Chapter 2

USE OF A TOTAL FLAMMABLE GAS DETECTOR IN MINE RECOVERY

J. E. Chilton

U.S. Bureau of Mines
Pittsburgh Research Center
Pittsburgh, PA 15236

ABSTRACT

Methanometers with catalytic heat-of-combustion sensors used in coal mines today will read low for flammable gases when oxygen (O_2) concentrations are low or when methane (CH_4) concentrations are greater than 10%. Thus, these methanometers may not be reliable during operations such as fire fighting or recovery of sealed mines. The U.S. Bureau of Mines developed a total flammable gas detector (TFGD) to measure CH_4 at concentrations up to 100% and to measure flammable gases in low O_2 concentrations. This paper describes the operation and construction of the TFGD and discusses measurements of flammable mine gases obtained from a mine in western Pennsylvania.

INTRODUCTION

Methane is encountered in the working atmospheres of many mines. These mines include most coal mines and some salt and trona (sodium carbonate) mines. The CH_4 concentrations in the atmosphere of these mines can accumulate to 5% to 15%, a mixture with air that is flammable or explosive. Figure 1 shows the hazardous range. In 1989, a CH_4 ignition killed 11 miners at the William Station Mine, KY, while they were moving a longwall mining system. In 1991, a CH_4 explosion killed two miners at the Firecreek Mine, KY. Such tragedies underscore the need to measure and control CH_4 in working mines to protect both life and property. The Mine Safety and Health Administration (MSHA) has promulgated ventilation rules for underground coal mines that require periodic testing for CH_4. These regulations also prescribe changes in the section ventilation, cut off of the section electrical power, or removal of miners from the section at designated CH_4 concentrations, U.S. Code of Federal Regulations (1989).

Workers commonly use portable, handheld CH_4 monitors (methanometers) to measure CH_4 concentrations in mines. Generally these methanometers have a range 0 to 5% CH_4 by volume[1] and use catalytic heat-of-combustion sensors. Methane reacting with O_2 at the surface of a heated platinum wire will add heat from the reaction to the wire, raising its temperature. The temperature increase of the wire and resultant change in the wire's electrical resistance are proportional to the concentration of CH_4. Rather than a

[1]All gas levels in this document will be expressed as % by volume unless otherwise specified.

simple platinum wire, most CH_4 sensors use a pellistor constructed from a thin platinum wire spiral coated with porous alumina and impregnated with metal catalysts such as platinum or palladium (figure 2). This structure is mechanically robust and allows the reaction of CH_4 with O_2 to proceed at reduced operating temperatures. In practice, two such pellistors are connected in a bridge circuit and heated by electrical current to the operating temperature. One pellistor is reactive to CH_4 and the other used as a reference. The reference pellistor is made nonreactive (poisoned) to CH_4. This circuit compensates for changes in ambient temperature. In most methanometers, the gas sample reaches the pellistors by diffusion through two separate flame barriers composed of either woven metal screen or porous sintered metal. The Auer M502 methanometer[2], (figure 3) uses a pump to draw a gas sample into a small volume containing both pellistors. Only the flammable gases within this volume are consumed during the measurement.

The requirements for the operation of a catalytic heat of combustion sensor are similar to the requirements for the propagation of fire as illustrated by the fire triangle. In the ordinary fire triangle, one corner represents the fuel, the second corner represents the oxidizer, and the third corner represents the ignition source. All three elements must be present for fire development. In the methanometer (figure 4), CH_4 is the fuel, O_2 from air is the oxidizer, and the heated platinum wire is the ignition source. All three elements must be present for catalytic heat of combustion sensor operation. Mines are continually ventilated with fresh air and usually have normal O_2 concentrations (approximately 20.9%). Thus low levels of methane or gases may be readily measured flammable with the standard methanometer.

[2]Reference to specific products does not imply endorsement by the Bureau of Mines.

However, if the gas sample contains no O_2, with any amount of CH_4, even up to 100%, there will be no reaction and thus no indication of CH_4. In coal mine fires and mine recovery operations, the atmosphere near the fire may have a low O_2 concentration, even less than 1%. The O_2 deficient atmospheres result from the reaction of O_2 with coal or other consumables in the fire, by dilution of O_2 from fire products such as carbon dioxide or by dilution in a sealed mine by continuous CH_4 emission. Mixtures of flammable gases without sufficient oxygen for complete combustion will not be accurately measured by a methanometer with a heat of combustion sensor.

