Naked Flame Tests for CO_2 in Limestone Caves & The Effect of CO_2 and O_2 on Humans.

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Cavers are quiet aware that if they are breathing heavily, have a headache or feel tired and lethargic, there may be a high concentration of carbon dioxide (CO_2) in the cave atmosphere which they are breathing. For those without sophisticated instruments, a simple "Naked Flame Test" is often done to verify their suspicion. This "Rule of Thumb" method of measuring the approximate percentage of CO_2 in caves has been used for many years. This raises a number of questions which this paper will attempt to answer. They include:-

- How accurate is the naked flame tests for measuring CO_2 concentrations?
- Are we measuring CO_2 concentrations or low oxygen (O_2) concentration in the cave when a naked flame is extinguished?
- Should we be looking at low oxygen concentrations as the life threatening component of the cave atmosphere instead of elevated CO_2 concentrations?
- Can we add butane fuelled cigarette lighters (eg. common disposable gas type) to the list below?

The simple naked flame methods of testing for CO_2 uses the following indications. *(Australian Caver, 1990).*

1% CO_2	a lighted match will go out.
4% CO_2	a lighted candle will go out.
6% CO_2	a carbide lamp will go out.

To answer the question of, "how accurate is the test", one must first look at the concentrations of CO_2 in caves and the concentrations of O_2 which are required to support combustion of various materials. To find out what is the most life threatening situation (low O_2 or high CO_2), one must look at cave air compositions that the human body can tolerate.

How does CO_2 get into caves and form pockets of high concentration?

As discussed in more detail in the article "Caves, Carbon Dioxide & you", *(Smith, 1993),* CO_2 enters caves by two main methods.

1. In this scenario, CO_2 is absorbed by the ground water as it passes through surface soil containing high concentrations of the gas, due to the decay of vegetation. This water percolates through the rock strata and enters the cave system, usually taking part in the calcite deposition cycle. In this instance the addition of extra CO_2 to the cave atmosphere displaces approximately equal quantities of O_2 and nitrogen (N_2). See *Table 2.*
   Halbert (1982), relates this "Foul Air Type 1" cave atmosphere to the introduction of CO_2 into the cave atmosphere and all other components are diluted - the source of the CO_2 is immaterial. An atmosphere resulting from purely a type 1 process occurs quite slowly and it requires five percent CO_2 to reduce the O_2 level by one percent.
2. In the second scenario the CO_2 is a by-product of organic and micro-organism metabolism or respiration by fauna such as bats or humans. In this instance the oxygen concentration is reduced in proportion to the increase in CO_2. The N_2 concentration stays constant. See *Table 3.*
   Halbert, (1982) "Foul Air Type 2" describes in great detail the relationship between consumption of O_2, and production of CO_2 in the metabolic process of living organisms. Essentially the volume ratio of CO_2 produced to O_2 consumed, called the "respiratory quotient" (RQ) is not constant and can vary between 0.7 and 1, depending on organic matter involved. ie. carbohydrates, fats or protein. If fats were utilised solely in the metabolic process the RQ = 0.7, and would result in a consumption of O_2 with a relatively smaller amount of CO_2 volume being produced in return.

3. The other factor which one has to consider is that in deep caves where air movement is minimal, CO_2 will build up in the lower part of the cave. So, even though the CO_2 may have entered the cave by one of the two above mentioned methods, a very still cave atmosphere may allow CO_2 to sink to the deepest part of the cave and displace O_2 and N_2. Thus building up the concentration of CO_2 to a higher concentration, at the lowest point in the cave. See *Table 4.*
*This **should not be confused** with Halbert's (1982) "Foul Air Type 3", cave atmosphere which has resulted from introduction of methane and nitrogen production and the non-respiratory uptake of O_2 as well as CO_2 stripping by water. Also falling into Halbert's third type is an atmosphere which has resulted from a combination of scenarios 1&2 with addition of another mechanism ("Foul Air Type 3"), which alters the gas concentrations.*
The CO_2 / O_2 relationship in caves has been discussed in more detail by *(Halbert. 1982) and (Osborne, 1981)*

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Elements required for Combustion

Before combustion can occur, three conditions must be satisfied.

1. There must be a fuel or substance which can be burnt.

2. The fuel must be heated to its *ignition temperature*. That is the lowest temperature at which combustion can begin and continue.

3. There must be enough oxygen to sustain combustion, either in the surrounding air or present in the fuel.

<u>Statistics of Gases.</u>

Specific Gravities at 25°C grams per litre at 1 atmosphere pressure.	Molecular weight	% in normal atmosphere
CO_2 = 1.931	CO_2 = 43.99	0.03%
O_2 = 1.404	O_2 = 31.98	21%
N_2 = 1.229	N_2 = 28.01	78%
		0.97% (rare gases)

Therefore we can calculate that at a given temperature, a volume of CO_2 is 1.57 times as heavy as N_2 (43.99/28.01 molecular weight ratio) and that CO_2 is 1.38 times as heavy as O_2 (43.99/31.98 molecular weight ratio).

