

ASSESSMENT OF THE EXPLOSIBILITY OF  
GAS MIXTURES AND MONITORING OF SAMPLE-TIME TRENDS

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ABSTRACT

Previous methods for the assessment of the explosive potential of gas mixtures have required the plotting of an explosibility diagram. These became cumbersome if a large number of assessments of various sampling locations over a period of time were required. This may make the approach of a dangerous situation more difficult to predict.

With the aid of a programmable calculator, a new method for the rapid assessment of the explosibility of coal mine sample gases has been developed. This method does not require that an explosibility diagram be drawn to indicate the explosive status of a gas mixture. Simple Cartesian co-ordinates representing the explosive potential of mixtures are obtained, which may readily be plotted to show changes with time.

INTRODUCTION

With the involvement of Department of Mineral Resources mobile gas analysis laboratories in colliery incidents, a rapid method for the assessment of the explosibility of sample gases obtained was required. Explosibility assessment of colliery atmospheres was considered necessary as an aid to ensuring the safety of personnel undertaking rescue operations after mine explosions or fires, or those involved in the recovery of previously sealed areas.

It was decided to base explosibility assessment methodology on the use of available, programmable, portable calculators. This approach was considered to have advantages in the speed and reliability of processing sample analysis data, the ability to readily check previous work and the reduction of the risk of misinterpreting graphical information when working under pressure.

Initially programs were developed based on previously published methods of explosibility assessment. However, shortcomings in these methods and in particular, difficulty in employing them to monitor time trends, resulted in the development of a new approach to explosibility assessment.

An improved method has now been developed for assessing the explosive potential of coal mine sample gases. It incorporates extensions to a previously accepted method with the added facility to readily monitor time-trends. This method is currently operational in conjunction

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with other facilities of the mobile gas analysis laboratories.

#### THE EXPLOSIBILITY OF GASES

Mixtures of flammable or combustible gases with air exhibit a concentration range over which the mixture, upon ignition, will propagate a flame independently of an external heat source (explosive range). If the concentration of flammable gas is below this range then the mixture is too lean to sustain combustion. At concentrations above this range insufficient oxygen is present to allow propagation of an ignition. The concentrations of flammable gas corresponding to the lowest and highest points of this range are termed the lower and upper explosive limits (LEL, UEL). The explosive range has also been termed the flammable range and its limits, the lower and upper flammable limits (LFL, UFL). The former terminology is more common in the coal mining industry and will be used here. Table 1 shows accepted values of the lower and upper explosive limits of methane, carbon monoxide and hydrogen in air under ambient conditions.

These ranges apply only to mixtures of the gas concerned with air. For mixtures of flammable gas, with an atmosphere deficient in oxygen, the explosive range is narrowed.

TABLE 1 - EXPLOSIVE LIMITS

<u>GAS</u>	<u>LEL</u>	<u>UEL</u>
CH <sub>4</sub>	5.0	15.0
CO	12.5	74.0
H <sub>2</sub>	4.0	75.0

Note: Gas concentration units in this and following tables are percentage by volume.

In general the lower explosive limit for a particular gas is raised only slightly but the upper explosive limit decreases markedly with increase in oxygen deficiency of the mixture.

The situation is further complicated if a mixture of flammable gases is considered, the components of which have widely varying explosive ranges. Such mixtures may be encountered in coal mines when, as the result of an explosion, heating or mine fire, carbon monoxide, hydrogen and higher hydrocarbons are present in addition to methane.

Commonly inert gas components are also present. These may be excess nitrogen (from oxygen depletion of original air) or carbon dioxide (from combustion) or both. These have a dampening effect on the explosibility of other gases. Figures expressing this effect as the volume of inert gas required to render a unit volume of combustible gas extinctive are given in Table 2. It can be seen that carbon dioxide is a more effective extinctive agent than nitrogen.

A number of methods have previously been developed to assess the explosibility of complex gas mixtures. The majority of these methods are based on the preparation and interpretation of explosibility diagrams, analogous to phase diagrams, and showing the possible explosive states of a gas mixture.

TABLE 2 - EXTINGTIVE VOLUMES<sup>1</sup>

<u>COMBUSTIBLE</u>	<u>INERT</u>	
	N <sub>2</sub>	CO <sub>2</sub>
CH <sub>4</sub>	6.0	3.2
CO	4.15	2.16
H <sub>2</sub>	16.55	10.2

<sup>1</sup> After Bajpayee (1976)

### METHODS OF EXPLOSIBILITY ASSESSMENT

Methods for the estimation of the explosive potential of gas mixtures have been the subject of a previous review. (Bajpayee, 1976). Of these, two were considered suitable for implementation with the mobile laboratories: that of Zabetakis et.al., (1957), and the approach of Hughes and Raybold (1960).

