Ignition of methane–air mixtures by laser heated small particles

Thomas H. Dubaniewicz Jr. , Kenneth L. Cashdollar, Gregory M. Green, Robert F. Chaiken

National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory, P.O. 18070, Cochrans Mill Road, Pittsburgh, PA 15236-0070, USA

Abstract

Optical technologies have progressed rapidly in the past 15 years. One application of laser technology in underground coal mines currently under evaluation is the remote measurement of explosive methane gas. Federal regulations require that atmospheric monitoring systems used in gassy underground mines where permissible equipment is required shall be intrinsically safe. Mine Safety and Health Administration criteria for the evaluation and testing of intrinsically safe apparatus and associated apparatus contain no specific guidance for optoelectronic components such as diode lasers. The National Institute for Occupational Safety and Health is conducting a study to help provide a scientific basis for developing appropriate safety guidelines for optical equipment in underground coal mines. Results of experiments involving ignition of methane–air mixtures by collections of small heated particles of Pittsburgh seam coal and black iron oxide are reported. The inert but more strongly absorbing iron oxide targets consistently ignited methane–air mixtures at lower powers than the coal targets. Minimum observed igniting powers for laser energy delivered by 200, 400 and 800 μm core fiber optic cables and directed onto iron oxide targets in methane–air atmospheres were 0.6, 1.1, and 2.2 W, respectively. Comparisons with the results of other researchers are made. A thermal layer theoretical approach to describing the process is included as an appendix.

---

1. Background

Today, laser diodes capable of producing several hundred milliwatts or more are found in industrial measurement and control applications (Cucci, 1996; Werthen & Andersson, 1996; Dubaniewicz & Chilton, 1995). Equipment that may contain intense laser sources include closed or open path optical analytical devices, fiber optic links for communication or power transmission, and others. Besides the risk of human exposure, one safety concern with these intense radiation sources is the potential for ignition of flammable gases, vapors, dusts, fibers or flyings often found in hazardous (classified) industrial settings (Magison, 1998). Recently, the ignition potential of optical equipment intended for use in hazardous (classified) locations was demonstrated by the US Bureau of Mines, Pittsburgh Research Center (USBM, PRC) (Dubaniewicz, Cashdollar, Green & Cucci, 1996). Observed ignitions underscore the need for appropriate safety guidelines for this emerging technology.

The National Institute for Occupational Safety and Health, Pittsburgh Research Laboratory (NIOSH, PRL) (formerly USBM, PRC) is conducting a study to develop safety recommendations for lasers used in areas of underground coal mines where permissible equipment is required (Dubaniewicz, Cashdollar & Monaghan, 1999). One application of laser technology in underground coal mines currently under evaluation is the remote measurement of explosive methane gas. Methane gas is often liberated during the mining process. Federal regulations require periodic methane measurements at the mining face, and abatement measures should methane concentrations exceed a threshold level.

The process of making methane measurements in the roof-fall-prone face area can require extensive safety precautions to prevent injury. The possibility of such injuries occurring, especially during extended cut operations, has been cited as a safety concern by the United Mine Workers of America. A simple-to-use remote

---

E-mail address: tcd5@cdc.gov (T.H. Dubaniewicz Jr.).

methanometer would therefore enhance miner safety in the roof-fall-prone face area.

Federal regulations also require that atmospheric monitoring systems used in gassy underground mines where permissible equipment is required shall be intrinsically safe. However, intrinsic safety applies primarily to preventing electrical spark or electrical heating ignition mechanisms. Little or no consideration had been given to optical ignition mechanisms because typical lasers used in mines had very low power. For example, the Mine Safety and Health Administration (MSHA) document "Criteria for the evaluation and test of intrinsically safe apparatus and associated apparatus" contains no specific guidance for apparatus containing optoelectronic components such as diode lasers (US Department of Labor, Mine Safety and Health Administration, 1995). Inadequate safety evaluation criteria are problematic in two ways. Obviously, allowing ignition capable optical beams in a potentially explosive environment is an invitation to disaster. Conversely, overly conservative evaluation criteria resulting from a lack of understanding of the phenomena could unnecessarily prohibit useful, potentially safety enhancing technology such as an optical remote methane monitor.

Of several identified optical ignition mechanisms, there is primarily one mode of ignition of methane–air atmospheres that needs serious consideration at the power levels common in current measurement and control applications (Magison, 1997, 1998, Chapter 12, pp. 493–512). This is the simultaneous presence of: (a) a flammable methane–air atmosphere, (b) a radiating energy source of the duration and intensity needed to cause ignition, and (c) an appropriate target to convert the optical energy to thermal energy. For example, material covering the end of a broken fiber optic cable could be heated by laser energy. The experimental approach to assessing this ignition mechanism is described below.

2. Technical approach

Combustion can take place in atmospheres containing 5–15% methane in air containing 21% oxygen. The most easily ignited mixture in this range can vary with ignition source. For example, the commonly accepted optimum mixture for electrical spark testing is 8.3% methane–air, whereas the accepted optimum mixture for hot wire testing is 7.7% methane–air (US Department of Labor, Mine Safety and Health Administration, 1995). Proust (1994) reported results using 7% methane–air mixtures when studying dust layers on Kaowool[1] mats irradiated with an open laser beam. Hills & Samson (1990) reported results using 8.3% methane–air mixtures when irradiating coal particles through optical fibers, citing electrical spark minimum ignition energy (MIE). Hills, Zhang, Sampson & Wall (1992) later reported minimum igniting powers when using 9.5% methane–air. In the current study, mixtures were varied between 5 and 10% methane–air (in 1% increments) to find the most easily ignited concentration and to better define the relationship between the ignition curve (igniting power versus gas mixture) and the selected ignition mechanism.