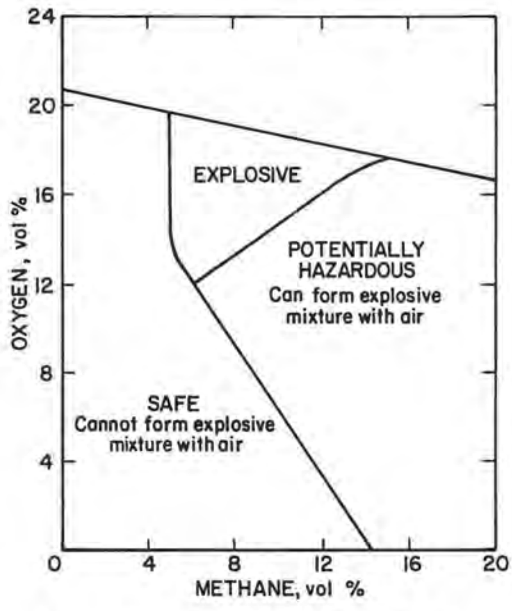

Figure 1. Explosive mixtures of methane and oxygen in air.

Several measurement techniques are used for estimation of CH_4 without requiring reaction with oxygen. These include measurement of refractive index of light and thermal conductivity. Both techniques can successfully measure CH_4 mixed with air or nitrogen at concentrations up to 100%. However, use of these techniques for measurement of multicomponent mixtures of combustible mine gases at the percent levels will result in significant errors in estimation of the total flammable gas content. For example, neither technique responds to carbon monoxide (CO). The Riken Model 18, with a refractive index sensor, reads 1% CH_4 for 1% carbon dioxide (CO_2) and -1% CH_4 for 1% hydrogen (H_2). The M510B, with a thermal conductivity sensor, is 5 times more sensitive to H_2 than to CH_4, Chilton and Kubala (1987). The Bureau chose a methanometer with a catalytic heat-of-combustion sensor which will react with all flammable gases for the work reported in this paper.

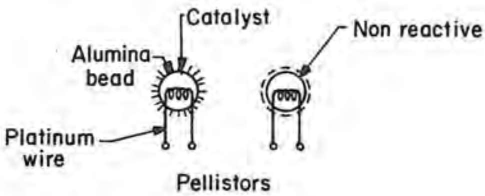

Figure 2. Catalytic heat of combustion sensor.

THE TOTAL FLAMMABLE GAS DETECTOR

In order to provide instrumentation for use in mine rescue and recovery operations, the Bureau developed the TFGD to measure all flammable gases, such as CH_4, ethane (C_2H_6) and other hydrocarbons, H_2, and CO, which may be in O_2 deficient atmospheres. The TFGD consists of a permissible Auer M502 methanometer, two peristaltic pumps, and a plastic fresh air bag housed in a metal enclosure (figure 5). The two peristaltic pumps are hand-operated and connected by a common shaft. One pump supplies a large volume of fresh air from the bag. The second pump supplies a smaller volume of mine gas (figure 6). The fresh air dilutes the mine gas sample so that there will be sufficient O_2 in the diluted sample to react with all the flammable gases present. Since the two pumps are connected, they deliver a fixed volume ratio of fresh air to mine gas sample.

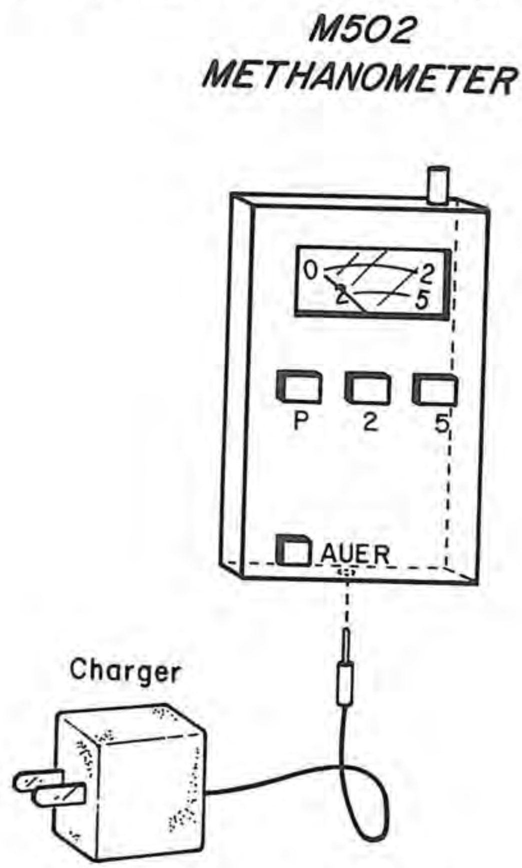

Figure 3. Aver Methanometer M502.

