Gas Chromatography Techniques in Detecting Toxic Exhaust Gases in Underground Mines

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Many gas emissions in mines can threaten human health. Gases can be emitted from mining sources such as geological strata, chemical treatment and exhaust emissions. Exhaust emissions include carbon monoxide, carbon dioxide, nitrogen and sulfur oxides and are considered as some of the most important and hazardous gases. These gases are dangerous in terms of human's health. They can cause toxic materials to be absorbed by the lungs and throat. They also can cause a situation under which an explosion may possibly occur. The Environmental Protection Agency (EPA) and Mine Safety and Health Administration (MSHA) specify maximum levels for various gases such as 50 ppm for carbon monoxide, 5000 ppm for carbon dioxide, 25 ppm for nitrogen monoxide, 5 ppm for nitrogen dioxide, and 5 ppm for sulfur dioxide. During this study, measurements have been taken by using GC (Gas Chromatograph) analyses to determine the amount and the concentration of each of the gases when high concentrations may indicate an emergency in a mine. The GC has been used in underground coal mines for over 30 years. Early models were too slow for high volume sampling and analyses required during a mine emergency. Improved GC models received wide acceptance in many industries and have become commonly used. The main use of a GC is for determining contaminants in air and water. This GC analyzing method can be useful in monitoring and investigating the underground mine atmosphere. Samples of mixed gases are often taken in bags and subsequently the gas is injected into the GC. Samples proceed through several analysis stages ending with the detector measuring the concentration of gases to provide accurate quantitative measurements of the different components of the gas mixture. Modern GCs provide high accuracy with fast analysis, have become popular analytical instruments and are considered as economical and reliable analyzers.

Keywords: Gas Chromatography, Exhaust Gas, Contaminents

1. Introduction

A gas chromatograph (GC) is used to isolate gas mixtures and analyze compounds that can be vaporized and injected into the instrument. The GC is commonly used in laboratories for gas mixture analysis. The GC consists of various components that help to separate, prepare and analyze the gas where the inert carrier gas is pumped continuously through coils that contain gas adsorbents. Small pulses of the gas mixture sample are injected into the line upstream from the GC columns. Initially, the coil materials absorb the selected gases and the continued flow of the carrier gas will cause desorption of each gas at a time and rate based on its particular adsorption characteristics. The result is that the gases leave the adsorbent columns as discrete and separated pulses. The subsequent concentrations can then be measured by using one or more of the detection techniques as described by McPherson, 1993. [1]

The GC technique can be used in detecting various kinds of naturally occurring mine gases. It is also used to detect engine exhaust gases from combustion processes such as carbon dioxide, carbon monoxide, hydrocarbons, and nitrogen oxides. GC laboratory testing can determine gas concentrations accurately. It can make accurate determination of gases found in the underground environment such as hydrogen, nitrogen, ethylene and ethane as described by Brady, 2008. [2]

Samples are often taken and stored in containers from which air has been totally evacuated. A container often used by NIOSH personnel is the 10-to-20 ml air-evacuated glass sampling tube. These are blood collection tubes that have at least 95% of air evacuated [3]. The other method for sampling gas is by using sampling plastic bags. These have been used successfully to collect air samples that contain organic and inorganic gases. This provides a simple, uncomplicated, and economical means of collecting and transferring gas samples. Also it offers an option of either short-term sampling or alternatively sampling for a full work shift depending on the size of the bag and the pump flow rate [4].

2. GC types

There are four GC types that are commonly used in determining mine gas concentrations based on the type of the detectors that have been incorporated.

