MEASUREMENT OF CARBON DIOXIDE EVOLUTION FROM DECOMPOSING MATERIALS USING CONDUCTIMETRY

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1986

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1. INTRODUCTION

This paper describes the practical details of a batch method for measuring the respiration and hence the rate of decomposition of organic materials. It is based on the absorption of carbon dioxide by an alkali in solution, and the subsequent assay of the amount absorbed using electrolytic conductivity.

The principle of alkali absorption has been quite widely used in this connection (Cowling & MacLean (1981), Anderson (1972), Van Cleve et al (1979), Kirita (1971) etc.), but usually in combination with some form of acid titration to determine the amount of carbonate produced. Conductivity is less often used, although a field respirometer developed by Chapman (1971) was based on it. This had the advantage of allowing continuous monitoring, but because of the complexity of the design, was unsuitable for any experiment involving more than a very few replicates. The method described here requires relatively simple apparatus and only a single conductivity cell.

It is possible to use conductivity in this way because of the fact that the mobilities of hydroxide and carbonate ions differ in the ratio 2.5:1 (approximately), so that when CO_2 is absorbed by an alkali, the conductivity of the solution steadily falls. To a first approximation, the reduction is determined only by the number of CO_2 molecules absorbed, and provided that the solution is measured at a standard volume (with no handling losses), its concentration need not be accurately known.

The conductivity meter in this application was the commercially produced PTI-10. One of a range of conductivity meters available from: Aqua Chemical Co., 166 Snargate Street, Dover, England. This has Automatic Temperature Compensation (ATC), and a display with 3½ significant figures (a maximum reading of 1999). It is battery powered and suitable for either field or laboratory use. It was

modified by us to include a facility for near simultaneous measurement of conductivity and temperature.

2. SETTING UP AND CALIBRATION OF THE CONDUCTIVITY METER

2.1 The Cell Constant (K)

The Cell Constant (K) is defined by:

$$K = C_s/C$$

where C is the measured conductance across the electrodes of the cell, and C_s is the conductivity (specific conductance) of the electrolyte. K has the dimension $(length)^{-1}$. Cells are designed to have a predetermined K value, although they may deviate slightly from the nominal due to manufacturing tolerances. They can be checked for accuracy by using the instrument to measure the conductivity of a standard 100 mM solution of potassium chloride at standard temperature, and applying the formula. C is then the meter reading and C_s a value derived either from data supplied with the instrument, or from published tables. At 18°C for example, Aqua Chemicals Co., gives 11,190 uS/cm.

2.2 Setting up the meter

The scaling of the PTI-10 meter has a tendancy to drift slightly from day to day (probably due to variations in ambient temperature), and should be checked and adjusted before making any measurements.

The instrument is supplied with a calibration plug, which serves as a temporary replacement for the conductivity probe. It contains a pair of fixed resistors which are substituted for the cell electrodes and thermistor (in an ATC system), and from the meter's point of view are equivalent to the probe being dipped into a standard electrolyte at standard temperature. The scale factor control on the meter is used to bring the reading to the 'target' value specified by the makers. For the PTI-10 it is given as 1000 for a reference temperature of 25°C, but can

be modified to cater for other temperatures. Its new value is then either calculated using the formula in section 3.2, or it can be determined empirically. The procedure then is to dip the probe in 100 mM KCl at the required temperature, and adjust the meter to give the conductivity reading appropriate to that temperature (at 18°C for example it would be 11,190 uS/cm). The corresponding reading with the calibration plug in place is then the new target.

Setting up using the calibration plug ensures that the meter is correctly scaled for a conductivity cell with a K value of 1.0, but the adjustment can also be used to cater for non-nominal cells by dividing the target reading by K.

3. THE TEMPERATURE PROBLEM

The main disadvantage in using conductivity as a measure of the ionic content of a solution is the fact that ionic mobility, and therefore conductivity, is temperature sensitive. Although it may be possible to avoid the problem by ensuring that the solutions are measured at a standard temperature, there are circumstances – for example in the field – when this is impractical, and the temperature of measurement must then be taken into account.

3.1 Temperature corrections

Some meters (including the PTI-10) have systems for Automatic Temperature Compensation (see below), which in many applications allow the temperature variable to be more-or-less ignored. They are inevitably imperfect however due to the fact that each ionic species has its own temperature response characteristic (Table 1). The correction applied is therefore reliable only when it is matched to a solution with unvarying ionic proportions: a condition that is certainly not met in the present application, where the uptake of CO_2 by an alkali causes a chemical change.