The former method requires the calculation of effective inert and combustible contents of the mixture and a factor relating the ratio of methane to other combustibles. These parameters are then plotted on an explosibility diagram which indicates the explosive status of the sample. A calculator program to perform the required calculations has been reported (Smith and Nugent, 1977). The method takes into account the greater extinctive effect of carbon dioxide in comparison to nitrogen and higher hydrocarbons may be taken into account as effective combustibles.

However the explosibility diagram on which this method is based is visually complicated. It rapidly becomes more so with changing proportions of methane to other combustibles and with the plotting of a number of sample points. Due to the complexity of the basic explosibility diagram and this diagram containing empirically derived curves, which would prove difficult to model in calculator programs, the latter method was chosen for further development.

The method of Hughes and Raybold is the current basis of explosibility assessment carried out by laboratories of the British National Coal Board (MacKenzie-Wood, 1980). It entails the calculation, with the aid of graphic diagrams, of parameters permitting the construction of an explosibility diagram for a gas mixture. The total combustible and oxygen contents of this mixture are then plotted allowing assessment of its explosibility. The original method does not take into

account the differing extinctive effects of carbon dioxide and nitrogen (this produces an error on the side of safety). The total concentration of higher hydrocarbons present is added to that of hydrogen, which has the broadest explosive range. This represents a "worst case" approach and results in any error, again, being on the side of safety.

### Mixtures of a Single Flammable Gas With Air.

Perhaps the most familiar means of illustrating the explosive characteristics of a flammable gas mixture was first published by Coward (1928-29). This explosibility diagram is known as a "Coward Diagram", a generalised form of which appears as Figure 1.

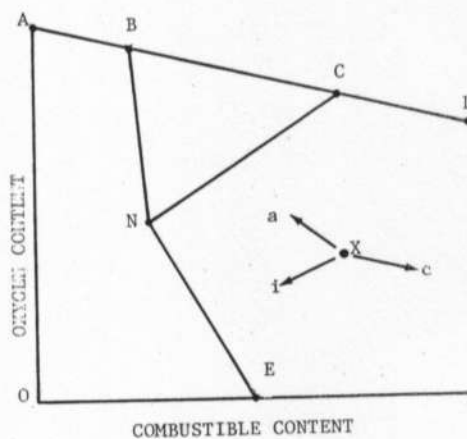


FIGURE 1

### GENERALISED COWARD DIAGRAM

In Figure 1, point A represents pure air and line AD mixtures of flammable gas with air. Point B represents the lower explosive limit and point C the upper explosive limit of the combustible gas in air. Point N, commonly termed the "nose point", represents the oxygen and combustible gas concentrations below which no mixtures are explosive. In constructing this diagram points B and C are initially plotted from the LEL and UEL of the mixture,

then point N from the oxygen and combustible content at the nose limit for the mixture. Line EN is then drawn such that, if continued it would pass through point A. The composition point, X, for the sample is then plotted from its oxygen and combustible gas content.

Three regions in the diagram are of interest. If a sample point lies in the area BCN it is explosive (capable of propagating flame after ignition). Samples lying in region DCNE are not explosive but would become so if they were diluted with air (potentially explosive). Samples lying in the region ABNEO are not explosive and are not capable of forming explosive mixtures with air dilution.

The diagram also conveys information on the effect of composition changes on explosibility. If a mixture is diluted with air, such as in the opening of a sealed area, its point on the diagram will move along a straight line toward point A (direction a, Figure. 1). This is especially important for samples initially in a potentially explosive condition, since air dilution means that they must pass through an explosive state.

Dilution with an inert gas will cause a sample point to move toward the origin, point O, (direction i). Increasing combustible content of the mixture causes a shift in direction c. An important aspect of this is that increasing combustible content of a mine atmosphere may result from not only the presence of increasing volumes of combustible gas but also from reducing the air supply to an area by sealing. This, under some conditions, could take the atmosphere through an explosive state.

