THE METHODOLOGY FOR THE USE OF INERT TRACER GASES IN RELATION TO CAVE METEOROLOGY

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Abstract

An outline of the various procedures for using the inert tracer gases, Freon 11, 12 or sulphur hexafluoride, to determine air movements in caves is discussed.

Practical examples proving air connection between two previously separate cave systems are given.

Problems inherent in using these tracer gases in caves are discussed and compared with the advantages of the system.

INTRODUCTION

Air tracing in caves has to date been carried out using such crude tracers as ethyl mercaptan (Fetrow, 1960). This type of tracer is not only harmful to the experimenters but has also been shown to kill some types of cave fauna (Muir, 1968).

Titanium tetrachloride (TiCl₄) has also been used to visualise air movements (Halbert & Michie, 1971). However, the authors do point out that hydrochloric acid (HCl) is produced during the hydrolysis of the TiCl₄. Although they indicate that HCl has no cumulative poisonous effects, its effects on speleothems and cave fauna are unknown and hence to be avoided if possible.

In view of the above problems, the use of inert tracers such as Freon 11 (CFCl₃), Freon 12 (CF₂Cl₂) or sulphur hexafluoride (SF₆) would allow the tracing of air movements in a cave system while having no known effect on the cave environment.

Glossop & Hamilton (1977) have outlined the procedure for the use of the above-mentioned inert tracers in above-ground tracing experiments. Using such tracers in the cave environment is a new and complex experiment.

Therefore, I report here the equipment and methodology necessary for air tracing experiments using these inert tracers in a cave system and also a discussion of the major complications that arise as a result of using tracer gases in the cave environment.

BASIC METHODOLOGY

Simply, the method involves releasing a tracer gas from a cylinder or, in the case of Freon 11, vaporising it and then collecting air samples at various times and at various points throughout the system under study. Thus the tracers can be used to determine the speed and direction of air movements in caves as well as to prove air connections between caves.

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INSTRUMENTATION

Low concentrations (ca 0.01 ppb) of tracer gases can be detected using gas chromatography with an electron capture detector. The detector giving the best reported result was a Nickel⁶³ electron capture detector which was capable of detecting 0.0002 ppb of SF₆ in air (Luckan & Mura, 1974).

In my experiments a tritium absorbed on scandium foil detector was used. Glossop & Hamilton (1977) report the limit of this detector as 0.018 ppb of SF_6 in air. Hence no matter which detector is used the method is obviously very sensitive.

Each tracer is best analysed on a different column: SF_6 on a 5 Å molecular sieve column, Freon 11 on a SF96/OV17 column and Freon 12 on a Porapak Q column (Glossop & Hamilton, 1977). Detection of Freon 12 requires a higher concentration, compared to Freon 11 or SF_6 , when using the Porapak Q column as the Freon 12 peak occurs on the oxygen tail.

SAMPLING

A number of sample containers have been tested for their ability to contain an air sample without absorbing or diffusing the tracer gas (Glossop & Hamilton, 1977; Luckan & Mura, 1974). These range from plastic bags of varying types to aluminium cans and glass containers.

Of these sample containers, the aluminium can would be the most suited to cave use as it is unaffected by water and robust. Unfortunately they are also expensive.

The glass containers offer limited use due to their fragile nature.

This leaves the Mylar and Saran Mags, of which the Saran bag has the advantage of storing low concentrations of tracer for up to two months without noticeable decrease in concentration (Luckan & Mura, 1974). However, it is available only in 12 litre and 50 litre sizes, so that when fully inflated, both the 12 L and 50 L bags are very bulky and storage and handling are problems. The cost of these bags is also prohibitive.

In regard to cost and ease of use, the Mylar bags described by Glossop & Hamilton appear to have the widest adaptability. However, these bags do suffer from one major disadvantage. The tracer diffuses out of the bag at a rate of 11% per day. Hence the bags must be analysed within two days of sampling, taking into account the relevant corrections for diffusion.