This is a problem fundamental to the conductivity method, and applies equally to attempts to apply temperature corrections by calculation. The approach then has to be based on an iterative procedure in which conductivity (with its implied ionic proportions) and the temperature correction are alternately re-evaluated – perhaps using a computer. The calculations can be applied to any meter, with or without ATC, but with due allowance for the fixed ATC correction rate in the former case.

3.2 Automatic Temperature Compensation

The ATC system works by sensing temperature through a thermistor built into the conductivity probe, and then automatically applying a scaling change so that the meter reading is correct for a solution at the reference temperature. For the reason given above, the correction rate must be a compromise, and in the present application would ideally match the temperature response of a partially carbonated alkali. The rate is not normally adjustable however (at least for the PTI range of meters), but set and specified by the makers. It is often expressed in as a percentage per °C, although it is not an exponential function as this would imply, but rather a linear one of the form

$$1/C_r = (1 - R(T_r-T_m))/C_m$$

Where C_r and C_m are conductivities at the reference temperature T_r, and the temperature of measurement T_m, and R is a constant.

R for the PTI-10 was measured as 0.00215 $(°C)^{-1}$, equivalent to a conductivity change of -2.04% per °C at 25 °C (see footnote) (the manual specifies -2.0%).

The plates of the electrolyte were temporarily replaced with a fixer resistor (the probe connector was modified for the purpose), and the probe (including the thermistor) immersed in water over a range of temperatures measured using a precision thermometer. The regression of pseudo-conductivity readings on temperature gave the value of R.

This compares with a response rate for 50% carbonated KOH of 1.86% per °C (Appendix 1). ATC therefore over-compensates by 0.18% per °C at this temperature. This is often small enough to ignore, especially if the solutions exposed to are being compared with unexposed blanks, and temperatures are fairly uniform. The error in the measurement of ΔC (conductivity change) may then be as low as 0.025% for every °C above or below the reference temperature (see Appendix 1 for the calculations).

3.3 Temperature measurement

Although the electrolyte temperature may not be critically important with ATC in use, it is worth measuring if only to ensure constancy within a batch of samples. Any thermometer may be used, but it is convenient in an ATC instrument to make use of the built-in thermistor. The method is the same as that used to evaluate the R factor, but with a permanent arrangement for switching between conductivity and temperature (Appendix 2 shows the circuit). The value of the fixed resistor determines the calibration. Meter readings are then converted to temperature using a formula derived by immersing the probe in a liquid over a range of accurately known temperatures. Routine conversion may be either from a table of equivalence, or from a graph.

4. CONCENTRATION OF THE ELECTROLYTE

When CO_2 is absorbed by a weak alkali solution (with a pH below 12.0), an appreciable proportion of the carbon exists as bicarbonate ion (HCO_3^-) rather than the carbonate ion (CO_3^{2-}), and since the two have different mobilities, the conductivity for a given CO_2 content is modified. Conversions from conductivity to carbon content are therefore greatly simplified if OH^- concentrations can be kept above about 7mM. Assuming that a given alkali absorbant is never more than 80% saturated with CO_2, the equivalent un-carbonated solution strength should not be less than about 35mM. (Hill and Evans (1986)).

The upper concentration limit is imposed by the conductivity meter. For the PTI-10 with a Cell Constant of 1.0 cm^{-1}, the maximum is 2000 $\mu S/cm$ (0.2 S/m), corresponding to KOH at a concentration of about 1.0M.

If CO_2 content is being derived by difference, it is not crucially important to know the precise concentration of the electrolyte, but it should be known approximately because of its effect on equivalent conductivity (due to decreasing dissociation with increasing concentration) (Fig. 1), and therefore on the conductivity/CO_2 calibration.

5. CONDUCTIVITY/CARBON CALIBRATION

Provided that the electrolyte is sufficiently concentrated to avoid bicarbonate formation, the conductivity/carbon relationship is linear, although the conversion factor is slightly affected by the concentration of the electrolyte, and by the choice of reference temperature. The factors given in Table 2 were derived by mixing pure solutions of KOH and K_2CO_3 together in various proportions (simulating carbonation of KOH by uptake of CO_2 gas).

6. GENERAL METHOD

The principle of the method is to enclose the respiring material (forest litter, soil etc.) in a sealed container (the respirometer), along with an absorbant in the form of an aqueous solution of alkali (usually potassium hydroxide). The absorbant is recovered after a measured time interval, diluted to a known volume with distilled water, and its conductivity measured. The amount of carbon dioxide absorbed can then be calculated by comparing the conductivities for the treatments (those exposed to CO_2), with the conductivity of unexposed blanks.