Calculating the Gas Concentrations in a Cave Atmosphere.

In dry air the total pressure (of a mixture of gases) is equal to the sum of their partial pressures. In simplified terms, the atmospheric or barometric pressure of dry air is equal to pNitrogen (pN_2) + pOxygen (pO_2) + pRare Gases (pRG) + pCarbon Dioxide (pCO_2).
However since a great majority of cave atmospheres contain high humidity, the water vapour component should be included in the equation.
Barometric Pressure = $pN_2 + pO_2 + pRG + pCO_2 + pH_2O$.

Halbert (1982) uses the Cave Air Index (CAI) to characterise gas mixtures found in caves on a dry atmosphere basis. The water vapour component in the calculation, slightly changes the concentrations of CO_2 and O_2, but does not affect the arguments derived from the data. Essentially the water vapour constitutes about 0.5% by volume of a saturated cave atmosphere at 20°C and conversely in a dry atmosphere it would be 0%. *(Halbert, 1982).* For simplicity cave atmospheres may be considered to consist of O_2, CO_2, and a Residue Fraction (RF) made up of rare gases, N_2 and water vapour (H_2O).

Table 1. ***Cave air scenario and*** **correlation with** ***Halbert's*** **"Foul Air Type" & Cave Air Index.**

Scenario	Foul Air Type *(after Halbert, 1982)*	Cave Air Index
1	1	between 4 & 5
1+2	1+2 combination	between 1 &4
2 and 3	2	between 0.75 & 1
--	3 or 2+3 combination	between 0 & 0.75

Cave Air Index =

$$\frac{\mathbf{CO_2}\ \text{Concentration}}{\mathbf{21 - O_2}\ \text{Concentration}}$$

The theoretical "Foul Air Type 3", where CAI = 0, is rarely know to exist in caves. In general cave atmospheres with CAI of < 0.75 are regarded as falling into the Foul Air Type 3. *Halbert (1982)* gives the example of "Foul Air Type 3" atmospheres containing 1% CO_2, 17% O_2, and 82% RF and another with 4.5% CO_2, 10.5% O_2, and 85% RF. He points out that a low absolute O_2 concentration does not need to be present. However in practice "Foul Air Type 3" atmospheres likely to be encountered in caves will have low O_2. Also this type of foul air may have deceptively low CO_2.

Some readings at Bungonia suggest a "Foul Air Type 3". They include atmospheres in Grill Cave with a composition of 1.4% CO_2, 12.0% O_2, 86.6% RF which gives a CAI of 0.16 and readings in Odyssey Cave of 2.8% CO_2, 14.5% O_2, 80.3% RF which gives a CAI of 0.43. *(Halbert, 1982)*

Table 2, Theoretical gas concentrations in cave atmosphere. Using scenario 1 with CAI = 4.

Total CO_2 concentration in Cave atmosphere	Total O_2 concentration in cave atmosphere	Total RF concentration in cave atmosphere
1%	**20.75%**	78.25%
2%	**20.50%**	77.50%
3%	**20.25%**	76.75%
4%	**20.00%**	76.00%
5%	**19.75%**	75.25%
6%	**19.50%**	74.50%
10%	**18.50%**	71.50%
24%	**15.00%**	61.00%

Table 3, Theoretical levels of gases in cave atmosphere, Using scenario 2. with CAI = 1.

Total CO_2 concentration in Cave atmosphere	Total O_2 concentration in cave atmosphere	Total RF concentration in cave atmosphere
1%	**20.00%**	79.00%
2%	**19.00%**	79.00%
3%	**18.00%**	79.00%
4%	**17.00%**	79.00%
5%	**16.00%**	79.00%
6%	**15.00%**	79.00%
10%	**11.00%**	79.00%
13%	**8.00%**	79.00%

Table 4, Theoretical concentrations of gases in a cave atmosphere, using figures in the second scenario plus the effect of CO_2 sinking (concentrating) to the lowest point in the cave and displacing approximately equal quantities of O_2 and N_2. This would represent the theoretical worst case CO_2 to O_2 volume percentage (possibly life threatening), which could be expected at the bottom of limestone caves. Using scenario 3. with CAI = 1.34

Total CO_2 concentration in Cave atmosphere	Total O_2 concentration in cave atmosphere	Total RF concentration in cave atmosphere
1%	**20.25%**	78.75%
2%	**19.51%**	78.49%
3%	**18.76%**	78.24%
4%	**18.01%**	77.99%
5%	**17.27%**	77.73%
6%	**16.52%**	77.48%
7%	**15.78%**	77.22%
8%	**15.03%**	76.97%
9%	**14.28%**	76.72%
10%	**13.54%**	76.46%
15%	**9.81%**	75.19%

Levels of O_2 and CO_2 required to extinguish a flame.

