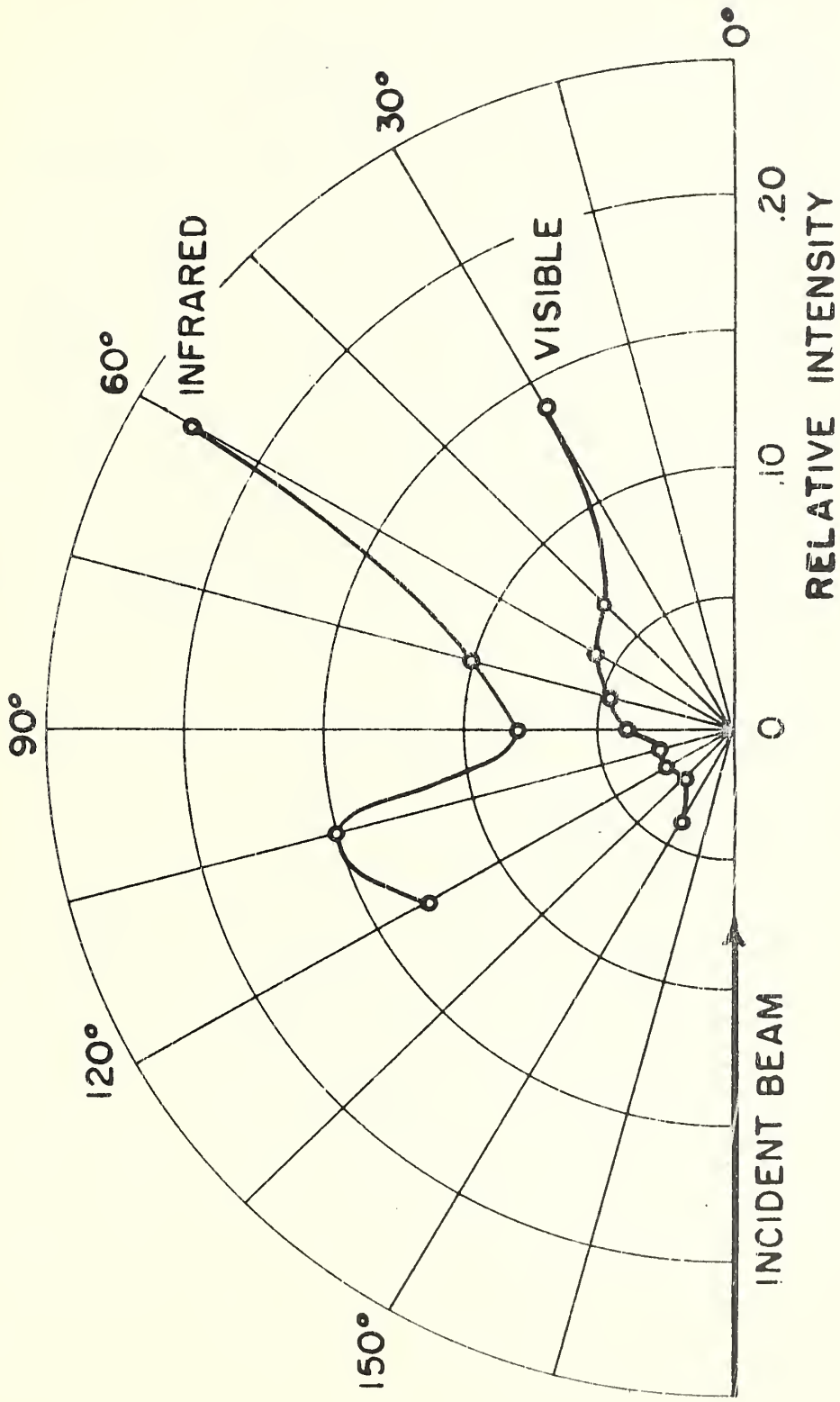


Figure 1. The observed relative intensity of energy deflected through various angles by a dispersion of commercial dry chemical.