Relevant properties of optical beams include energy, area, and duration. These properties define the optical beam in terms of energy, energy density, power, and power density. Energy and energy density criteria are appropriate for short duration, high peak power optical pulses. A continuous wave (CW) laser was used in this study, with power and power density being the relevant beam properties. The relationship between igniting beam power and irradiated area is nonlinear. In cases of very large and very small areas, ignition potential appears to approach asymptotic limits that can be approximated in terms of a limiting power (for small areas) and a limiting power density (for large areas) (Carleton & Weinberg, 1994). McGeehin (1994) proposed safety criteria for limiting power and power density based on testing of flammable mixtures of carbon disulfide or ethyl ether in air. Limiting power and power density safety criteria specifically for methane–air mixtures have not been proposed. Hills reported ignition results for methane–air atmospheres using 50 and 100 μm core diameter optical fibers tipped with coal particles (Hills & Samson, 1990; Hills et al., 1992). In the current study, 200, 400, and 800 μm diameter optical fibers were used to better define the relationship between igniting power and target area for selected methane–air mixtures. Targets were selected to match the surface area of the fiber tips, thus providing a convenient way to vary target surface area while ensuring almost all of the laser energy was absorbed.

The ignition requires the conversion of optical energy to thermal energy by absorption in an appropriate target. The target needs to attain a minimum ignition temperature for a given ignition volume in order to ignite the surrounding gas. Some relevant target properties include absorbance, surface area, volatility, and reactivity with air. There is consensus in the literature that strongly absorbing targets facilitate ignition. The role of target surface area, volatility, and reactivity is less clear. For example, small, volatile or combustible targets may vaporize, dissipating the laser energy before igniting the surrounding gas. Larger combustible targets may have sufficient mass to contribute significant heat of combustion to ignite methane–air more easily than a similar sized inert target. Also, larger heated targets can ignite methane–air at lower temperatures than smaller targets, but require higher incident powers to attain similar tempera-

---

[1] Mention of any company name or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

tures as small targets. Small targets that vaporize near appropriate ignition temperatures may ignite gases more readily than other small targets by achieving a minimum volume (Carleton & Weinberg, 1994). All of these issues are relevant to coal targets. Electrical spark research may provide insight as far as volatility is concerned. The sensitivity of the spark test apparatus increases when using electrode materials with progressively lower boiling points, under certain test conditions (Peterson, 1992). In the current study, optical fiber core sized targets of black iron oxide and coal particles were tested to better define the role of surface area, volatility and reactivity in methane–air ignition.

3. Test setup

Ignition experiments were conducted in a 20-l test chamber (Fig. 1) designed for explosion testing of dusts, gases, and their mixtures (Cashdollar & Hertzberg, 1985). It can be used to measure lean and rich limits of flammability, explosion pressures and rates of pressure rise, minimum ignition energies, minimum oxygen concentrations for flammability, and amounts of inhibitor necessary to prevent explosions. The chamber can be used at initial pressures that are below, at, or above atmospheric as long as the maximum explosion pressure is less than 21 bar, which is the rated pressure of the chamber. For these tests, chamber instrumentation included a pressure transducer and a high-speed (200 frames per second) video camera.

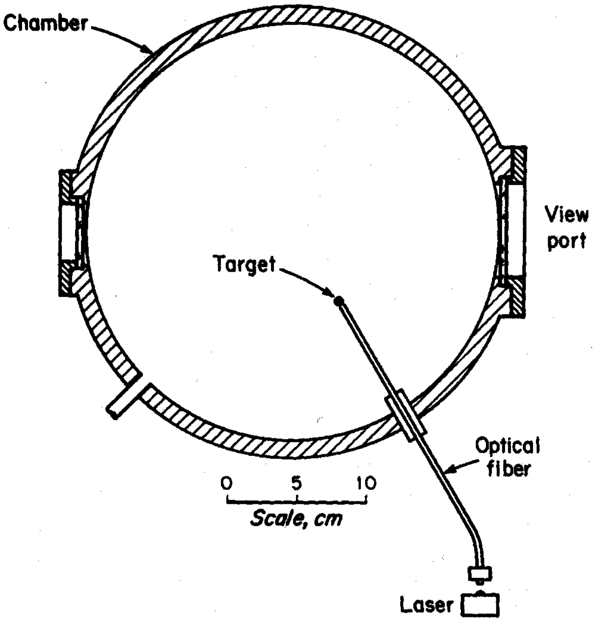

Fig. 1. Horizontal cross section of the 20-l chamber methane–air ignition test setup.

The laser used was a SDL model 8110-B Integrated Laser System (ILS). The ILS output power is variable up to 10 W out of a 400 μm diameter aperture. The laser diode wavelength is centered at 803 nm in the near infrared region. The ILS was operated in constant power mode which eliminated overshoot, and produced a 100 ms rise time. An SMA bulkhead adapter provides fiber optic coupling. The ILS also contains a low power visible aiming laser which proved useful in setting up experiments.

Three sizes of fiber optic cable were used. The smallest had an output core diameter of 200 μm. This was a Fiberguide Anhydroguide plastic clad silica (PCS) 400–200 μm fiber optic taper. The next size was a Spectran 400 μm core, 430 μm clad Hard Clad Silica cable, 0.4 numerical aperture (NA). The third cable was a Fiberguide Anhydroguide PCS, 800 μm core, 900 μm clad diameter, 0.4 NA cable.

Selected targets included Pittsburgh seam coal (PC) and black iron oxide. Black iron oxide was chosen because of its excellent optical absorption and inertness. Welzel, Bothe & Cammenga (1994) found it to be a worst case target when placed on optical fiber tips under certain test conditions. The iron oxide used in the NIOSH study is a combination of ferrous (FeO) and ferric (Fe_2O_3) oxide having a theoretical formula of Fe_3O_4. The manufacturer's data sheet indicated particle size is uniform with an average diameter of approximately 0.4 μm. Pittsburgh seam coal is used in standardized MSHA dust blanketing tests for intrinsic safety evaluations. The standardized test calls for dust fine enough to pass through a 200 mesh (75 μm) screen. However, very fine PC particles with a mass median diameter of 3 μm were used in one series of tests for a better comparison with iron oxide test results. For ignition tests with these fine particles, a coating of particles was placed on the fiber optic tip sufficient to block a visible aiming laser. Larger individual coal particles approximately the size of the fiber optic core diameter were used in another series of tests to investigate potential heat of combustion contributions from progressively larger coal particles.