In fire fighting terms, the main extinguishing mechanism of CO_2 is its ability to dilute the O_2 concentration in the atmosphere to a level that will not support combustion. If we take the extremes, and add a non toxic gas such as nitrogen, argon, neon or helium, to an atmosphere at about 17% concentration by volume, it will displace O_2 to a life threatening level. *(Safe Handling of Compressed Gases, 1992).* Bear in mind that in fire fighting terms the aim is to dilute O_2 to a concentration which will not support combustion.

From *Table 5*, it can be seen that the addition of CO_2, to dilute the O_2 concentration, will result in a CO_2 rich atmosphere which will not support human life. For this purpose much higher concentrations of CO_2 are present, than would be found in caves.

Nitrogen can also be used to dilute the O_2 concentration, however since N_2 is less dense than CO_2, extinguishing the flame would require almost twice the volume of N_2 to achieve the same result.

Table 5, Minimum volume ratios of CO_2 or N_2 to air which is required to prevent burning of various vapours at 25°C.

Vapour	Carbon Dioxide CO_2/air	The resulting atmosphere from addition of CO_2 would consist of				extra N_2/air	The resulting atmosphere from addition of N_2 would consist of			
		%O_2	%N_2	%CO_2	Rare Gases		%O_2	%N_2	%CO_2	Rare Gases
Carbon disulfide	1.59	**8.11%**	30.12%	61.40%	0.37%	3.0	**5.2%**	94.5%	0.0075%	0.243%
Hydrogen	1.54	**8.27%**	30.71%	60.64%	0.38%	3.1	**5.1%**	97%	0.00732%	0.237%
Ethylene	0.68	**12.50%**	46.43%	40.49%	0.58%	1.00	**10.5%**	89%	0.015%	0.485%
Ethyl eithe	0.51	**13.91%**	51.66%	33.79%	0.64%	0.97	**10.66%**	88.83%	0.015%	0.492%
Ethanol	0.48	**14.19%**	52.7%	32.45%	0.66%	0.86	**11.3%**	88.17%	0.016%	0.522%
Propane	0.41	**14.89%**	55.32%	29.1%	0.69%	0.78	**11.8%**	87.64%	0.0169%	0.545%
Acetone	0.41	**14.90%**	55.32%	29.1%	0.69%	0.75	**12.0%**	87.43%	0.017%	0.554%
n-Hexane	0.40	**15.0%**	55.71%	28.6%	0.69%	0.72	**12.2%**	87.21%	0.0174%	0.564%
Benzene	0.40	**15.0%**	55.71%	28.6%	0.69%	0.82	**11.54%**	87.91%	0.0165%	0.533%
Methane	0.33	**15.79%**	58.65%	24.83%	0.73%	0.63	**12.9%**	86.5%	0.0184%	0.595%

Table 5. (After Friedman. R.,1989). Data calculated from tabulations by Kuchta (1985.)

To calculate the final volume percentages of each gas from the (volume ratio) of CO_2 added to air. The following formulae are used.

$R+V=Y$

Where R = *Volume of CO_2 needed to give CO_2/ air volume ratio. (from table No.4)*
V = *Volume of air which CO_2 added to (=1)*
Y = *Total volume of gases when CO_2 and air is mixed.*

To find the percentage of gases in the new atmosphere (which will not support combustion of various vapours because the O_2 has been diluted). Using the known percentage of gases in air. ie. $O_2 = 21\%$, $N_2 = 78\%$, $CO_2 = 0.03\%$ and Rare gases = 0.97% It must be noted that R value must be added to air CO_2 of 0.03%

Gas % (fire retarding atmosphere) = % of gas (in normal air) ÷ Y

Example.
*To calculate the O_2 % in an atmosphere which **will not** support combustion of Propane vapour, CO_2 ratio is 0.41 from chart above.*
Therefore $Y = 0.41+1$
$Y = 1.41$
Gas % = 21 ÷ 1.41 = 14.89% oxygen in the new atmosphere.
(The same calculations can be made for gas concentrations if Nitrogen is added to an atmosphere.)

Looking at the fuel components of the "Naked Flame Test"

Matches.

There are two main types of matches, "Strike-anywhere" and "Safety". This paper will only deal with "Safety" matches as they are the only type readily available in Australia. In general, "Safety" matches can only be lit by striking them across a special surface on the side of their box or packet. The head is made of a mixture containing potassium chlorate, sulphur and other components, which will ignite at a temperature of approximately 182°C. The coating on the box is made of amorphous phosphorus and sand.