The Bureau fabricated two different TFGD systems. One has a dilution ratio of 30. This system would dilute a 100% CH_4 sample to 3.3%, a level within the measurement range of the M502 (0 to 5%). This system was designed for measurement of concentrations of mine gases up to 100% CH_4 as found in some sealed gassy mines. The second TFGD system has a dilution ratio of 15. In this case, the system would dilute a 60% CH_4 sample to 4%, which is in the measurement range of the methanometer. The second unit would measure CH_4 in the potentially explosive range, 5% to 15% CH_4 in air, with better resolution.

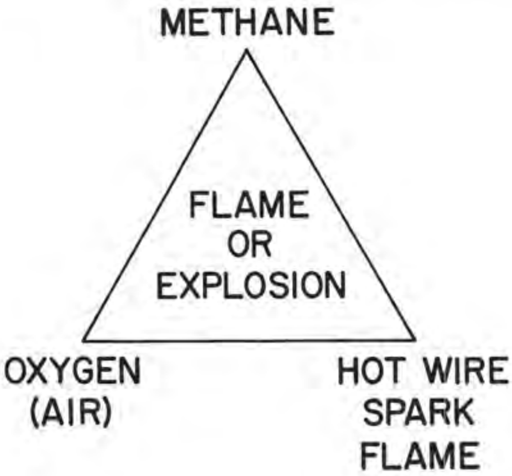

Figure 4. Methanometer fire triangle.

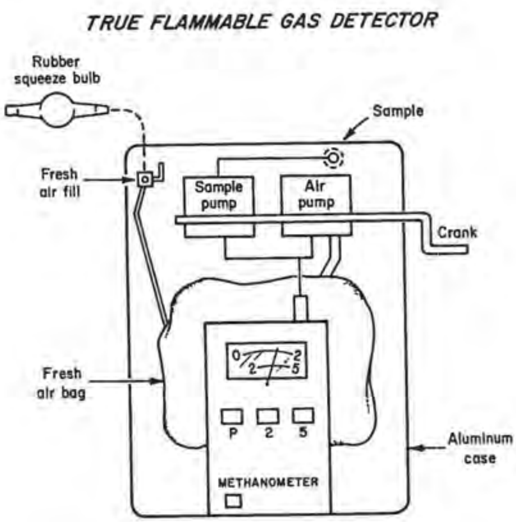

Figure 5. Total flammable gas detector - TFGD.

The methanometer in the TFGD indicates the concentration of the diluted gas. The original mine gas concentration is calculated by multiplying the indicated value by the TFGD dilution ratio. The dilution ratio is experimentally determined by sampling either 100% or 50% CH_4 gas standards and measuring the response on the M502 methanometer for the diluted gas. The dilution ratio is calculated from the ratio of the known CH_4 gas standard concentration to the methanometer indication. The measured dilution ratio is marked on each TFGD unit. Since most users prefer direct indication of the original gas concentration during mine operations, a nomograph (fig. 7) is placed on the side of each TFGD system. To find the original mine gas concentration, the user simply notes the value on the nomograph across from the value indicated by the methanometer.

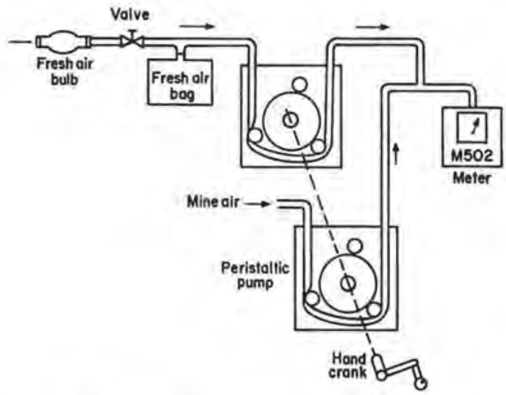

Figure 6. TFGD operation.

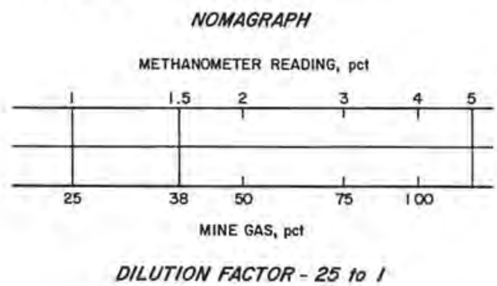

Figure 7. Nomagraph.