2.1 Flame ionization detector-type gas chromatograph (GC - FID)

This type is used for low gas concentrations and is constructed of a small volume chamber into which the gas chromatograph's capillary column is directly plumbed. Usually the small diameter capillary column is

fitted directly into the bottom of the detector's jet. The gaseous eluents from the column are mixed with separately delivered H_2 and air and all are burned on the jet's tip. After H_2 and O_2 are introduced to the Flame Ionization Detector (FID), the flame is lit using an electronic ignitor. The charged particles in that combustion process create a current between the detector's electrodes. The gaseous products leave the detector chamber through the detector's exhaust as shown in Fig 1. The detector housing has been heated so that gases produced by combustion do not condense before leaving its exhaust [5]. This type of GC is very sensitive and can detect a large range of concentrations. The FID is a relatively inexpensive instrument and needs low maintenance. FIDs can measure organic materials concentrations at very low substances. The FID flame is oxidizing all the mixture that is passing through. This analytical method destroys the gas sample [3,5].
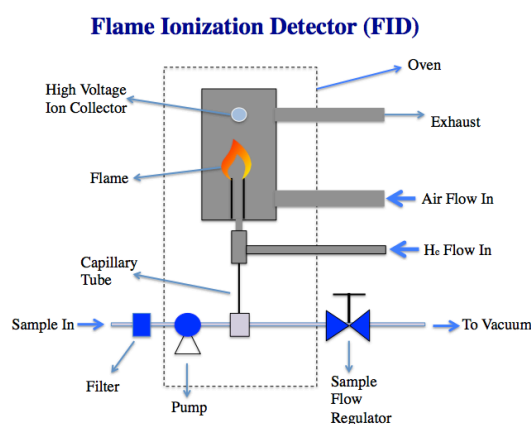

Fig. 1. Illustration of the GC – FID type.

2.2 Thermal conductivity detector-type gas chromatograph (GC – TCD)

The thermal conductivity detector – type gas chromatograph (GC-TCD) is used to analyze inorganic gases and small hydrocarbon molecules. It compares the thermal conductivity of two gas flows – the pure carrier gas and the sample. Changes in the temperature of the electrically heated wires in the detector are affected by the thermal conductivity of the gas which flows around it. The changes in this thermal conductivity are sensed as a change in electrical resistance and then can be measured [6]. The GC – TCD type is used in the presence of high gas concentrations. Unlike the FID, the TCD does not destroy the sample and it is less sensitive.
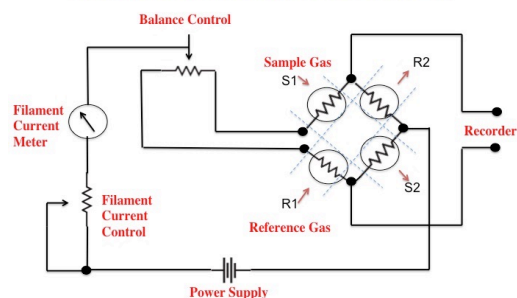

Fig. 2 . Illustration of the GC – TCD type.

2.3 Gas Chromatography – Mass spectrometry (GC – MS)

This type of GC is a combination of gas – liquid chromatography and gas spectrometry that will allow identification of different substances in a test sample. It identifies substances by electrically charging the specimen molecules, accelerating them through a magnetic field, breaking the molecules into charged fragments and detecting the different charges. A spectral plot displays the mass of each fragment. A technician can use a compound's mass spectrum for qualitative identification. The technician uses these fragment masses as puzzle pieces to piece together the mass of the original molecule, the "parent mass [7]. The GC – MS is popular for detecting engine exhaust gases analysis. From a mining perspective it is efficient in detecting gases in case of fire and explosives investigations. In addition it can identify the organic materials. On the other hand, the GC – MS requires pure samples to be injected in in order to give accurate measurements.
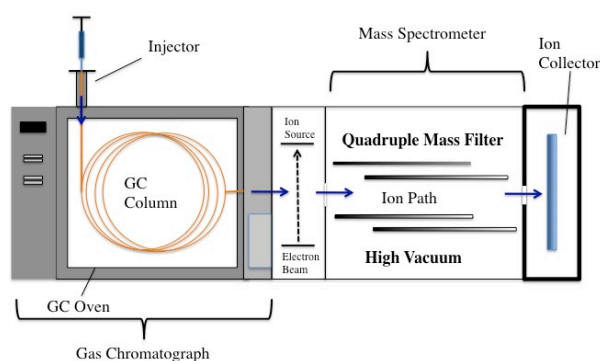

Fig. 3. The GC – MS type components.