Wooden "Safety" matches are generally made of poplar wood, which is dried to reduce moisture content to below 7%, then the "splint" is treated with an anti-afterglow solution (*retardant*) which prevents embers from forming after a flame is blown out. The second stage in production is dipping approximately 10 mm of the tip end into paraffin. This provides a base to carry the flame from the head to the wood. Then the tip (sometimes called a bulb) is added. Some match manufacturers add a final chemical coating that protects the match from moisture in the air.

When a match is scraped across the box striking surface, it begins a chemical reaction between the potassium chlorate and amorphous phosphorus which in turn ignites the sulphur component of the head. The heat generated in the head vaporises the paraffin coating on the splint and the flame is drawn down from the head. Moisture is driven out of the timber, the retardant is burnt off, allowing the wood volatiles to vaporise and ignite. The head will fizz and not burst into full flame when there is a lack of O_2 in the atmosphere, since it is burning due to the O_2 in the potassium chlorate contained in the head.

Book matches are a type of "Safety" match made of heavy paper (called *paperboard*) and the row or rows (called *combs*) of matches are bound into a paperboard cover. The paperboard is also treated with an anti-afterglow solution and paraffin as with wooden matches. *(The World Book Encyclopedia, 1992).*

Candles

A candle burning in an area without draft will produce a steady flame. The flame's heat vaporises just enough candle wax to keep the flame burning at the same height. This is influenced by the length and type of wick and the type of wax. The wick serves as a place for the flame to form. When lit by another heat source, the heat from the burning wick melts the wax at its base and the liquid is drawn up the wick to the flame by capillary action. The heat in the flame vaporises the molten wax which then burns. Most candles today consist of beeswax or paraffin. The latter being the most common.

Paraffin is a wax obtained from petroleum and is a mixture of hydrocarbons which melt between 32 to 66°C and vaporises at between 150 and 300°C.

Cigarette Lighter (Butane type).

Butane is a colourless, flammable gas which can be readily kept in a liquid state while under pressure at ordinary temperatures. Once the pressure in the lighter reservoir drops below 265 kPa at 25°C, the liquid butane begins to vaporise until the pressure increases to an equilibrium point and further vaporisation ceases. When the lighter is operated, gas from the reservoir is liberated through a fine jet and a hot spark from the flint easily ignites the gas. Ignition temperature of butane can vary between 482 and 538°C, however the hot flint spark is sufficient to begin combustion of the gas. At atmospheric pressure the normal vaporisation point of butane is -0.5°C.

Laboratory Combustion Tests

To verify the O_2 concentrations required to support combustion of matches, candles and cigarette lighters, a series of tests were conducted in a controlled atmosphere chamber. A large inflatable glove chamber made of clear plastic was filled with normal atmospheric air. The "Glove Bag^{TM}" Model X-37-27, was pre-loaded with all the components required for the experiment, then sealed from the outside atmosphere. A stand was used to hold a burning candle and another stand held a mini video camera (ELMO 120 with 15mm lens). The chamber full of normal air, was then purged with argon to reduce the O_2 concentration. The O_2 concentration (as % by volume) was measured using a Teledyne Portable Oxygen Analyzer, (Model 320). A small bleed line, vented excess hot air and fumes from the chamber as the argon gas reduced the O_2 concentration. At each 0.5 % drop in O_2 concentration, four separate matches ("Kangaroo" brand) were lit and a video recording made of their burning. The lowest O_2 concentration reached in the chamber was 7.5%.

When the match tests were complete, the chamber was slowly re-filled with fresh air and a butane cigarette lighter was struck at each 0.5% rise in oxygen concentration. The level at which the butane would remain alight was noted. Then the O_2 concentration was reduced to verify the exact percentage which would extinguish the flame. Both ignition and extinguishing of the flame occurred between 14.25% and 14.5% O_2.

The atmosphere in the chamber was then returned to normal atmosphere air and a candle lit. Argon was slowly purged into the enclosed atmosphere until the candle went out. This occurred at an O_2 concentration of 15%.

The results of the tests are summarised in *Table 6*.