The M502 was selected for the TFGD system because it is the only one in commercial production that uses a fixed sample reaction volume (2 to 3 ml). Seven turns of the hand crank pumps approximately 10 ml sample volume through the TFGD. This pumped volume insures complete renewal of the gas within the pumps, internal tubing, and the methanometer sample volume for each measurement. The sample reaction volume in the M502 is small, minimizing the amount of air used for each reading. This feature helps increase the total number of samples (approximately 30) that can be run before having to refill the fresh air bag carried within the unit. All other commercial methanometers operate by continuous gas sample diffusion and convection. These methanometers cannot be used in the TFGD; delivering a continuous sample to the sensor during the measurement would rapidly exhaust the fresh air supply in the TFGD.

The TFGD system was initially designed for in-mine use where the mine atmosphere sample would enter the unit directly during hand operation of the pumps. One common method of controlling or helping to extinguish mine fires, though, is to seal the mine from outside air. Before the rescue team can reenter a sealed mine, they must sample the mine atmosphere. Often, companies drill boreholes from the surface into an area close to a fire to facilitate mine gas sampling. The TFGD can measure the flammable concentration of the mine gas sampled through tubing in the mine from a surface borehole as indicated in figure 8. The mine gas sample is first pumped from tubing through the borehole into a flexible gas bag. The gas bag is then connected to the TFGD. After the sample is hand-pumped into the unit, the methanometer is operated to indicate the diluted CH_4 or flammable gas concentration.

MINE FIRE MEASUREMENTS

A coal mine in southwestern Pennsylvania caught fire near the Thomas Portal shaft on October 17, 1990. This shaft and all other mine openings were sealed with slag and fly ash to extinguish the fire. The company drilled boreholes at several locations to allow monitoring the fire by mine gas sampling. They installed plastic tubing extending into the mine in the casing at each hole and sealed the casing heads with polymeric foam. MSHA collected gas samples at each site using a gasoline engine-powered electric generator to drive an electric powered air pump to obtain the mine air samples. At first, MSHA monitored the mine gas composition onsite with a portable gas chromatograph housed in a van. After several weeks, they collected gas samples at each site for later analysis at their Pittsburgh laboratory.

GAS SAMPLE FROM BOREHOLE

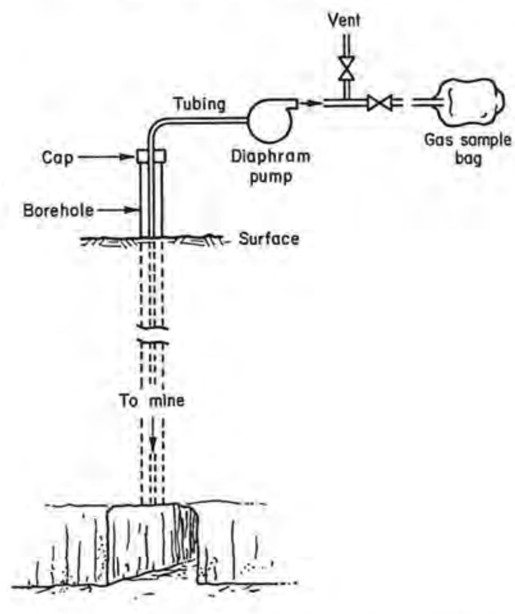

Figure 8. Gas sample from borehole.

MSHA personnel also helped collect mine gas samples to test the TFGD. First, the mine air samples were collected in a plastic bag. Then, a sample was drawn from the filled bag into the TFGD by operating the air pumps. Measurements were also taken with methanometers, CO meters, and O_2 meters from the flowing mine gas sample at the air pump outlet. Bureau researchers drew additional gas samples into glass Vacutainers for analysis at the Bureau's laboratory by gas chromatography (GC). The CH_4 and O_2 measurements were taken with the National Mine Services (NMS) MX240, an instrument that contains detectors for both gases. The sensor for CH_4 is catalytic heat-of-combustion; the sensor for O_2 is electrochemical. CO measurements were taken with a NMS CO260, which has an electrochemical sensor. Measurements taken at the Thomas Portal were as follows: On October 26, 1990, the MX240 read 0.9% CH_4 and 1.8% O_2. Samples analyzed by GC reported 3.72% CH_4, 0.33% C_2H_6, 1.51% H_2, and 1.01% CO for a total flammable gas concentration of 6.6% CH_4 equivalent (see appendix). The TFGD measured 5% CH_4 equivalent. On November 20, 1990, the MX240 read 1.9% CH_4 and 2.4% O_2. Samples analyzed by GC found 2.77% CH_4, 0.088% C_2H_6, 0.8% H_2, and 1.11% CO, for a total flammable gas concentration of 4.4% CH_4 equivalent. The TFGD yielded 3.4% CH_4 equivalent.