SAMPLING PROCEDURE AND PRECAUTIONS

The sampling bag (Fig. 1) is connected to a plastic hand pump which has been flushed for about 30 seconds prior to sampling. It is generally wise to remove the glass stopper a short time before the sample is to be taken as sometimes it may be very difficult to extract.

The actual sampling time (the time required to pump up the bag) can be varied by the rate of pumping and also by the use of a capillary constriction in the neck of the plastic pump.

Some important precautions when using Freon 11 or 12 are to ensure that samplers have not used any insect repellants, deodorants or aftershaves prior to sampling.



Fig. 1. Sampling Bag (not to scale).

Also ensure that the sample bottles are clearly labelled and the code explained to the samplers.

BACKGROUND LEVELS OF FREON 11, 12 AND SULPHUR HEXAFLUORIDE

Freon 11 has many known sources including propellants from spray cans such as insecticides, spray deodorants and aftershaves (varying significantly with brand). Freon 12 background is known to be 10% higher (Fraser, 1975, cited by Glossop & Hamilton, 1977) than Freon 11 but can not be detected using the Porapak Q column as the peak occurs in the oxygen tail. Freon 12 also occurs in spray cans.

A sample of ten sites in the Perth metropolitan area produced an average concentration of $1 \ \mu g/m^3$ for Freon 11 (Glossop & Hamilton, 1977). Therefore background levels must be measured before an air trace is conducted.

Sulphur hexafluoride has the advantage of a background level that is not ordinarily measurable. However, to be sure, blanks should be taken to show that no SF₆ was present before release.

CHOICE AND QUANTITY OF TRACER

When choosing which tracer to use you must consider the following:

1. The possibility of high background levels of Freons 11 and 12 from industrial sources.

2. The availability of the tracer.

3. The ease of transporting the tracer (In my experiments a small "lecture bottle" cylinder was found to be excellent for underground use).

The choice of the quantity of tracer to be released depends upon the type of experiment to be undertaken and the volume of the cave in which the gas is to be released.

For example, if the cave is large or long (ca 5 km) and you are attempting to prove air connection to an adjacent system, then several hundred grams of tracer will be adequate. However if you are trying to establish an air flow chart for a long (ca 5 km) system then a release of about 10 g of tracer should provide measurable concentration gradients at sampling points, whereas the previous example is only likely to afford a positive or negative result. This presumes that some air movement is occurring in the cave.

A PRACTICAL EXAMPLE

THE EASTER TO JEWEL CAVE (AU-14 TO AU-13) CONNECTION USING FREON 11 AND SF6

Easter and Jewel Caves are situated a few kilometres north of the Augusta town site in the south-west of Western Australia.

The Gondolin Extension in Easter Cave was thought to be the closest point to nearby Jewel Cave. The survey of Gondolin was not complete at the time of the experiment and hence the distance between the caves was not known.

The Freon 11 air trace. As the retention time of the tracer in the cave was not known, Freon 11 was chosen for the first trace so that SF_6 could be used at a later date in a more sensitive trace

On 30 June 1978, approximately 200 g of Freon 11 was vaporised in the Gondolin Extension of Easter Cave. For a period of eight hours after this release air samples were collected every hour from The Dome area in the Flat-roofed Chamber of Jewel Cave. Further samples were taken from the entrances of Jewel and Easter Caves, also hourly for eight hours. The samples were then transported to Perth and analysed the next day.

The tracer was detected in all eight Jewel (Flat-roofed Chamber) bags although the bulk of the tracer reached Jewel after three hours. It was not possible to determine if the tracer in the first two samples was a true indication of the tracer levels at the time of sampling as the concentration of Freon 11 was so high after three hours that diffusion into these early samples over the remaining five hour period could have accounted for the observed levels of Freon 11. The Jewel entrance samples gave further proof that the air connection was positive, as high levels of tracer were detected after seven hours. On the other hand, no tracer was detected at the Easter Cave entrance.

During this experiment the overall cave breathing was observed to be in at the Easter entrance, away from the Easter entrance at the first duck into the Gondolin Extension, and out at the Jewel Cave tourist entrance (the natural entrance being blocked).

With the basic knowledge that a connection did in fact exist, a second air trace was designed to isolate the points of connection between the two systems.