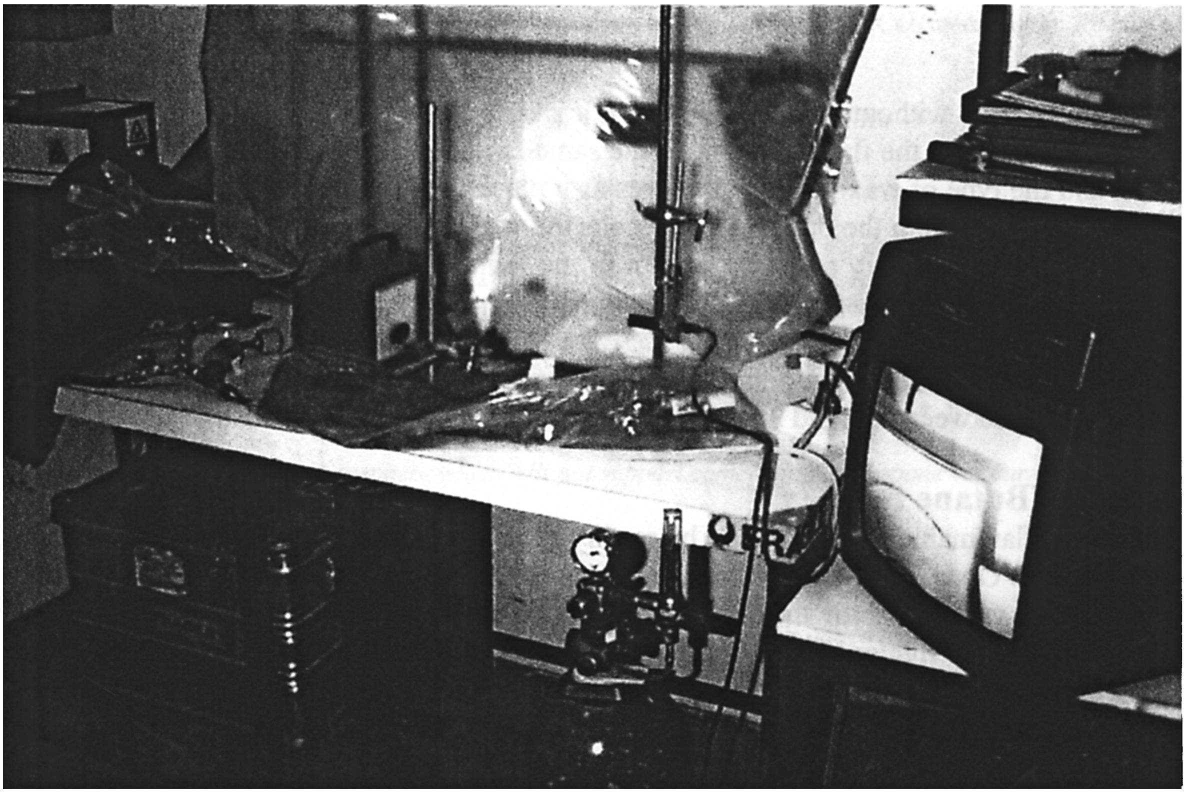

Figure 1. Testing setup using a Teledyne Portable Oxygen Analyzer, and large inflatable glove chamber to measure oxygen concentrations which would extinguish various fuels. ie matches, candles and butane cigarette lighter.

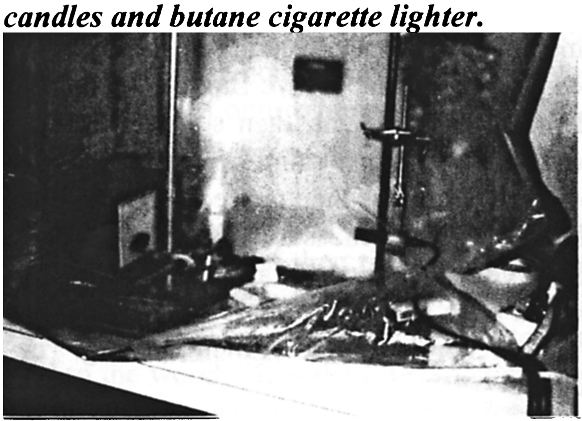

Figure 2. Closeup of experiment. Note, mini video camera - centre right.

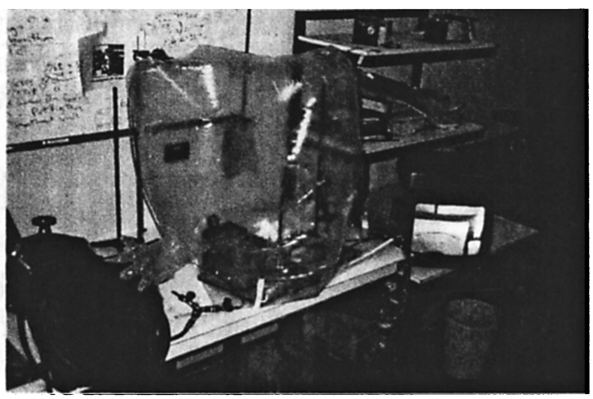

Figure 3. Overall view of experimental setup. Video recorder and argon gas bottle on right

Results of the Test.

On the whole the match tests were very consistent, with about half a percent variation in the O_2 concentration required for the ignition of paraffin on different matches from the same box observed. The test with "Kangaroo" brand matches (made in Sweden) did not show any sign of fizzing slowly like a sparkler as I have seen in the cave environment. One can only assume that the matches used in a cave on those occasions had absorbed some moisture which retarded combustion of the match head or that different brands behave differently because of variations in retardant or head composition. The candles and butane lighters were extremely sensitive to changes in O_2 concentrations at their critical combustion points.

