An Electrolytic Field Device for the Titration of CO₂ in Air

By F. Delecour*, F. Weissen*, and C. Ek**

*Centre d'Etude des Sols forestiers de la Haute Belgique, I.R.S.I.A., Faculte agronomique, Gebbloux, Belgium

**Laboratoire de Geologie et Geographie physique, Universite, Liege, Belgium

An Electrolytic Field Device for the Titration of CO₂ in Air

By F. Delecour*, F. Weissen*, and C. Ek**

ABSTRACT

A technique for determining the CO_2 content of cave air is described. The titration set, used by agronomists and soil scientists for the analysis of soil atmosphere, has proved to be practical and easily manipulated underground. The procedure is based upon an electrolytic titration of CO_2 absorbed by a 0.1 N NaCl solution. The apparatus is enclosed in a portable wooden case.

Some preliminary results are reported. Attention is given to the gradients of the amount of CO_2 in the atmosphere of some caves: along a shaft, along a scree fan extending from a fractured zone, and along a subterranean stream. The observed range of CO_2 content of cave air ranges from that in the free atmosphere to nineteen times more in a fissure. The most frequent values are two to eight times in spacious caves, compared to free air.

INTRODUCTION

An interesting method for the measurement of CO_2 in soil air has been described by H. Koepf in 1952. It has been used by (among others) F. Hilger (1963), and at the Centre d'Etude des Sols Forestièrs de la Haute Belgique, Gembloux, Belgium. This method is also suitable for atmospheric CO_2 determinations and has been shown by F. Delecour (1965) to be accurate and reproducible.

The determination is based upon the electrolytic titration of the carbonic-acid gas of a known volume of air, absorbed in a 0.1N NaCl solution, that has been colored with phenolphthalien. The electrolysis of this solution produces NaOH, which neutralizes the absorbed carbon dioxide. The current is kept constant during the whole titration. One measures the time necessary to produce enough NaOH to neutralize the absorbed carbon dioxide, which is indicated by the phenolphthalien turning red. The carbon dioxide content of the sample can be computed from the current (mA), the time (seconds) and the air-sample volume (ml).

The apparatus, packed in its case, is shown in figure 1. It weighs 15 kg. It is easily carried, so that measurements can be made in the field (or in a cave).

APPARATUS

Referring to figure 2, the components of the apparatus shown in figure 1 are: A - voltammeter, B - battery compartment, C - rheostat, D - NaCl solution storage flask, E - compartment for titration cells, and F - cover

*Centre d'Etude des Sols forestiers de la Haute Belgique, I.R.S.I.A., Faculte agronomique, Gebbloux, Belgium

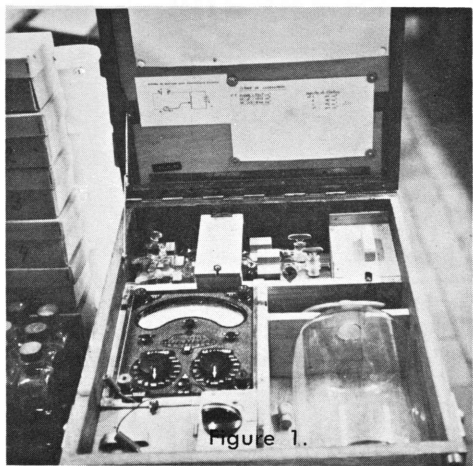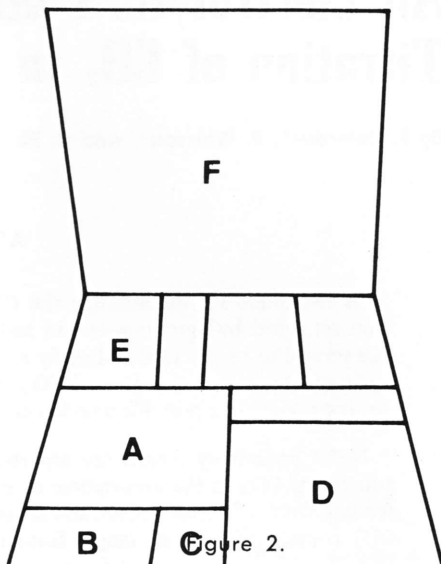**Laboratoire de Geologie et Geographie physique, Universite, Liege, Belgium

Figure 1.