Measurements were taken at the Linden Portal (2 miles from the Thomas Portal) as follows: On November 20, 1990, the MX240 read 3.5% CH_4 and 16.2% O_2. Since the O_2 concentration was over twice the CH_4 indication, the methanometer value is reliable and TFGD unit was not used. The total flammable gas by GC data, principally CH_4, was 3.3% CH_4 equivalent. A summary of the gas analysis is given in Table 1.

Table 1.--Gas Analysis Summary

LOCATION	ANALYSIS UNIT	TOTAL FLAMMABLE %	OXYGEN %
Thomas 10/26	MX240	0.9	1.8
	GC	6.6	2.8
	TFGD	5.0	-
Thomas 11/20	MX240	1.9	2.4
	GC	4.4	2.7
	TFGD	3.4	-
Linden 11/20	MX240	3.5	16.2
	GC	3.3	16.5

Gas Analysis Summary

In both of the mine samples at the Thomas Portal, the O_2 concentration was too low for complete reaction with all the flammable gases. Thus the flammable gas measurements with the catalytic heat-of-combustion methanometer were too low. The TFGD measurements were closer to the total flammable gas concentrations.

The deviation of the TFGD-measured values from the calculated CH_4 equivalent values is caused by the M502 methanometer response characteristics. When calibrated for CH_4, the M502 read 90% of calculated response for CO and 70% of calculated response for H_2. Other catalytic heat-of-combustion methanometers have been found to read 100% of the calculated response for both of these gases. Most likely, the lower response of the M502 results from incomplete poisoning of the M502 reference pellistor to CO and to H_2. Any response of the reference pellistor to CO or H_2 would effectively subtract from the response of the active pellistor in the bridge circuit. If true, repoisoning the reference pellistor in the M502 would improve the agreement between measured and calculated CH_4 equivalents for these flammable gas measurements.

In the measurements taken on October 26, 1990, the sample gas was also fed directly into a CO monitor with a range of 0-2000 ppm CO. The instrument read greater than full scale. Subsequent GC analysis showed the CO concentration to be 1.01% (or 10,100 ppm). For the next measurement on November 20, 1990, an extra TFGD was modified. The mine gas from the gas collection bag was diluted and fed by pumping continuously into a CO monitor until the display gave a constant indication. The original gas concentration was then calculated from the product of the measured value for the dilute gas (384 ppm) and the dilution ratio (27.8). The calculated CO concentration of 1.07% was compared to the value of 1.13% determined by GC. This result affirms the validity of the dilution principle for CO as well as for other flammable gases. This single measurement took several minutes of steady pump operation and consumed more than half the fresh air supply within the TFGD. This procedure, requiring continuous gas sample dilution, is not practical for work in mine recovery where sources of fresh air may be limited.

SUMMARY

- The total flammable gas detector unit will measure flammable gases inside the mine during recovery operations or will measure the flammability of mine gas samples pumped through boreholes.
- The TFGD successfully measured total flammable gases from an actual mine fire when O_2 levels were low. TFGD measurements agreed well with GC analyses. In these same conditions, flammable gas measurements made with catalytic heat-of-combustion sensors were unreliable.
- The TFGD can measure high concentrations of CO in mine gases by dilution of the gas sample fed into a low range CO monitor.
- This study confirmed that a methanometer with catalytic heat-of-combustion sensors with a range 0 to 5% CH_4 will reliably measure low concentrations of CH_4 and other flammable gases only when the sample contains sufficient O_2 to react completely with all the flammable gases.

REFERENCE

Chilton, J. E., and T. Kubala, 1987, "True Flammable Gas Detecting System," BuMines IC 9163, 11 pp.

U.S. Code of Federal Regulations, July 1, 1989, Title 30-Mineral Resources; Chapter I-Mine Safety and Health Administration, Department of Labor; Subchapter D-Ventilation; Part 75 Mandatory Safety Standards-Underground Coal Mines, sec. 75.308; p. 511.

APPENDIX

Equation 1 calculates the total CH_4 equivalent in percent by volume units for all of the flammable gases in the sample:

$$CH_4 \text{ equivalent} = 5 \bullet \Sigma(fLFL_i), \quad (1)$$

where $fLFL_i$ is the fraction of lower flammable level (LFL) for each flammable gas. The fractional value is calculated by dividing the percent by volume of each flammable gas (as determined by GC analysis) by the %LFL for that gas. The %LFL values used in this calculation are 5% for CH_4, 3% for C_2H_6, 12.5% for CO and 4% for H_2.