Table 6. Gives condition of flame in relation to percentage of oxygen in the controlled atmosphere.

Match	Candle	Butane lighter
21% - 18% easily burns all of match .	>19% normal flame.	
17.5% Burns head and flame transfers down paraffin to wooden splint on most occasions	17% - 16.5% burns with elongated flame.	
17% - 16.5% ignited head and on nearly every occasion, burns down onto paraffin coating then extinguishes.	16.5% - 16% flame begins to shrink, but candle remains alight.	
16% - 15.5% ignited head just ignites paraffin coating on splint (some matches only)	16% burns slowly with small flame	
15% - head burns briefly with whispery flame & goes out.	< 15.0%, A burning paraffin candle is extinguished.	> 15% O_2, A Butane Cigarette Lighter can easily be lit and will stay alight.
		14.5% - weak blue flame with orange top, just stays alight
		<14.25% - Flame will extinguish
14% match head burns very briefly & goes out.		14% - 13% Large flashes of flame but will not stay alight.
<13% head flares & extinguishes immediately (less than 0.5 seconds)		12.5% sparks with partial ignition, small fireballs
		<10% - no ignition, only hot sparks from flint.

Should we be looking at O_2 deficiencies as life threatening while underground?

If we consider an atmosphere consisting of just N_2 and O_2, where the O_2 is at a lower concentration than the normal atmosphere, the human body would be affected in the following manner. *(Laboratory Safety Manual, 1992)*

- O_2 reduced from 21 to 14% by volume. First perceptible signs with increased rate and volume of breathing, accelerated pulse rate and diminished ability to maintain attention.
- O_2 concentration between 14 to 10% by volume. Consciousness continues, but judgment becomes faulty. Rapid fatigue following exertion. Emotions effected, in particularly ill temper is easily aroused.
- O_2 reduced from 10 to 6% by volume. Can cause nausea and vomiting. Loss of ability to perform any vigorous movement or even move at all. Often the victim may not be aware that anything is wrong until collapsing and being unable to walk or crawl. Even if resuscitation is possible, there may be permanent brain damage.
- O_2 reduced below 6% by volume. Gasping breath. Convulsive movements may occur. Breathing stops, but heart may continue beating for a few minutes - ultimately death.

The above data indicates that very little difficulty is caused by short-term exposure to O_2 / N_2 mixtures down to about 10% O_2. From *Tables 5 & 6,* it can be seen that the percentage of O_2 which will just not support combustion is approximately 15%. This is well above the concentration which will support human life. In *Tables 2, 3 & 4,* the theoretical cave atmospheres contain sufficient O_2 concentration to support life, however the CO_2 concentrations is sufficiently high to be dangerous to cavers, see *Table 8*.

The Le Chatelier's principal.

This states that *"any system in equilibrium shifts the equilibrium, when subjected to any constraint, in the direction which tends to nullify the effect of the constraint"*.
If the example of a Butane (cigarette lighter) flame is used.

Butane + Oxygen $\longrightarrow$ Carbon Dioxide + Water

$$2C_4H_{10} + 13O_2 \longrightarrow 8CO_2 + 10H_2O$$

Simply this means that if the CO_2 concentration is raised and /or the O_2 concentration is reduced, then the reaction will slow down and eventually stop. The CO_2 concentration will have a much lesser effect than the O_2 concentration. The experimental data and that of *Kuchta (1985)*, indicate that a 1% increase in CO_2 concentration will raise the O_2 concentration required to support combustion of a given substance by less than 0.05% O_2.

In the majority of cave atmospheres it is the low concentration of O_2 which stops this reaction, not the high concentration of CO_2.

Properties of Carbon Dioxide (CO_2).

Even though CO_2 is 1.57 times heavier than nitrogen and 1.38 times heavier than O_2, it will have a tendency to disperse in an isolated volume of air, due to molecular diffusion. In other words a mixture of gasses will not separate into layers of various density gases if they are left for a long time in a still chamber. On the other hand various gasses purged separately into a closed container will become uniformly mixed over a period of time. A possible explanation of the high concentration of CO_2 in deep caves (with a relatively still atmosphere), is that CO_2 is being produced metabolically or entering the cave via ground water at a greater rate than the gas can diffuse into the cave atmosphere, thus settling at the bottom of the cave because it is a dense gas.

Carbon dioxide is "regarded as a `hot gas' due to its low thermal conductivity, heat is not conducted away as rapidly as in normal air, so a person standing in it feels warm about his lower limbs". *(Strang, 1990)*

How fire fighting research is aiding cavers.