The titration set in its wooden case.

with a white screen for comparing colors. During the electrolysis, the apparatus is arranged as shown in figure 3.

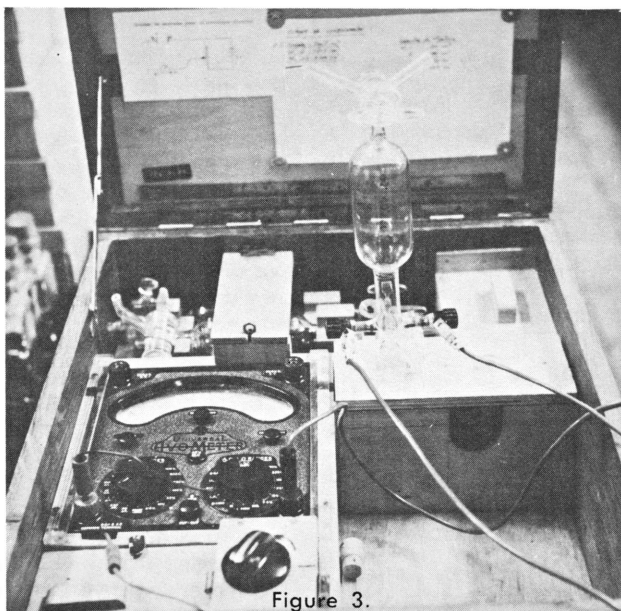Figure 2.

Components of titration set (see text).
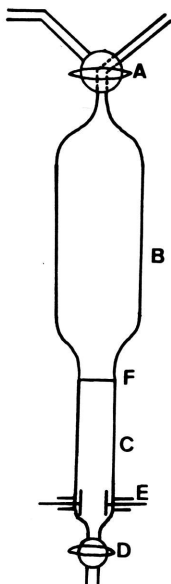

Figure 3.

Arrangement of the apparatus during electrolysis.

Figure 4.

The titration cell (see text).

Figure 5.

Stabilized current source.

Figure 4 is a schematic of the titration cell. Its components are A - three-way stopcock, B - cylindrical bulb (about 3.5 x 9.5 cm), C - lower tube (about 1.5 x 6.5 cm), D - lower stopcock, E - platinum electrodes (1 cm², 1 cm apart, and at least 3 cm below F), F - guage line. The total volume of parts B and C is about 100 ml. This must be accurately determined. The volume of C below the guage-line is 10 ml.

The NaCl storage flask is a 3 to 4 liter glass or polyethylene bottle with a stopcock at the bottom. During an analysis, the upper opening is fitted with a soda-lime absorption tube.

The transitor-stabilized current source (0-10 mA) is shown schematically in figure 5. The current strength is regulated by an adjustable 10-k ohm rheostat. Temperature effects are cancelled by the Zener-diode ZL 3.9. Power is supplied by drycells (12-14 volts).