A sample of iron oxide, minus 200 mesh PC, and limestone rock dust ($CaCO_3$) were analyzed by Labsphere, Inc. to determine their absorption characteristics (Fig. 2). The samples were measured for hemispherical reflectance factors using a double beam ratio recording integrating sphere reflectometer. The reflectometer was made up of a Perkin-Elmer Lambda-19 spectrophotometer and a Labsphere reflectance accessory. The absorbance was then calculated as the Log $(1/R)$, where R is the reflectance factor measured at a particular wavelength. Results show the iron oxide is a slightly stronger absorber than the coal over the wavelengths measured. Both are much stronger absorbers of radiation than limestone rock dust, a material commonly applied in underground coal mines to prevent coal dust explosions.

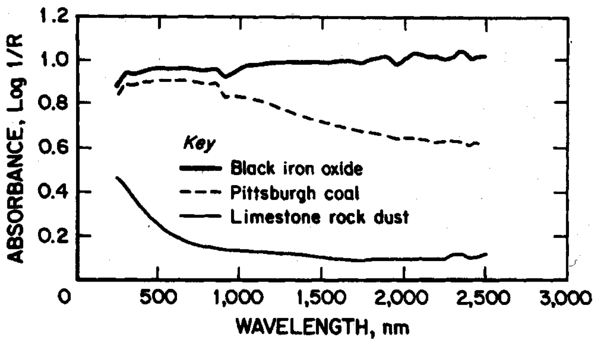

Fig. 2. Absorbance of iron oxide, Pittsburgh coal, and limestone rock dust samples.

An adequate length of fiber was pulled through a feedthrough in the 20-l chamber (Fig. 1) to allow preparation of the fiber tip. A fiber optic cleaver (York model FBK 11C) provided a flat, perpendicular, optical surface for each ignition test with the 200 and 400 μm core fibers. The 800 μm core fiber required a manual cleaving tool. Before each test, the power emanating from the cleaved end of the fiber was measured using a laser power meter (Scientec Model D200PC) with attached calorimeter (Scientec Model AC2501). This power measurement was taken as the total power absorbed by the target for the ensuing ignition test. The laser was then turned off and targets attached to the fiber end. Excess fiber was pulled back through the feedthrough until the target was placed near the center of the chamber atop the vertically aligned fiber. The visible low power aiming laser was then used to verify that the target completely covered the fiber end.

The 20-l chamber was sealed and evacuated, and the flammable gas–air mixture was introduced into the chamber by partial pressures. The pressure transducer detected ignitions in conjunction with the high-speed video camera. A personal computer-based high-speed data acquisition system recorded the pressure data. Targets were heated to incandescence in all tests whether or not an ignition was produced. Tests were determined to be nonignitions and terminated after the video camera showed the intensity of incandescence dropped considerably or ceased. In most cases tests were terminated within about 1 min after turning on the laser. The flammability of the gas–air mixture was periodically verified using electric matches when experiments resulted in nonignitions. The primary criterion for ignition was the visual appearance of flame on the high speed video. Ignition was also confirmed by the explosion over pressures, which were about 4–7 bar (55–100 psi) for 6–10% methane–air. Peak pressures were much lower for 5% methane–air ignition, about 0.14–0.36 bar (2–5 psi). Tests considered nonignitions generally produced pressure rises less than 0.01 bar (0.2 psi).

4. Experimental results

Various methods were used to attach targets to the fiber tip in preliminary ignition tests. The very fine iron oxide particles did not appear to adhere adequately to the optical fiber tip and, as a result, ignition tests were not very repeatable. In these tests, a sample of iron oxide particles was mixed with isopropyl alcohol, applied to the tip of the fiber until the aiming laser was no longer visible, and allowed to dry before sealing and evacuating the chamber. Mixing the very fine particles with an inert lubricant (Krytox) provided better adhesion in subsequent tests, producing more repeatable results, and the lowest igniting powers. The Krytox to particle ratio of the mixture was about 1:3 by volume. Krytox is a fluorinated lubricant that has good temperature stability (low outgassing up to about 355°C), and is nonflammable. Adhesives (such as cyanoacrylate) were not used extensively with the very fine particles because of potential heat of combustion contributions. The fiber-sized coal particles required an adhesive (cyanoacrylate) to adhere adequately to the fiber tip. Absorbance characteristics of particle–adhesive mixtures were not measured, although the color of the mixtures did not appear to vary substantially from the fine particles themselves. Fiber-sized coal particles were carefully affixed to the fiber tip under a microscope. A comparison of minimum igniting powers of various targets on a 400 μm fiber is shown in Fig. 3. The 4 W value for the iron oxide-only target (total of 16 tests) in Fig. 3 may indicate weak adhesion to the fiber tip.

Two tests were also conducted with a graphite powder and isopropyl alcohol colloid applied to the tip of the 400 μm core fiber placed in 7% methane–air. The manufacturer's data sheet indicated the graphite particle size was 2 μm or less, with a sublimation point of about 1920°C and oxidation point between 426 and 482°C. The isopropyl was allowed to evaporate before sealing and evacuating the chamber. Applying 1.5 W produced incandescence lasting about 0.5 s, but no gas ignition. This was a shorter duration of incandescence than for tests with other targets. No further tests were attempted since other targets produced ignitions readily under similar test conditions (see Fig. 6).

More detailed results are shown in Figs. 4–6. In each series of tests with a particular fiber diameter, the methane concentration was varied to find the minimum igniting laser power. In general, each set of tests at a particular methane–air concentration were discontinued after three nonignitions were obtained. This was not the case for fiber-sized coal particles as shown in Fig. 5. More tests were conducted after obtaining four nonignitions in one case because the irregular shapes and reflective (glossy) facets of the larger particles made it difficult to block the aiming laser. Minimum igniting powers for PC (3 μm)–Krytox targets (Fig. 4) were 0.9 W for the 200

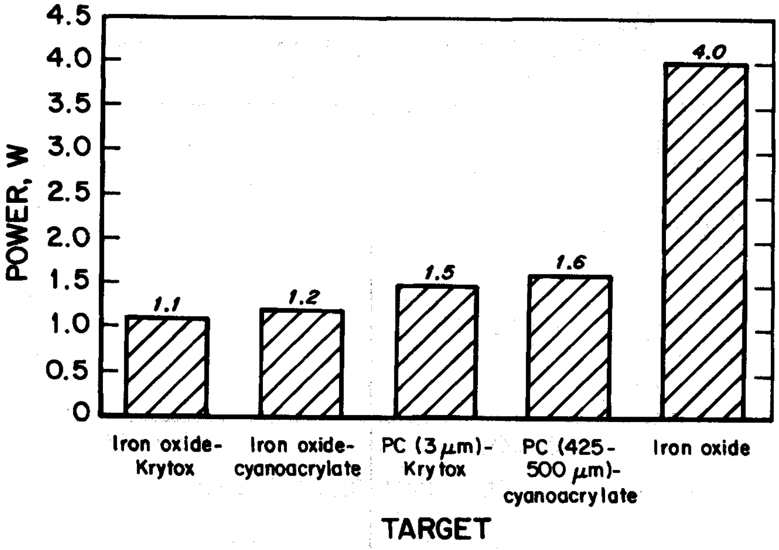

Fig. 3. Minimum igniting powers with selected targets placed on a 400 μm core optical fiber placed in flammable methane–air mixtures.