A paper by *(Fields, 1992)* studies the use of a new fire extinguishing gas mixture, designed to be used in enclosed spaces. While the actual percentages are not given in the paper, the gas called "Inergen" appears to consist chiefly of argon (Ar) with some CO2 added. The function of the gas mixture is to reduce the ambient oxygen concentration to less than 15%. The study then goes into great detail about the affect on human life when the O_2 concentrations are reduced to between 15.0% and 12.4%, while the CO_2 concentration is increased to between 3.1% and 4.3%. The research found that the addition of CO_2 was beneficial as it induced an immediate and sustained stimulus to increase breathing rates of persons caught in areas flooded with this gas mixture. It was the increase in CO_2 and to a much lesser extent the decreased O_2 which stimulated the respiratory response. For fire fighting "Inergen", would be injected into an enclosed space at between 0.4 and 0.7 cubic metres for every cubic metre of room volume. At 40% dilution there would be 3.1% CO_2 and 15.0% O_2, while at 70% dilution there would be 4.3% CO_2 and 12.4% O_2. The paper concludes that the elderly or people with heart diseases (eg. coronary artery disease) but not heart failure would be at some risk of clinically significant hypoxia when breathing 70% Inergen mixture at sea level, but not when breathing a 40% mixture. The use of Inergen was considered at altitudes with barometric pressure down to 650mm Hg, (Sea level atmospheric pressure $\approx$ 760mm Hg). There was an overall increase in risk, however not significant enough to warrant a change in the mixture. At sea level an average healthy person would be at low risk of suffering any affects other than reducing their capacity for physical exertion, to less than half the maximum they could normally sustain while breathing fresh air.

An increase in CO_2 would cause increased breathing rates and could impose serious limitations on the degree of physical exertion achievable by a person with lung disease, cardiovascular disease, anaemia or carbon monoxide poisoning.

One thing lacking in this paper is any real mention of time scales of exposure to this concentration of CO_2 and O_2.

Table 7. The % volume, composition of the two Inergen / air mixtures.

	40% Inergen in air	**70% Inergen in air**
Resulting volume % of gases in atmosphere which will extinguish fire	N_2 = 70.0 %	N_2 = 66.5%
	Ar = 11.4%	Ar = 16.4%
	CO_2 = 3.1%	CO_2 = 4.3%
	O_2 = 15.0%	O_2 = 12.4%
	Trace gases = 0.5%	Trace gases = 0.4%

After Field., 1992,

Interesting phenomena with cigarette lighter in O_2 deficient air.

A cigarette lighter when lit in an atmosphere which will support combustion of butane will burn with the flame extending directly from the jet. When this lit cigarette lighter is slowly lowered into an atmosphere that will not support combustion (lower O_2, higher CO_2 concentration), an interesting phenomena occurs. The flame will magically stay burning where the atmosphere will support combustion, just above the interface between the high and low CO_2 concentration, while the lighter is several centimetres below the interface.

In the CO_2 Pit of Gaden Cave (WE-2), a demonstration by Mike Lake showed that the flame extended to about 100 mm above the lighter as it was gradually lowered into the higher concentration in the Pit. At one stage a 25mm high flame flickered some 75 mm away from the lighter. Because of the low concentration of O_2 (proportional to high concentration of CO_2) there was no flame for the first 75mm out from the lighter jet.

This phenomena can not occur with the other solid fuels, such as matches and candles, as the heat from the flame is required to vaporise the volatiles which then burn.

A cigarette lighter which does not have adjustment for the flame can also be used to some degree to check for low O_2 concentrations. A subtle change in the flame height occurs as the O_2 concentration decreases. A longer flame indicating that the O_2 concentration is decreasing. This test is probably more desirable than the matches or candle method as unpleasant odours are not produced. However this method is not recommended for the novice as it requires some experience for reliable interpretation.

Why should we be aware of CO_2 concentrations?

Gases which create a hazard simply by displacing oxygen are called simple asphyxiants. However it is not the lack of oxygen in a cave which causes the physical symptoms or in extreme cases death, rather it is the increased concentration of CO_2. For example a person can survive several hours in an atmosphere with 3% CO_2 and 12% O_2. On the other hand an atmosphere of 8% CO_2 and 18% O_2 **could** result in suffocation and death within a few minutes. The exact percentage and timing will depend on the individuals physiological makeup and tolerance, however several minutes exposure to a concentration of >10 CO_2 will certainly result in death. For instance exposure to 25% CO_2 or greater, will result in death within one minute, even if there is 20 % O_2 in the atmosphere.

The *"Laboratory Safety Manual (1992)",* quotes 0.5% CO_2 as the `Threshold Limit Value Time Waited Average' (TLVTWA). This is the concentration to which a person may be exposed, 8 hours a day, 5 days a week, without harm. The manual also quotes 5% $CO_2$ and above as being `Immediately Dangerous To Life and Health' (IDLH). This is the concentration that will cause irreversible physiological effects after 30 minutes exposure.

Effect of CO_2 on the Human Body.