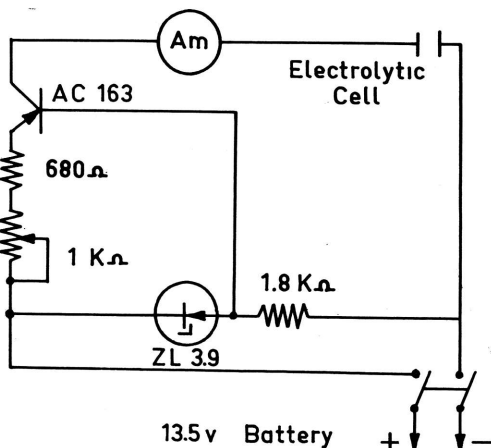Several reagents are required. These are a) a 0.5% solution of phenolphthalein in 0.1 N NaOH; b) 0.1 N NaCl, adjusted to a pH between 0.9 and 9.1 by means of solution a, for which about 3±.15ml per liter of solution are required. The NaCl solution then exhibits a definite pink color; c) 2.5% KCN-AgCN, prepared by dissolving 2.5 g KCN in about 70 ml of distilled water, dissolving 2.5 g AgCN in this solution, and bringing the volume to 100 ml ; d) 2% KCN, prepared by dissolving 2 g KCN to a volume of 100 ml.

PROCEDURE

Before use, the anode of the electrolytic cell must be silvered. This silver layer reacts with the chlorine released at the anode, removing it from the reaction system. Silvering of the anode is accomplished using the KCN-AgCN solution (a above), with a current strength of 10mA, for one hour. This may be done with the current-source already described, connected in reverse to the electrodes. About 50 ml of the silver solution is pipetted (caution!) into the titration cell and the circuit is switched on. The solution is allowed to drip from the cell at the

rate of one drop every 8-10 seconds by means of the stopcock D (figure 4). After silvering, the cell is thoroughly rinsed.

It is necessary to clean the electrodes of any grease before the first silvering. This can be accomplished by electrolysis (0.2-0.4 mA) of a concentrated sodium hydroxide solution, with frequent current reversal.

During determinations, the silver-plated anode becomes progressively black and must be regenerated after eight to ten determinations. The accumulated AgCl layer is removed by shaking with the 2% KCN solution (d) and the electrode re-plated.

A gas sample is introduced into the system as follows: the bottom stopcock of the NaCl flask is connected to the lower end of cell with a rubber tube. Stopcocks A and D are opened and the bulbs filled by lifting the flask. In order to discard the NaCl solution which has been in contact with air, at least 10 ml of the solution is allowed to flow out through A. Both A and D are then closed, and the cell may be taken to the place where the sample of air is to be taken.

Sampling is accomplished by opening A and D, allowing the NaCl solution to run out until it comes to the level of the guage line F. The stopcocks are then closed. The air-sample volume is that of bulb B.

By vigorously shaking the cell, for four or five minutes, the CO_2 in the sample is absorbed in the NaCl solution, which becomes acidic and hence colorless. The cell is then connected to the current source (figure 5) for electrolysis. A current of 2.2 mA is advantageous for the subsequent calculations. The duration of the electrolysis is recorded to the second (for example, with 2.2 mA, the duration of electrolysis is of the order of 50-55 seconds for a sample of free air). During the electrolysis, NaOH is formed at the cathode and the solution becomes red again. The cell is then disconnected and shaken, as above, for four or five minutes. The color of the solution is then compared with that of a control tube. If the solution in the cell is less colored than that in the control, it should be electrolysed further, until the colors are the same. After every new electrolysis, the cell is shaken, for 30 to 45 seconds, before the colors are compared.

If the solution in the cell is more colored than that of the control, an acidifying electrolysis should be made, by reversing the connections and operating as described earlier, until the colors are the same in the cell and in the control tube.

The CO_2 content of the sample, expressed as mg/1, is computed from the formula where

$$CO_2 \ (mg/1) = \frac{0.456 \ (i) \ (t_1 - t_2)}{V}$$

i is the current in mA; t_1 the duration of direct electrolysis, in seconds, t_2, the duration of reverse electrolysis in seconds; and V the volume of the air sample in ml.

If the current i is 2.2 mA, (0.456 i) is very near 1.0, which simplifies the calculation even further.

Koepf (1952) found that the range of maximum precision lies between 0 and 5 mg CO_2/1. Beyond 5 mg/l, the results are somewhat low (about 5% for CO_2 content of 7 mg/1).