2.4 Gas Chromatography Infrared Spectrometry (GC-IR)

The combination of Chromatography and Infrared Spectrometry enables the separation of the mixture and identifies the component. The Infrared spectrophotometer determines the relative strengths and positions of the infrared region and it measures the IR absorption spectrum of the measurement target gas

introduced into the gas cell. The measured IR absorption spectrum is used for qualification and quantification. The analysis can be completed rapidly without pretreatment.

3. Previous research

There are many studies that have been done to investigate mine atmospheres by using gas chromatography techniques to analyze the collected gas samples and to identify their type as well as measuring their concentrations.

Within a study done by [9] a gas chromatograph equipped with thermal conductivity detector was used. Two gas chromatographic columns were used where column 1 consisted of a 3 m of Porapak Q, 50-80 mesh, in series with 1.5 m of Porapak R, 100-120 mesh, in 3.2 mm internal diameter teflon tubing. Column 2 consisted of 25 mm of calcium sulphate in series with 3 m of Porapak Q, 50-80 mesh, and 1.5 m of Porapak R, 100-120 meshes, in 3 mm internal diameter Teflon tubing. The detector is maintained at a temperature of 200° C and 200 milliamps detector current. The Porapak is a packing material that delivers separated volatile compounds. It consists of cross linked polystyrene beads. There are different types of Porapak packing materials and for each there are three different kinds based on mesh size and temperature limit. Table 1 illustrates some types of Porapak.

Lamb, Larson and Tollefson have used the Q types as it is very effective with hydrocarbons, organic compounds in water and oxides of nitrogen. R types are useful because they have moderate polarity.

Table 1. Some types of the Porapak packing materials.

Porapak type	Mesh sizea	Temp. Limits
P	50 - 80	250° C
	80 - 100	250° C
	100 - 120	250° C
Q	50 - 80	250° C
	80 - 100	250° C
	100 - 120	250° C
R	50 - 80	250° C
	80 - 100	250° C
	100 - 120	250° C

Column 1 has been immersed in dry ice for about 15 mins after a sample was injected into the column and the column maintained at minus 78° C until the CO was eluted approximately 15 mins after sample injection. The column was then removed and left to adjust to room temperature. Methane and all inorganic components except NH_3, NO_2, and H_2O were obtained from the analysis using this column.

Column 2 was maintained at 160°C for the duration of the analysis of about one hour. The analysis of hydrocarbon components including methane was performed on this column. Ammonia analysis was not possible in this column.

The results showed that column 1 gave an excellent separation of O_2 and CO. The component separations indicate that these separations suggest that column 1 could be used with great facility in the study of NO reduction by H_2 or CO and in the study of the formation of nitrous oxide (N_2O) as an intermediate in the reduction process. Most of components used in column 1 are eluted. In column 2 it is apparent that CO_2 and N_2O have equal retention times.

This study showed that the combination of the column packings Porapak Q and R in a single column could be used for partial gas chromatographic analysis of automobile exhaust gas mixture components including hydrocarbons, oxides of nitrogen (except nitrogen dioxide which is detected in- directly when present in sufficient quantity) and carbon monoxide. [9].