#### Mixtures Containing a Number of Flammable Gases.

The original method of Coward treated only mixtures of one combustible gas with air. Hughes and Raybold developed extensions to

the method enabling Coward diagrams to be constructed for mixtures containing a number of combustible components. To calculate the limit of compositions of mixtures of combustible gases, it is assumed that Le Chatelier's principle is valid. This principle states that if each component of a mixture is at a limit composition then the mixture as a whole is also at limit composition. Mathematically:

$$L_m = \frac{100}{\sum (p_i / L_i)}$$

where:  $L_m$  is the limit of the complex mixture  
 $L_i$  are the limits of the separate gases  
 $p_i$  are the concentrations of each combustible gas as a percentage of total i.e.  $\sum p_i = 100$

This principle provides a means of calculating the lower and upper explosive limits and nose point compositions of mixtures of gases from the limit compositions of each combustible gas in air and excess inert. Table 3 gives combustible and oxygen contents at the nose limits for mixtures of methane, carbon monoxide and hydrogen in air and both excess nitrogen and carbon dioxide.

TABLE 3  
Nose Limit Contents

	OXYGEN		COMBUSTIBLE	
	N <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
CH <sub>4</sub>	12.24	15.07	5.93	6.66
CO	6.07	8.80	13.78	18.0
H <sub>2</sub>	5.12	7.61	4.30	5.73

As a result of these calculations a Coward diagram is obtained which conveys the explosibility characteristics of a complex mixture of gases. The method is outlined in more detail in the Appendix.

This method, as originally published, did not take into account the differing extinctive powers of carbon dioxide and nitrogen. For composition limit calculations a number of graphs were employed relating combustible and oxygen content at limit points to the percentage of each combustible in total combustibles. Adapting this method to a programmable calculator provided the opportunity to eliminate these intermediate graphical steps and to conveniently include the effect of carbon dioxide in the calculations.

Because of the widely differing explosibility characteristics of methane, carbon monoxide and hydrogen, Coward diagrams for mixtures of these gases vary greatly with differing proportions of each gas. Provided the proportions of each gas do not alter, a single diagram is adequate and can conveniently be used to monitor explosibility as a function of time. However, it may be expected that in a post explosion, heating or fire environment, or in situations where direct attack with water to a fire is used, these proportions would vary considerably. In monitoring the progress of these situations, this would rapidly lead to either a large number of differing explosibility diagrams or a complex single diagram, thus making assessment difficult and the possibility of error greater. This was the primary consideration in developing the extension to the Hughes and Raybold approach later described.

#### Use of An Explosibility Index

As a means of predicting the onset of a dangerously explosive situation an explosibility index has been suggested (Mitchell and

Burns, 1979). This index, a modification of previous German and Russian methods, is given by:-

$$E = E_c ( O_2 / MAO )$$

where  $E$  = Explosibility Index  
 $E_c$  = Effective combustible content of the mixture  
 $= (CH_4 + 1.25 H_2 + 0.4 CO) \%$   
 $MAO$  = Maximum allowable oxygen content of the mixture.  
 $= 5 + \frac{7 CH_4}{(CH_4 + H_2 + CO)} \%$

With the plotting of this index as a function of time, trends towards an explosive condition of sampled gases may be visualised. This method was however, considered unsuitable for further development and use due to a number of major deficiencies. These, as outlined by Mitchell and Burns are:

- a) Critical values of the index, indicating an explosive or potentially explosive situation may vary and prior experience in a situation is required before values can be selected.
- b) These values may be different for different sampling locations and for a given location could change with different conditions in the area.

#### AN EXTENDED METHOD OF ASSESSMENT

The method developed is essentially an extension of that of Hughes and Raybold. It provides an efficient means of data reduction leading to much simplified assessment of explosibility, both currently and as a function of time. Basically, a transformation is performed on the Coward diagram for a gas mixture, yielding Cartesian co-ordinates, (x,y), which convey essential explosibility information.

In the unmodified method, the explosive

status of a gas mixture is a function of: the lower and upper explosive limits (LEL, UEL); the combustible and oxygen content of the mixture corresponding to the nose point ( $C_N, O_N$ ); and the actual combustible and oxygen contents of the sample ( $\Sigma C, O_2$ ). The simplifying transformation may be expressed:

$$f(\text{LEL, UEL, } C_N, O_N, \Sigma C, O_2) \rightarrow f(x_m, y_m)$$

where  $x_m$  and  $y_m$  are modified co-ordinates for the mixture. Details of, and formulae used in this transformation are given in the Appendix.

The effect of this transformation and the correspondence between the regions of a Coward diagram and the modified diagram are shown in Figure 2.