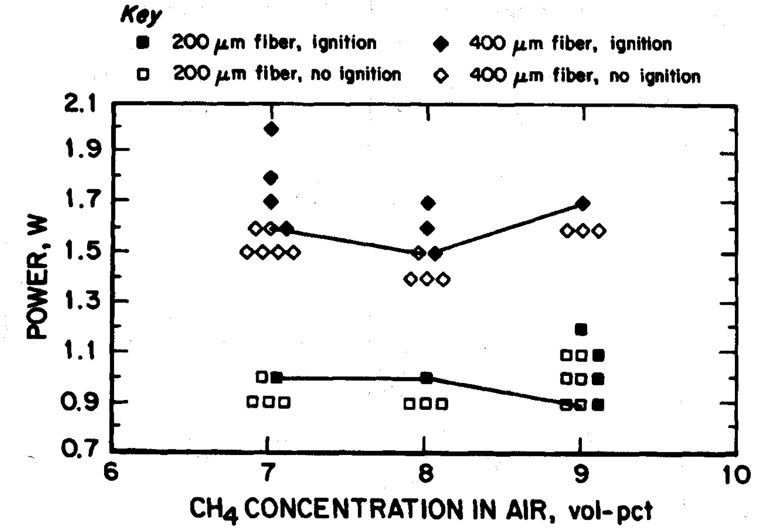

Fig. 4. Igniting powers for optical fibers tipped with PC (3 μm)–Krytox mixture, placed in flammable methane–air mixtures.

μm core fiber and 1.5 W for the 400 μm core fiber. Minimum igniting powers for fiber sized PC–cyanoacrylate targets in 8% methane–air (Fig. 5) were 1.6 W for the 400 μm core fiber and 2.7 W for the 800 μm core fiber. The fine and fiber-sized coal particle tests were generally less repeatable than the iron oxide tests. Additional coal particle tests over a range of methane–air concentrations are warranted to confirm minimum igniting powers.

Minimum igniting powers (Fig. 6) with iron oxide–Krytox targets were 0.6, 1.1, and 2.2 W with 200, 400, and 800 μm core diameter fibers, respectively. The relatively flat response with methane concentration resembles autoignition temperature (AIT) phenomena more so than electrical spark MIE phenomena. Limiting thermal phenomena such as AIT are also characterized by large ignition lag times. This trend is indicated in Fig. 7. Ignition lag times were estimated by observing video tape recorded by the high speed camera system. Ignition lag was taken as the time between the first noticeable target glow and first noticeable flame front emanating from the target. In several cases barely discernible flame fronts emanating from the target were followed by clearly visible flames appearing from other portions of the chamber, typically about 100 ms afterwards in this chamber. Ignition lag times of 5% methane–air were not discernible from the video tape, and are not included in Fig. 7.

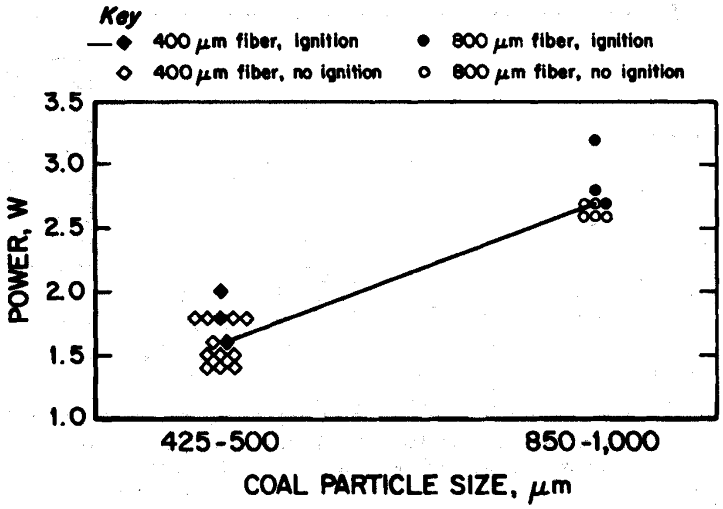

Fig. 5. Igniting power vs. coal particle size for optical fiber tipped with fiber-sized PC–cyanoacrylate targets, 8% methane in air.

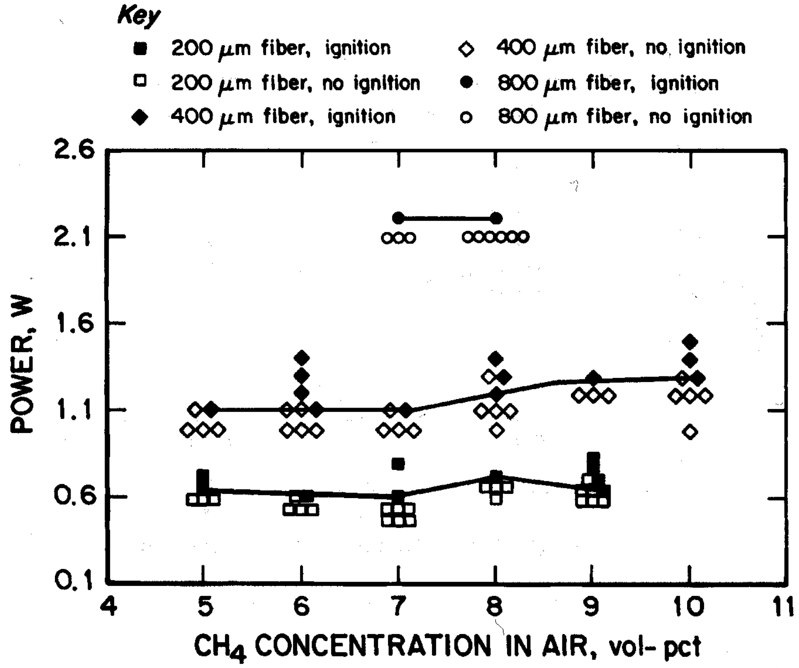

Fig. 6. Igniting powers for optical fibers tipped with iron oxide–Krytox placed in methane–air mixtures.