RESULTS

Some preliminary measurements, carried out during the spring and summer of 1966, displayed encouraging results. All were recorded in Belgium, in limestone caves, at altitudes ranging from 100 to 250 meters above sea level. Additional observations will be reported in the Annales de Speleologie.

In figures 6 and 7 are shown the results of measurements made along steep slopes in Comblain-au-Pont Cave and Rochefort Cave. It can be seen that the CO_2 content of the air may increase downward or upward. The top of the Comblain shaft is open to the outer atmosphere while the top of the "Hell" chamber in Rochefort Cave is connected by fissures with the soil of a wooded doline.

Two factors may induce these CO_2 gradients. In the Rochefort "Hell Chamber", diffusion from a fissure is probably the main factor. At Comblain, the CO_2 gradient can
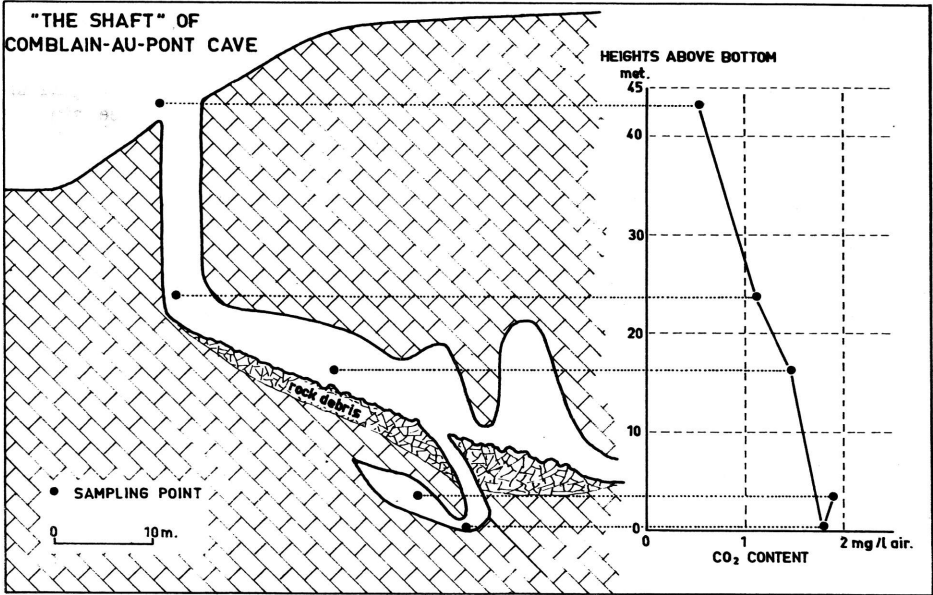
Figure 6.

Cross section from Comblain-au-Pont Cave showing sampling locations and CO_2 measurements.
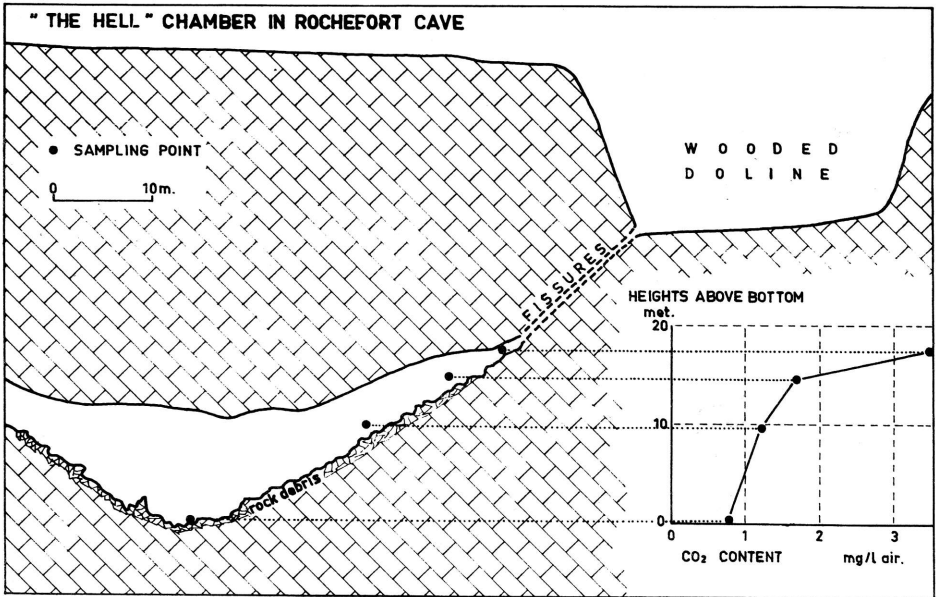