Exposure to just 1 to 2% CO_2, for some hours will result in acidosis, even if there is no lack of oxygen. This acid-based disturbance will occur in the human body when the increase in partial pressure of CO_2 (pCO_2) is greater than 44mm Hg.* Acidemia will result and secondary mechanisms are initiated by the body that attempt to prevent drastic changes in pH and tend to return the pH toward normal. "Intracellular buffering, via red cell haemoglobin, phosphate, and protein, exchange intracellular sodium and potassium for the excess extracellular hydrogen ion. In addition, hypercapnia leads to an increase in renal hydrogen ion secretion and net acid excretion, as well as an increase in bicarbonate reclamation. Although this response begins early, the maximum effect takes several days." *(Clinical Management of Poisoning & Drug Overdose).*

Table 8. Generally accepted physiological effects of CO_2 at various concentrations. *(Strang, 1990)*

Concentration	Comments
0.03%	Nothing happens as this is the normal carbon dioxide concentration in air.
0.5%	Lung ventilation increases by 5 percent.
2.0%	Lung ventilation increases by 50 percent, headache after several hours exposure.
3.0%	Lung ventilation increases by 100 percent, panting after exertion, headaches.
5 - 10%	Violent panting and fatigue to the point of exhaustion merely from respiration & severe headache. Prolonged exposure could result in unconsciousness and death.
10 - 15%	Intolerable panting, severe headaches and rapid exhaustion. Exposure for a few minutes will result in unconsciousness and suffocation without warning.
25% to 30%	Extremely high concentrations will cause coma and convulsions within one minute of exposure.

Treatment for exposure to CO_2

For persons exposed to high concentrations of CO_2, remove to a well ventilated atmosphere, keep the person warm and avoid exertion. In severe cases administer oxygen if available but be aware that vomiting and nausea often follows. Persons who have been exposed for short periods, generally recover without serious after effects.

Conclusion

If a paraffin candle which is alight and is then moved to an atmosphere in a cave which will not support combustion, the flame will be extinguished. From *Table 5*, it can be seen that a controlled atmosphere with about 15% O_2, will not support combustion of a number of organic compounds. The laboratory test results in *Table 6*, confirm that 15% O_2 extinguishes a paraffin candle when argon is used as the diluting gas. In *Table 7*, a fire fighting company recommends the use of a gas mixture which when released into confined areas will dilute the O_2 to 12.4% and increase the CO_2 to 4.3%. This is sufficient to extinguish general fires and sustain human life without long term adverse effects. In both cases, reducing the O_2 concentrations from normal atmospheric 21% O_2 to below 15%, appears to be sufficient to extinguish a flame. From *Table 3*, it can seen that a cave atmosphere with a concentration of 6% CO_2 could theoretically result in a 15% O_2 concentration where organic metabolism has been the major contributor to gas concentrations. This O_2 concentration is the same as that which the match head and butane cigarette lighter extinguished.

It would appear conclusive that the flame test is measuring primarily the O_2 concentration and that the CO_2 concentration has a much lesser influence. The accepted CO_2 concentration from "Naked Flame Test", adopted as the ASF Cave Safety Guidelines, 27th Jan. 1990 (Australian Caver 1990) are essentially meaningless other than to indicate an atmosphere which could be hazardous or life threatening .

The rule of thumb "Naked Flame Tests" using different fuels appears to be a very accurate indicator of the O_2 concentrations in a cave. The O_2 concentration being an indication in most cases, of the elevated CO_2 concentration. In general a high CO_2 concentration is the most life threatening situation encountered underground while a life threatening low O_2 concentration, is encountered to a much lesser extent. Therefore a flame test is not an accurate measure of the CO_2 concentration in a cave, but merely an indicator that there is an elevated concentration.

In the worst case limestone cave atmosphere scenario *(Table 2)*, O_2 at 15% correlates with 24% CO_2. This concentration of CO_2 is particularly life threatening despite the O_2 concentration being within human survival range. However in practice, cave atmospheres of this type, tend to be made up of a combination of scenario 1 & 2 and would have a Cave Air Index of between 1 and 3. This still results in an extremely dangerous CO_2 concentration at the critical flame extinguishing concentration of 15% O_2.

Without sophisticated measuring instruments, one can only speculate about the exact concentration of CO_2 in a cave, so if any one of these flame indicators will not burn, it is time to get out.

If sophisticated measuring equipment is not available, the best advice is to carry out a "Naked Flame Test" when you or a member of your group experiences the first signs of labored breathing, headaches, clumsiness, loss of energy or any of the other signs associated with elevated concentrations of CO_2. Ideally cavers should become aware of the subtle changes to a cigarette lighter flame associated with O_2 concentrations down to 13%. This will reduce the amount of unpleasant fumes emitted from matches burnt by people experimenting in the confines of a cave. The best advice is, "If in doubt, get out", in an orderly manner.

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