A summary of minimum igniting powers versus core diameter is shown in Fig. 8 and listed in Table 1. Results reported by Hills (Hills & Samson, 1990; Hills et al., 1992) are included for comparison in Fig. 8. Hills found minimum methane–air igniting powers of about 300 mW when 38–45 μm diameter coal particles placed in a glass dish were illuminated by single mode and 50 μm core diameter optical fibers. Ignition of an 8% methane–air mixture was also reported when a 40 μm particle attached to a 100 μm core diameter optical fiber was heated by 360 mW. This graph shows that inert but more strongly absorbing iron oxide–Krytox targets consistently ignited methane–air mixtures at lower powers than coal targets in this study. Minimum igniting power densities for iron oxide–Krytox targets calculated by dividing the igniting power by the surface area of the fiber core produces values of 19.2, 8.7, and 4.4 W/mm^2 for 200, 400, and 800 μm fibers, respectively. Comparing these calculations with Fig. 8 shows that smaller core fibers required lower incident powers for ignition than larger core fibers, but larger power densities.

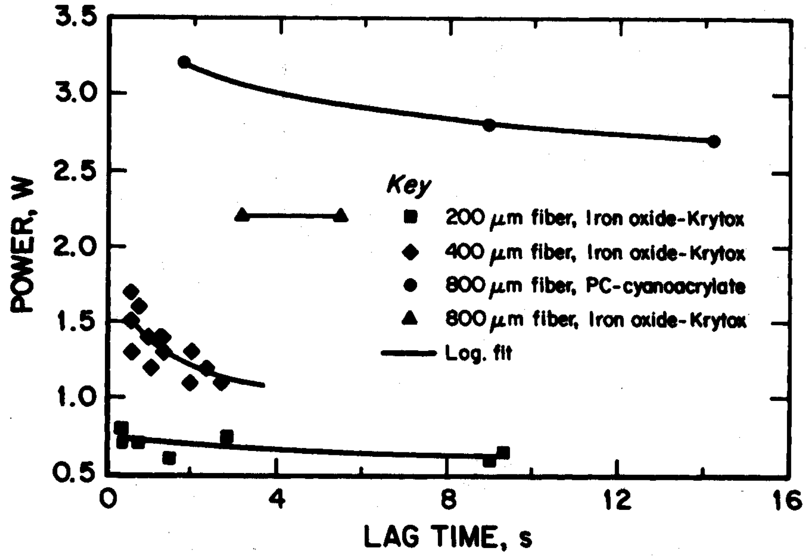

Fig. 7. Igniting power vs. lag time for various targets placed in flammable methane–air mixtures.

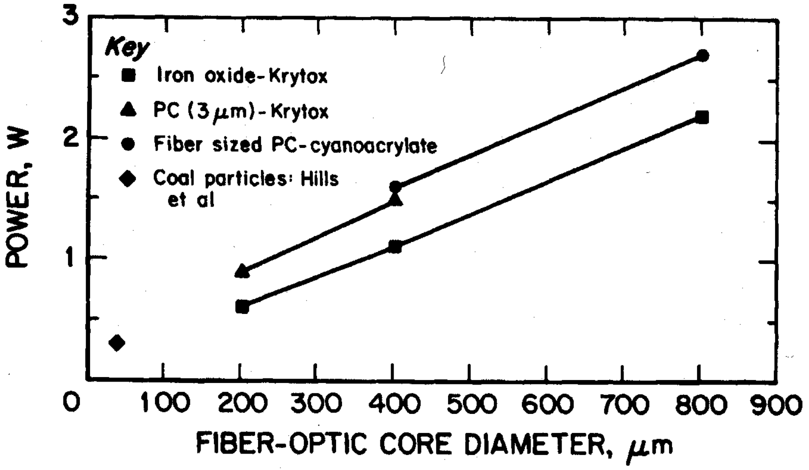

Fig. 8. Minimum igniting power vs. fiber optic core diameter, various targets.

Table 1
Minimum igniting powers (W) for various fiber optic core diameters and targets

Fiber optic core diameter (μm)	200	400	800
Iron oxide–Krytox	0.6	1.1	2.2
PC (3 μm)–Krytox	0.9	1.5	–
Fiber sized PC–cyanoacrylate	–	1.6	2.7

5. Discussion

Experimental approaches to assessing minimum igniting phenomena require a large number of tests to account for statistical variations in test conditions. The number of nonignitions per test series in Figs. 4–6 is roughly 10. In comparison, MSHA tests each electrical circuit for 1000 revolutions in a spark test apparatus, with multiple sparks for each revolution, resulting in at least 5000 make–break sparks. For this reason, a conservative safety factor should be applied to the curve in Fig. 8 at the current state of knowledge. Results do suggest larger core fibers are significantly less likely to cause ignition in methane–air mixtures, under certain test conditions. The likelihood of significant intensity fluctuations in multimode optical fibers from modal variations or focusing effects from stretched and/or broken fibers, for example, may need to be considered where appropriate. Fiber optic tapers should prove useful in evaluating the failure mode where a multimode fiber is stretched to the breaking point with a concurrent reduction in diameter. Test results showed 400 μm fiber tapered down to 200 μm produced lower igniting powers and approached limiting ignition lag times more quickly than untapered 400 μm fiber.