The SF₆ air trace. To avoid the problem of diffusion of tracer into samples once they had been collected, the Mylar bags were housed in a one litre plastic bottle with a screw cap. These plastic bottles were tested to determine if SF₆ could penetrate the plastic if left in an atmosphere with a high SF₆ concentration for five days. No SF₆ could be detected in the blank air sample after the said period.

After choosing two possible points of connection in the flat-roofed Chamber of Jewel Cave (marked 1 and 2 on Fig. 2), an attempt was made to repeat the first experiment on 9 July 1978. Samples were also collected in the Gondolin Extension at the points marked 4 and 5 on Fig. 2.

Approximately 100 g of SF₆ was released and samples were collected at three sites in both Jewel and Easter caves. Unfortunately this experiment did not have the luck of the first. Analysis revealed that the gas had reached sampling point 1 in less than *one minute*. However, then the unpredictable happened. During the first 15 minutes after release the overall cave breathing either stopped or changed direction. As a result sampling point 3 never detected the SF₆ (although they could see point 1) and point 2 had only one positive sample and that was after five hours.



In Easter Cave the only valuable information that was obtained was that the SF₆ pulsed through Gondolin Chamber (point 4 on Fig. 2) during the first minute, decreased in concentration, then pulsed again at 24 minutes, most likely in the opposite direction as the cave breathing changed direction. The samples taken at Gondolin Beach (point 5 on Fig. 2) indicated that the cave was not breathing strongly as little tracer was detected but the pulse at 24 minutes was observed.

Overall these two experiments were a success in that an air connection between the two caves has been proven and a cave breathing flow chart has been commenced. Also possible points of connection have been established.

Advantages and disadvantages of the method. The major problem that was uncovered is the unpredictability of cave breathing. With studies of cave breathing patterns it may be possible to reduce the incidence of attempted air traces in periods when gross cave breathing changes are likely to occur. I envisage, however, that cave breathing changes and even internal fluctuations will always be a problem when conducting an air trace.

Another problem stems from the ease with which the tracer is conveyed in a cave. This means that once release has occurred samplers are virtually confined to a small area until sampling is complete. This can make sampling a difficult job especially if samples have to be collected for twelve hours or longer.

The choice of a time for an overall sampling period is difficult, for it will vary with each type of air trace and hence the sampling time should always be exaggerated to cover most possibilities.

The plastic bottles used as sample bag containers were of great assistance when transporting the samples through lakes and crawlways. Their only drawback is that some samples were lost through samplers overinflating the sample bags causing them to burst when the sampling neck was forced back into the bottle. Hence some care, by samplers, must be exercised here.

Following the Freon 11 air tracing experiment weekly samples were collected from Jewel Cave for one month. The concentration of freon 11 dropped drastically over the first week and then approximately halved each week thereafter. However the final sample was still well above the background level and would have required at least another month, at the same rate of decrease, to reach it. Therefore before attempting an air tracing experiment thought must be given to the possible need for a second trace to either verify or extrapolate the results of the first. If this is to occur, with the same tracer, and the cave breathing is poor, then some considerable time period may be necessary before the tracer is expelled from the cave.

When tracing between two caves with large entrances that are in close proximity care must be taken to avoid the tracer making the above-ground connection. This can be detected by using entrance and even surface sampling points.

One final disadvantage is that the air samples can not be analysed in the cave and hence many hours may be lost on experiments which fail completely.

The major advantage of these tracer gases is that they are chemically inert and hence the chance of them having any adverse affect on the cave environment or cave speleothems is very unlikely. With regard to cave animals the effects of SF₆ are almost certainly nil (Lester & Greenburg (1950) have shown that rats can exist in an 80%:20% atmosphere of SF₆:0₂ for 16-24 hours with no detectable physiological effects). Freon 11 or 12, however, could cause suffocation if used in very high concentrations in a confined space. This

problem is virtually overcome by another advantage of these tracers and that is their sensitivity. From experience I can say that the use of small quantities of tracer (ca 10-20 g) will give the best results, even in large systems. Hence high concentrations of tracer should not occur.

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