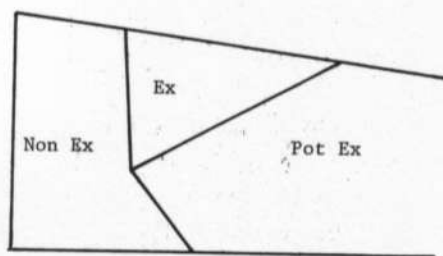


FIGURE 2

CORRESPONDENCE: COWARD/MODIFIED DIAGRAM

All mixtures whose ( $x_m, y_m$ ) co-ordinates lie in the first quadrant are explosive, those in the second and third quadrants non-explosive and those in the fourth quadrant potentially

explosive. The explosive status of a gas mixture is, therefore, indicated by the signs of  $x_m$  and  $y_m$ . If this is the only information required, a diagram need not be drawn.

Figure 3 shows the results of the above approach for three gases which illustrate the three possible explosive states. Compositions and other parameters for these mixtures are listed in Table 4.

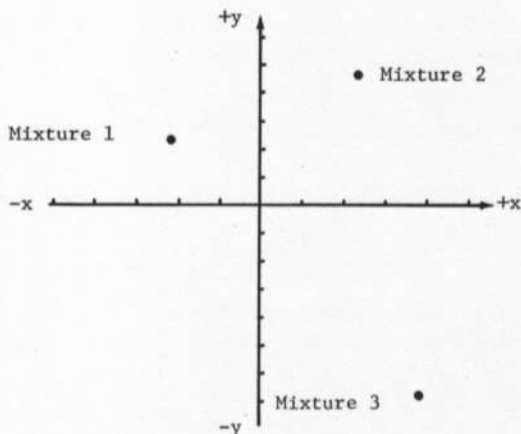


FIGURE 3

EXAMPLE GAS MIXTURES

TABLE 4 - GAS MIXTURE DATA (FIGURE 3)

MIXTURE	1	2	3
CH <sub>4</sub>	1.93	3.3	3.18
CO	1.4	4.3	0.83
H <sub>2</sub>	4.0	4.9	-
CO <sub>2</sub>	5.32	13.8	2.62
O <sub>2</sub>	11.89	2.8	13.46
C	7.33	12.5	4.01
LEL	4.89	5.61	5.71
UEL	36.48	36.4	17.96
C <sub>N</sub>	5.50	6.49	6.75
O <sub>N</sub>	7.09	7.71	11.71
X <sub>m</sub>	2.26	3.84	-2.22
Y <sub>m</sub>	4.61	-6.74	2.37

CONDITION EXP. POT. EXP. NON. EXP.

NOTE These compositions are those given by Hughes and Raybold as examples. Different values for combustible and oxygen contents at the nose point, ( $C_N, O_N$ ) are the result of taking into account the extinctive effect of carbon dioxide.

Directional information of the Coward diagram with regard to air or inert dilution or increasing combustible content is retained in the modified diagram. In general, air dilution causes shift of a sample point toward top left of the modified diagram, inert dilution toward bottom left and increasing combustible content toward bottom right.

Figure 4 shows co-ordinates obtained for 58 different gas mixtures plotted on a single diagram. Table 3 gives the composition of strategic points on the diagram, together with the overall concentration ranges involved. The methane concentration as percentage of total combustibles in the mixtures varied from 47 to 65 per cent.

In Figure 4 point V represents an initial, oxygen deficient atmosphere. The segment V-W shows the effect of increasing combustible content in this atmosphere with transition from a non-explosive to a potentially explosive state. The segment W-X illustrates the effect of dilution with nitrogen of this atmosphere, as in the inertisation of a sealed area, and return to a non-explosive condition.

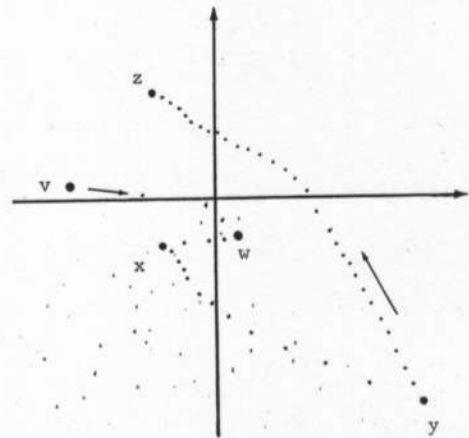


FIGURE 4  
LONG TERM SAMPLE SEQUENCE

Segment X-Y again illustrates the effect of increasing combustible content. Line Y-Z shows the effect of air dilution on mixture Y and its transition through an explosive state. If it were necessary to ventilate, with air, an area containing an atmosphere such as Y then co-ordinates for points in the dilution could be plotted with time and an estimate of when the atmosphere would become explosive would be obtained.