A thermal layer theoretical approach to describing this ignition process is included as Appendix A by Robert F. Chaiken. Although this is a preliminary model, some initial results are presented here. The model indicates minimum laser power for ignition (P) is of a form

$$P = A + Br_0 \quad (1)$$

where A and B are factors that depend on the ignition temperature appropriate for the experimental condition, and r_0 is a target radius (taken to be equivalent to the fiber core radius in subsequent calculations). The model indicates a linear relationship between igniting power and target radius, tending towards a constant value with decreasing radius. This is consistent with experimental data presented here (Fig. 8). Minimum power calculations from the model are in reasonable agreement with experimental data (see Fig. 11). The fiber was observed to glow several millimeters back from the target during tests, suggesting the fiber acts as a significant heat sink. The model includes terms accounting for this conductive loss and also radiative loss to the environment, but does not consider possible effects due to convection. The mathematical treatment in the model is partially based on small target heating times compared with the overall time to ignition. Therefore, application of this model to high peak power optical pulses may not be valid. These situations are outside the scope of the current study.

The cladding to core diameter ratio of the 800 μm fiber is 4.5% larger than that of the 400 μm fiber. This represents a significant increase in proportional fiber tip surface area if considering overall cladding diameters. As the applied targets covered the entire fiber tip, including the cladding, the thermal energy produced during the 800 μm tests will be dissipated to a disproportionally greater extent than with the other fibers tested. This may account for the 800 μm data occurring slightly above the line drawn through the 200 and 400 μm iron oxide data in Figs. 8 and 11.

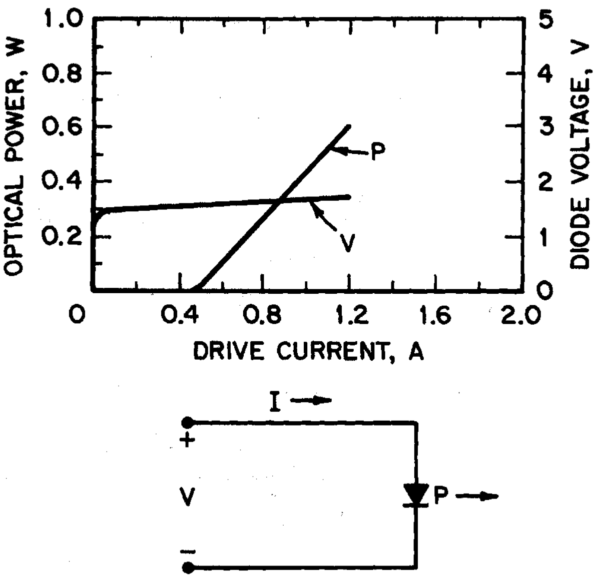

Fig. 9. Laser diode electrical input and CW optical power output characteristics.

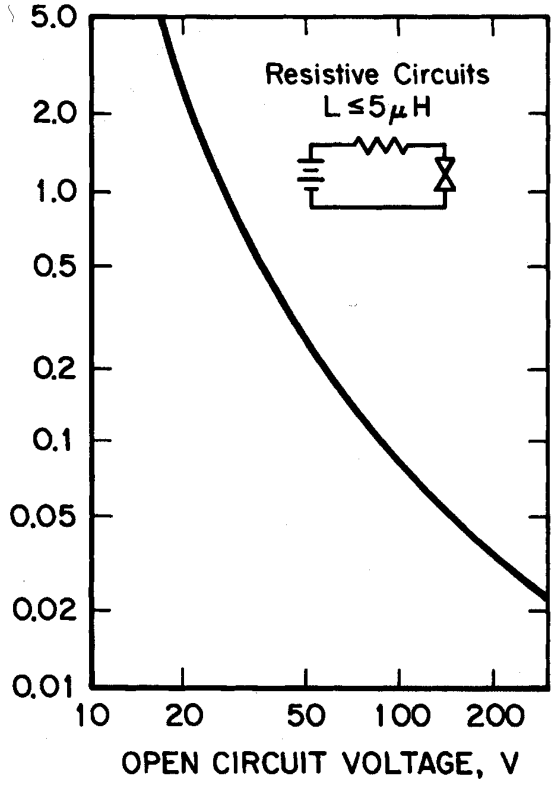

Fig. 10. MSHA accepted ignition curve for resistive circuits.

Test results have important implications for intrinsic safety evaluations. In lieu of relevant safety guidelines for optoelectronic components, one may be tempted to make safety evaluations based upon the driving circuitry. Fig. 9 shows voltage, current and CW optical power characteristics for a commercial laser diode. The power is measured out of a 100 μm fiber-optic pigtail. Fig. 10 shows the MSHA accepted electrical spark ignition curve for resistive circuits, plotting short circuit current versus open circuit voltage. Even at maximum drive current producing upwards of 600 mW optical power, the laser diode drive circuit could be well within the safe boundary from an electrical spark point of view (below and to the left of the ignition curve). Considering also that optical conversion efficiency is less than 40%, the laser diode and drive circuit might be considered safe without further evaluation. However, 600 mW optical power out of 100 μm core diameter fiber is above the ignition curve of Fig. 8, indicating further evaluations are prudent.

Larger coal particles required higher incident powers to ignite 8% methane–air mixtures in this study (Fig. 5), indicating heat of combustion contributions were negligible (coal particles were heated to white-hot incandescence in all tests). This does not necessarily apply to situations where much larger accumulations of coal dust may ignite. MSHA intrinsic safety evaluations also contain provisions for coal dust blanketing tests where appropriate. The second phase of the current study will involve laser ignition of coal dust layers modeled after the MSHA test. Ignition potential of coal dust suspensions will also be studied. For industries outside of MSHA jurisdiction, these situations may be more appropriately handled by Class II hazardous location type guidelines. ISA—The International Society for Measurement and Control has formed the SP12.21 Fiber Optics committee to address these and other issues for fiber optic systems used in hazardous locations.

Appendix A. Model for laser ignition of combustible gas mixtures: a thermal layer approach to describing the process by Robert F. Chaiken

Laser heated solid particles positioned at the end of an optical fiber can cause ignition of combustible gas mixtures (e.g. CH_4+air). In the description which follows, the ignition mechanism is taken as thermal in nature, i.e. an adequate volume of gas is heated to an adequate temperature by thermal conduction from the surface of the hot particle. By adequate, this means satisfying a minimum ignition temperature and achieving a minimum ignition volume capable of propagating a flame into the gas. Due to the poor absorptivity of the gas, any radiation from the particle will be to some external ambient temperature environment (e.g. container walls). Hence, such radiation will not contribute to the heating of the gas surrounding the particle, but will simply increase the laser power required to cause ignition.