Figure 7.

Cross section from Rochefort Cave showing sampling locations and CO_2 measurements.

be due to an accumulation by gravity. However diffusion may be responsible for the higher CO_2 content in the little chamber situated 3.5 m over the bottom.

Five measurements were carried out along an underground river, at 20 cm above the water level, between the exsurgence of the river and the terminal sump, at the very end of the cave. The results are shown in figure 8.
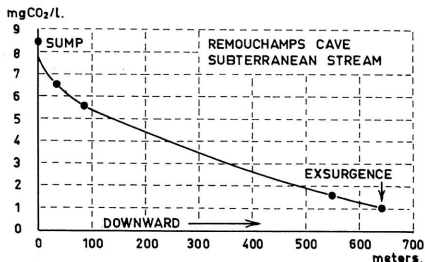

Figure 8.

Subterranean stream in Remouchamps Cave. CO_2 content of air 20 cm above water level. The distance is measured along the stream.

One might assume that the progressive lowering of CO_2 content of the air, downstream, shows variations of equilibrium between the air and the water. However calculations from water analyses show that this is not true. The following possible explanation might then be proposed: the water is in equilibrium with high CO_2 values when the river emerges from the sump and enters accessable passage and, at first, the diffusion rate of CO_2 from water to air is very high. Further downstream, both the excess CO_2 in the water is lower and cave ventilation is improved, leading to lower CO_2 concentrations in the air.

Conclusions

Values observed (75 measurements) ranged from 0.55 mg/l, for free air, to 10.62 mg/l in a fissure of a shallow cave, under wood and pasture. In the majority of cave atmospheres, values were between 1 and 3 mg/l; they can be a little lower in some passages of big caves, or somewhat higher in small cavities.

The high CO_2 content in fissures (frequently 10, or even 19, times higher in narrow fissures than in the free atmosphere) seems to indicate that air with high CO_2 content flows through these fissures, and that its diffusion in caves is slow. A faint, increasing gradient of CO_2 downslopes was observed twice. It is possibly due to accumulation by density, but the values were not very high at the bottom (less than 3 mg/l).

One might conclude that most of the features reported here were either known or suspected, but the scarcity of measurements in cave air has prevented general conclusions from being drawn. One hopes that the device presented here will contribute to the multiplication of measurements in all seasons, in other climates, at various altitudes, and so forth.

Since atmospheric CO_2 is a *prime mover* in dissolution of limestone, we firmly believe that measurements such as described above will prove to be valuable for furthering our general understanding of karst processes.

LITERATURE CITED

Delecour, F.
1965 Détermination des activités biologiques par la méthode de Koepf. Standardization et essai de la technique de dosage de CO_2. Note de recherches no. 2, Centre d'Ecopédologie forestière, Gembloux, Belgium.

Hilger, F.
1963 Activité respiratoire de sols équatoriaux: Application de la méthode respirométrique *in situ*: Bull. Inst. Agron. Stat. Tech. Gembl., v. 31, pp. 154-182.

Koepf, H.
1952 Laufende Messung der Bodenatmung im Freiland: Landw. Forsch., v. 4, pp. 186-194.