Following this sequence on conventional explosibility diagrams would entail the preparation and interpretation of either a large number of diagrams or a reduced number of very complex diagrams. The extended method over-

TABLE 3  
COMPOSITION AND RANGE DATA OF MIXTURES IN FIGURE 4

	V	W	X	Y	Z	Range
CH <sub>4</sub>	1.2	4.1	3.06	13.4	2.31	0.5 - 5.36
CO	0.5	2.8	2.1	5.36	0.93	0.1 - 1.84
H <sub>2</sub>	0.1	1.7	1.27	1.84	0.32	1.2 - 13.4
CO <sub>2</sub>	1.5	4.4	3.3	7.19	1.24	1.24 - 7.19
O <sub>2</sub>	10.0	7.5	5.62	1.75	17.62	1.75 - 17.62

comes the problems associated with previous approaches in that a single diagram can be used to monitor complex explosibility situations over a period of time.

CONCLUSIONS

It is considered that the extended method of explosibility assessment outlined above leads to the following advantages:

- (a) allows the explosive status of a complex gas mixture to be ascertained without the need to plot an explosibility diagram.
- (b) facilitates the plotting of explosive potential as a function of time thus aiding estimation as to when a situation may become dangerous.
- (c) retains the essential directional information of "Coward Diagrams" as to the effect of air dilution, inert dilution and increasing combustible content of gas mixtures
- (d) reduces the number of parameters required to define an explosive condition, thus will facilitate the transfer of information between remote sampling points, fresh air bases and central control points during an incident.
- (e) permits modelling of the outcome of intended actions, given the knowledge of an area concerned and estimated input and output volumes of gases.

Footnote

Software for this method of explosibility assessment is currently available for Hewlett-Packard HP67 and HP41C calculators. The programs may be copied onto blank magnetic cards supplied, and listings and further information obtained by contacting the author.

ACKNOWLEDGEMENT

Is given to Messrs. A.P. MacKenzie-Wood and C.G. Ellis, the former for his advice and editing assistance and the latter for suggesting that polar co-ordinates may prove useful.

APPENDIX

The following equations follow a calculation procedure analogous to that of Hughes and Raybold except for equation 1.2 and 1.3 which include the extinctive capacity of carbon dioxide.

(a) Lower and Upper Explosive Limits

$$L_{L,U} = \frac{100}{\sum(p_j/L_j)} \dots\dots 1.1$$

- where:  $L_{L,U}$  = lower, upper explosive limits of mixture
- $p_j$  = concentration of combustible gas, j, as a percentage of total combustibles.
- $L_j$  = LEL, UEL for combustible gas, j.

(b) Combustible Content at the Nose Point

$$C_N = \frac{N_2}{T} \left[ \frac{100}{\sum(p_j/n_{1,j})} \right] + \frac{CO_2}{T} \left[ \frac{100}{\sum(p_j/n_{2,j})} \right] \dots\dots 1.2$$

- where:  $C_N$  = combustible content at the nose point for the mixture.
- $n_{1,j}$  = nose limit for gas, j, in air and excess nitrogen.
- $n_{2,j}$  = nose limit for gas, j, in air and excess carbon dioxide.

$$T = N_2 + CO_2$$

(c) Oxygen Content at the Nose Point

$$X_L = \frac{N_2}{T} \left[ \frac{\sum(v_{1,j} p_j)}{\sum(p_j/n_{1,j})} \right] + \frac{CO_2}{T} \left[ \frac{\sum(v_{2,j} p_j)}{\sum(p_j/n_{2,j})} \right] \dots\dots 1.3$$

$$O_N = 0.2093 (100 - X_N - C_N) \dots\dots 1.4$$



where;  $X_L$  = excess inert at the nose point  
 $O_N$  = oxygen content at the nose point  
 for the mixture

$u_{1,j}$  = volume of nitrogen required to  
 render unit volume of gas, j,  
 extinctive

$u_{2,j}$  = volume of carbon dioxide required  
 to render unit volume of gas, j,  
 extinctive.