This model assumes that the particle is at uniform temperature (i.e. the solid particle has a high thermal conductivity relative to that of the gas), and the heat transport at the solid/gas interface is spherically symmetrical and primarily conductive.

Consider now the immersion of a solid sphere at constant uniform temperature, T_s, into a quiescent gas at initial temperature, T_0. Heat will be conducted from the surface of the sphere to the gas at a rate

$$Q_{\text{out}}=4\pi r_0^2\lambda_g\left(\frac{\partial T}{\partial r}\right)_{r_0} \tag{A1}$$

where r is the region of gas $\geq r_0$, the radius of the particle, and λ_g is the thermal conductivity of the gas.

From Chaiken, R.F. (1995). *Combustion and Flame*, 3, 285–290 (also see Carslaw, H.S., & Jaeger, J.C. (1947). *Conduction of heat in solids*. Oxford University Press, p. 209), we can write directly for the time-dependent surface gradient

$$\left(\frac{\partial T}{\partial r}\right)_{r_0}=\frac{(T_s-T_0)}{\delta(t)} \tag{A2}$$

$$\delta(t)=\frac{r_0}{1+\dfrac{r_0}{\sqrt{\pi\kappa_g t}}} \tag{A3}$$

where $\kappa_g=\lambda_g/\rho_g c_g$, the gas thermal diffusivity (~1.5 cm^2/s at 1000 K).

$\delta(t)$ can be considered a gas thermal layer around the particle that grows outward with time. Its value essentially linearizes the gradient where the temperature T_s at r_0 decreases to T_0 at $r=r_0+\delta$. For long times and/or small particles, $\delta(t)$ will approach a maximum value, r_0, leading to a minimum value of Q_{out} for a given T_s.

Now Q_{out} is exactly the power needed to be absorbed by the particles to maintain T_s constant. If other thermal losses from the particle were negligible (which they are not), Q_{out} at a given T_s for ignition would define the laser power level at that temperature; particularly when the time to heating the sphere to T_s is small compared with the overall time to gas ignition. The laser power level that would maintain T_s at a constant level would be given by

$$P(t)=Q_{\text{out}}=4\pi r_0\lambda_g(T_s-T_0)\left[1+\frac{r_0}{\sqrt{\pi\kappa_g\tau}}\right] \tag{A4}$$

Setting T_s to some constant minimum temperature, T_{ig}, which results in ignition, infers that there will be a specific time, τ, which defines the power required to maintain T_{ig} at a constant value. The value of τ will be some characteristic of the ignition process, e.g. time to reaction runaway. The value of Q_{out} will then be the minimum laser ignition power, i.e.

$$P(\tau)=4\pi r_0\lambda_g(T_{ig}-T_0)\left[1+\frac{r_0}{\sqrt{\pi\kappa_g\tau}}\right] \qquad \text{(A5)}$$

The thickness of the thermal layer at that time is

$$\delta(\tau)=\frac{r_0}{1+\frac{r_0}{\sqrt{\pi\kappa_g\tau}}} \qquad \text{(A6)}$$

which varies with particle size.

The process of ignition at T_{ig} results from the build-up of sufficient energy in the thermal layer surrounding the solid sphere so that the outward flow of heat results in a propagating flame front. This minimum energy density can be expressed in terms of a minimum "thermal pressure" (i.e. cal/cm^2) needed to cause the combustion reactions to rapidly accelerate, i.e.

$$F_{ig}=\rho_g c_g\delta_{ig}(T_{ig}-T_0) \qquad \text{(A7)}$$

It is reasonable to assume that F_{ig} is a constant of the combustible gas mixture; hence,

$$\delta_{ig}(T_{ig}-T_0)=\frac{F_{ig}}{\rho_g c_g}\approx\text{constant} \qquad \text{(A8)}$$

For a given ignition geometry higher temperatures will require smaller gas volumes, whereas larger gas volumes will require lower temperatures. For the spherical geometry under consideration here, the maximum value of δ_{ig} from Eq. (A6) is r_0, which leads to

$$P(\tau)=4\pi\kappa_g F_{ig}\left[1+\frac{r_0}{\sqrt{\pi\kappa_g\tau}}\right] \qquad \text{(A9)}$$

At this point, the laser power level being considered is used only to ignite the gas mixture. It varies directly with the sphere diameter which is taken to be the same as the optical fiber diameter. However, there are heat losses from the tip of the optical fiber that can occur which will contribute to the laser power requirements but not to the effective thermal layer in the combustible gas mixture. Radiation of heat from the optical fiber tip to the far walls of the chamber is one such heat loss. Another is heat conduction from the fiber tip back along the optical fiber itself. Thus, in terms of a measured laser power for ignition, we need to add to Eq. (A9) terms accounting for radiation and heat conduction.

Radiation can be accounted for by

$$P_{rad}=4\pi r_0^2\varepsilon\sigma(T_{ig}^4-T_0^4) \qquad \text{(A10)}$$

where ε is the emissivity of the solid sphere and σ is the Stefan-Boltzman constant, 5.67×10^{-12} W/cm^2-K^4.

Factoring the fourth power terms in combination with Eq. (A8) leads to

$$P_{rad}=4\pi\kappa F_{ig}\frac{r_0\varepsilon\sigma}{\lambda_g}(T_{ig}^2+T_0^2)(T_{ig}+T_0) \qquad \text{(A11)}$$

Heat conduction back along the optical fiber is assumed to be linear, and can be described by Eq. (A5) with $r_0/\sqrt{\pi\kappa t}\gg1$ (also see Eq. (A6)), and where the transport and material constants refer to the optical fiber (subscript f). Utilizing Eq. (A8) leads to the following expression for the conductive heat loss term:

$$P_{cond}=4\pi\kappa_g F_g\left(\frac{\lambda_f}{\lambda_g}\right)\frac{r_0}{\sqrt{\pi\kappa_f\tau}} \qquad \text{(A12)}$$

Summing Eqs. (9), (11), and (12) then leads to the total minimum laser power for ignition of the combustible gas mixture.