Another study was conducted by Bagley and others, [10]. The researchers undertook this project to ensure a safe atmospheric condition in an underground mine after the use of modern, electronically controlled, low emission diesel engines in a mine. DPM samples were collected in the underground mine and analyzed by using two separate gas chromatography/mass spectrometry (GC-MS) methods. The first method was used to quantify the polycyclic aromatic hydrocarbon. The second GC-MS method was used for the measurement of nitro-polycyclic aromatic hydrocarbon. Researchers have analyzed separate aliquots of DPM-associated soluble organic fractions (SOF) for nitro - polycyclic aromatic hydrocarbon. Aliquots in the range of 5.0 to 6.0 ml of the SOF extracts were spiked with 4-nitro-biphenyl and then concentrated to a final volume of 1.0 ml. 1.0 μl of the concentrated extract was introduced in the GC/MS instrument with the injector and transfer line at 300°C and the GC oven at 65°C. The injector and transfer line are held at constant temperature throughout the sample analysis and the column was ramped to 240° C at a rate of 30°C per minute followed by a ramp to 300°C at a rate of 10°C per minute. After reaching the final temperature the column was held at the final temperature for 20mins as shown by Bagley, and others, 2002. [10]

The usage of GC- MS was vital for this study to obtain the results. However, the researchers concluded that the use of electronically controlled, modern diesel engines with a low sulfur fuel in Cote Balanch Mine (and underground salt mine) resulted in large reductions in DPM and all DPM-related components. The measured potentially health related components showed similar reductions. However, the use of electronically, controlled, modern engines cannot be relied upon to reduce concentrations below 0.15 mg/m^3 in all circumstances. A substantial reduction in DPM levels was observed at the downwind sampling location in this study. The traditional metric and the $< 0.8 \, \mu m$ respirable fraction were reduced by $> 60\%$ and 43%, respectively. The nontraditional metric continuous reading instruments such as diffusion charger, photoelectric aerosol sensor, and condensation particle counter all showed 50% reduction.

Another study was conducted by (Heaton, and Wentworth, 1959) [12] based on the necessity of studying distinct hydrocarbons in vehicle emissions. The organic elements of vehicle exhaust have given rise to the common recognition that these mostly consist of hydrocarbons. A suitable method for defining emission hydrocarbons should qualitatively and quantitatively regulate distinct hydrocarbons. In addition it is important to ensure a sensitivity of above of 10 ppm, without intrusion of non-hydrocarbon constituents. The analysis should not be costly, and should be quick, precise, correct, functional, simple to adjust, and give easily understandable and interpretable results. There is a void in previous approaches regarding the study of emission gas that provides for the necessity of understanding and solving the gas emission problems in mines.

Gas chromatography can give the required separations of gas mixtures but typical current energy sensors are not sensitive enough without the sample being concentrated. The mass spectrometer detectors are relatively expensive and do not have an ease of adjustability or understandings of the resulting data. Furthermore, an improved type of GC, Gas Chromatography Infrared Spectrometry (GC-IR) has been developed that generally meets the aforementioned pre-requisites.

Through the use of the GC – IR the information conveyed for emission hydrocarbons associated with untainted hydrocarbon fuels led to the conclusion that there were considerable quantities of unreacted fuel. The emissions from scented fuels held the most unreacted fuel, while olefin fuels emission held the least. It was found that 45 percent of all hydrocarbons in emissions were unreacted isooctane when utilizing isooctane energy sources. Furthermore, scented fuels travel within the engine with fewer cracked products, which were defined as components no more present in the original fuels than non-scented fuels. These outcomes qualitatively correlate with the given data. With the concentration of olefin in the gasoline there was a transmission of strong variances regarding the olefin concentration in the emission. The investigational indications gave the conclusion that the amount of olefin within the emission grew as the amount of olefin within the fuel was enlarged. Finally, the majority of the analysis and evidence conveys that the emissions hydrocarbon structure is contingent on the fuel structure.

4. Conclusions

The gas chromatograph with its different types and features can be very useful for determining the exhaust gases concentrations that they give accurate readings and measurements that the researchers can rely on. The GCs vary in hardware types and the variety of the detectors that can be built in them, which give a flexibility to choose the appropriate type of GC and detector based on the feature of the sample. However, the GC sometimes requires time to analyze the sample where a real time reading is not given since the samples are taken to the laboratory. Also, some of the gas chromatography might be too expensive and sensitive – a reason why they might not in preference to be used. Nevertheless, the GC is a favored instrument for gas or liquid analysis as it gives accurate concentration readings.

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