$L_L, L_U, C_N, O_N, O_2$  (sample) and  $\Sigma C$   
 (total combustibles in sample) can then  
 be used to plot a Coward diagram for the  
 gas mixture.

An abbreviated form of such a diagram  
 is shown in Figure A.1. In this figure point  
 X represents a sample composition shown here  
 for convenience as potentially explosive.

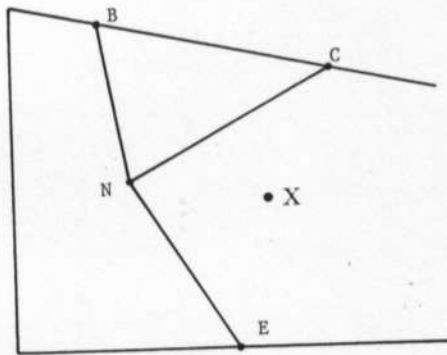


FIGURE A. 1.

PRE TRANSFORMATION DIAGRAM

Steps in the Extended Coward Diagram

Calculations.

1. Calculation of the co-ordinates of points  
 B, C, and E.

$$B \quad (LEL, 0.209 \text{ LEL} + 20.93)$$

$$C \quad (UEL, -0.209 \text{ UEL} + 20.93)$$

$$E \quad \left[ \begin{array}{c} -20.93 \text{ } C_N \\ O_N - 20.93 \end{array} , 0 \right]$$

2. Co-ordinate transformation to move the  
 origin to the nose point.

$$(x, y) \rightarrow (x - C_N, y - O_N)$$

3. Conversion of new co-ordinates of points  
 B, C, E and X to polar form with the origin at  
 the nose point.

$$B \rightarrow r_B \angle \theta_B \quad C \rightarrow r_C \angle \theta_C$$

$$E \rightarrow r_E \angle \theta_E \quad X \rightarrow r_X \angle \theta_X$$

4. Calculation of modified angular co-ordinates  
 $r_m, \theta_m$  for the sample point, x

- (a) Explosive Case ( $\theta_B > \theta_X > \theta_C$ )

$$r_m = r_x$$

$$\theta_m = \left[ \frac{\theta_X - \theta_C}{(\theta_X - \theta_C) + (\theta_C - \theta_X)} \right] \cdot 90$$

- (b) Potentially Explosive Case ( $\theta_C > \theta_C$  or  $\theta_E > \theta_E$ )

$$r_m = r_x$$

$$\theta_m = \left\{ \left[ \frac{\theta_X - \theta_E}{(\theta_X - \theta_E) + (\theta_C - \theta_X)} \right] \cdot 90 \right\} + 270$$

- (c) Non-Explosive Case

$$r_m = r_x$$

$$\theta_m = \left\{ \left[ \frac{\theta_X - \theta_B}{(\theta_X - \theta_B) + (\theta_E - \theta_X)} \right] \cdot 180 \right\} + 90$$

5. Conversion of modified angular co-ordinates  
 to rectangular (Cartesian) co-ordinates for the  
 sample point.

$$r_m \angle \theta_m \rightarrow (x_m, y_m)$$

6. The co-ordinates  $(x_m, y_m)$  then convey the  
 explosive state of the analysed gas mixture  
 according to:

State	$x_m$	$y_m$
Explosive	+	+
Potentially Explosive	+	-
Non-Explosive	-	+
	-	-

They may also be plotted on simple rectangular,  
 X-Y axes to allow time trends to be observed.

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DISCUSSION

I. ROBERTS (Queensland Department of Mines):  
The two disasters which have occurred in Queensland in the last decade both occurred at a weekend, the Box Flat disaster occurred on a Sunday and the Kianga one on a Saturday. Add to this the fact that the West Wallsend explosion was one which occurred at a weekend and during a mine shutdown. These explosions were the result of events which occurred over the weekend, and it is understood that the Appin belt fire occurred over a weekend. This should be drawn to the attention of the people at this Conference. It highlights the need for surveillance at weekends, perhaps more than has been applied in the past. This is prompted by

a remark which Mr. Lyne made, perhaps made rather lightly, about removing Friday from the calendar, and this would only be a short term remedy if the Australian dream is realised and a five-day weekend is achieved.

B. LOVELY (Queensland Department of Mines): Dr. Ellicott is to be congratulated very much on his paper. Anything that can simplify the deduction of conclusions from gas analyses needs to be applauded and at this stage it is appropriate to consider what this new diagram is going to be called. It could be foreseen that it could be quite happily referred to as the Ellicott diagram.