$$P_{laser}=4\pi\kappa_g F_{ig}\left[1+\frac{r_0}{\sqrt{\pi\kappa_g\tau}}+\left(\frac{\lambda_f}{\lambda_g}\right)\frac{r_0}{\sqrt{\pi\kappa_f\tau}}+\frac{\epsilon\sigma r_0}{\lambda_g}f(T_{ig})\right]$$

$$f(T_{ig})=(T_{ig}^2+T_0^2)(T_{ig}+T_0) \qquad \text{(A13)}$$

which has the form

$$P_{laser}=A+Br_0 \qquad \text{(A14)}$$

The value of the factors A and B would depend on the T_{ig} that is appropriate for the experimental condition, but it would seem that the minimum laser power for ignition is linear with optical fiber diameter. While calculations to establish values of A and B could be a numbers game without some sound data on the various material parameters that are involved, Fig. 11 shows the results of one set of calculations based on the following assumed values for those parameters which have been treated as constants: F_{ig}=0.00125 cal/cm^2; τ=0.25 s; λ_g=0.00015 cal/cm-s-deg; κ_g=1.8 cm^2/s. λ_f=0.003 cal/cm-s-deg; and κ_f=0.003 cm^2/s. Lines are shown for values of T_{ig} from 1000 to 2500 K.

Also shown in Fig. 11 are data from Fig. 8 for black iron oxide coated optical fibers in methane–air mixtures. The calculated results are in reasonable agreement with the data. It might be pointed out that some of the transport properties (e.g. κ) could vary significantly with temperature. While the temperature dependency has not been considered at this time, it should be considered in subsequent evaluations of the laser ignition experiments.

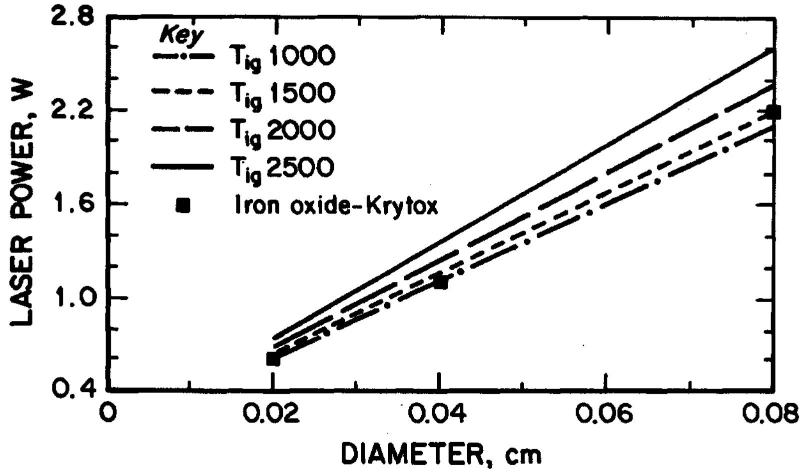

Fig. 11. Plot of minimum laser power for ignition for various ignition temperatures, compared with experimental data for iron oxide from Fig. 8.

References

Carleton, F.B., & Weinberg, F.J. (1994). Annex I: Final Summary Report, Imperial College. In P. McGeehin, Optical techniques in industrial measurement: safety in hazardous environments. European Commission Report EUR 16011 EN, 15 pp.

Cashdollar, K. L., & Hertzberg, M. (1985). 20-Liter explosibility test chamber for dusts and gases. *Review of Scientific Instruments*, *56*, 596–602.

Cucci, G. R. (1996). Remote measurement and environmental monitoring using transmitters powered by fiber optics. In (pp. 165–169). *Proceedings of the 41st Annual ISA Analysis Division Symposium, 29.*

US Department of Labor, Mine Safety and Health Administration (1995). Criteria for the evaluation and test of intrinsically safe apparatus and associated apparatus. CDS No. ACRI2001, RR 1, US Department of Labor, Mine Safety and Health Administration, Triadelphia, WV.

Dubaniewicz, Jr., T.H., & Chilton, J.E. (1995). Optically powered remote gas monitor. USBM RI 9558, 9 pp.

Dubaniewicz, T. H. Jr., Cashdollar, K. L., Green, G. M., & Cucci, G. R. (1996). Ignition tests with a fiber optic powered instrument. In (pp. 175–184). *Proceedings of the 41st Annual ISA Analysis Division Symposium, 29.*

Dubaniewicz, T. H. Jr., Cashdollar, K. L., & Monaghan, W. D. (1999). Laser ignition of flammable gas. In *Proceedings of the 1999 International Laser Safety Conference, Orlando, FL, 8–11 March 1999* Orlando, FL: Laser Institute of America, in press.

Hills, P. C., & Samson, P. J. (1990). Explosion hazards of optical fibres in combustible environments. In *Proceedings of the 7th Optical Fibre Sensors Conference, 2–6 December, Sydney, N.S.W.* (pp. 63–65).

Hills, P. C., Zhang, D. K., Sampson, P. J., & Wall, T. F. (1992). Laser ignition of combustible gases by radiative heating of small particles. *Combustion and Flame*, *91*, 399–412.

Magison, E. C. (1997). Are optical beams an explosion hazard? *Intech*, *44* (9), 61–66.

Magison, E. C. (1998). *Electrical instruments in hazardous locations.* (4th ed.). Research Triangle Park, NC: ISA—The International Society for Measurement and Control.

McGeehin, P. (1994). Optical techniques in industrial measurement: safety in hazardous environments. European Commission Report EUR 16011 EN, 15 pp.

Peterson, J.S. (1992). Influence of electrode material on spark ignition probability. USBM RI 9416, 19 pp.

Proust, C. (1994). Annex V: Final Report. In P. McGeehin, Optical techniques in industrial measurement: safety in hazardous environments. European Commission Report EUR 16011 EN, 15 pp.

Welzel, M.M., Bothe, H., & Cammenga, H.K., Annex II: Final Report, PTB. In P. McGeehin, Optical techniques in industrial measurement: safety in hazardous environments. European Commission Report EUR 16011 EN, 15 pp.

Werthen, J. G., & Andersson, A. G. (1996). Optically powered sensors. In (pp. 145–152). *Proceedings of the 41st Annual ISA Analysis Division Symposium, 29.*