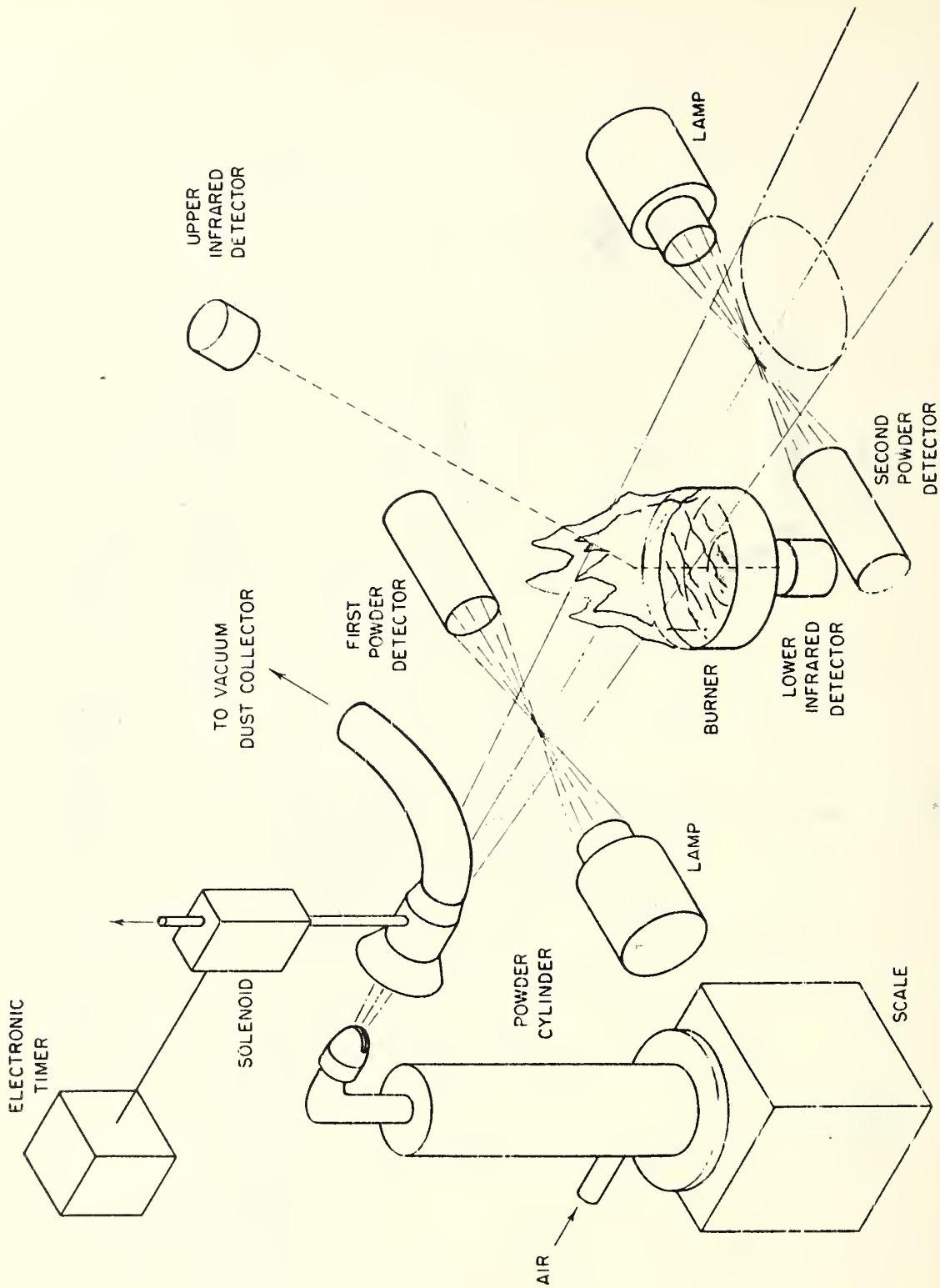


Figure 2. Equipment used to measure the transmittance and concentration of powder clouds.

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