All the absorbants in any one batch of respirometers should be taken from the same stock solution, and the volume used should be the same throughout. The absorbant is normally dispensed using an adjustable, self-priming dispenser fitted with a non-stick (PTFE) piston (to avoid the problem of adhesion that often occurs when alkalis are used with glass-glass contact). The 'Zippette' is a commercially available version.

Concentration and volume should be chosen so that for a given exposure time, about half of the hydroxyl ions are converted to carbonate. This gives maximum sensitivity without the risk of running into non-linearities due to bicarbonate formation.

The absorbant is recovered at the end of the scheduled period by pouring the dish contents into a bottle (often a 500 ml Mason jar) primed with rather less than the volume of distilled water required to give the desired dilution. Some of the solution is used to briefly rinse any residual absorbant into the bottle. The bottles are then sealed and transferred to the laboratory.

The volume of absorbant can change during the course of a run, due to evaporation or condensation, and a final topping-up with distilled water is used to bring the nett volumes (or more usually the nett masses which are quicker to measure) up to a standard.

All the conductivities in a batch are if possible measured at the same temperature. The bottles can be equilibrated on the bench or in an incubator set to the reference temperature (usually 18°C), but the actual temperature of measurement should be checked (the cell thermistor may be used as explained in Section 3.3).

In a large container there is a time lag between the release and subsequent absorption of a CO_2 molecule. The real time available for take-up is therefore less than the apparent time, and rates of CO_2 production tend to be underestimated. The approximate mean residence time T (hours) can be calculated using the Hill and Evans (1986) formula.

$$T = \frac{V}{0.2 \times A \times \sqrt{C}}$$

where V is the respirometer volume (m^3)

A is the surface area of the absorbant (m^2)

and C is the concentration of the absorbant (mM).

In a typical case using a 2.5 l container, and a 100 mM KOH solution with a surface area of 100 cm^2,

$$T = 0.125 \text{ hours.}$$

Since such an experiment would commonly last for 24 hours, errors arising would usually be small enough to ignore.

6.1 Laboratory method

Various respirometers have been used ranging in size from 500 ml polypropylene Mason jars to 11.5 l plastic bins (similar to 10 l paint containers). The former are suitable for small samples of very active material (litter for example), and are used by dispensing the absorbant into the jar itself (not using a dish), and holding the specimen in a small open tub suspended from the screw-top. The same jar can then be used for dilution and conductivity measurement by detaching the tub. The arrangement is shown in Appendix 3. The scale of the apparatus allows the temperature of quite large batches to be controlled using an incubator.

The large bins are generally used for relatively bulky materials such as wood or soil in flower pots. They differ mainly in that the absorbant must be contained

in a dish. Temperature control is difficult because of the bins being too big for most incubators.

All respirometers should if possible be closed and sealed out-of-doors. This is because the CO_2 content of the air inside a building is often above the normal level in the atmosphere (about 0.034% in 1986). Perfect sealing of containers is important but can be suprisingly difficult to achieve. Petroleum jelly smeared on the lid contact surfaces is usually effective however.

The absorbant should have a surface area large enough to allow an adequate rate of uptake. In general, one should aim to use the largest dish that will fit comfortably into the respirometer, and a volume of absorbant sufficient to cover the base of the container to a reasonable depth - not so shallow that evaporation could empty it. The strength of the absorbant is then chosen to give about 50% carbonation in the time available.

For most of our experiments we have used rectangular plastic dishes with a basal area of 100 cm^2, and 50 ml of absorbant, giving a depth of 0.5 cm. The alkali strength was usually in the range 50 to 500 mM.

As a precaution against undetected spillage, fluorescein may be added to the absorbant. This has a small but constant effect on conductivity, and makes any spillage immediately distinguishable from, for example, condensed water.

6.2 Field method

Our main field application was for _in situ_ measurement of litter and soil respiration in coniferous plantations and on clear-felled sites. We attempted to isolate vertical cores of material by partially burying lengths of 160 mm PVC drainpipe. Installation involved making a preliminary circular incision with a

sharp knife, and then pressing the pipe sections into the soil. Obstacles were if possible removed by careful excavation. Pipes were generally sunk to a depth of about 50 mm, leaving about 50 mm above ground. When the ground sloped, the pipes were kept vertical, but cut obliquely on their lower edges so that the depth of penetration was still even. Strips of PVC were glued to the inside of each pipe to form a ledge upon which the rectangular absorbant dish could be supported clear of the ground surface. The installations were intended to be left in place semi-permanently, but without covers, so that litter accumulation and breakdown could continue more-or-less normally (there was inevitably a sheltering effect due to the above ground portions of the pipes).

For respirometry each chamber was closed by a 'top hat' also made of 160 mm piping with a flat PVC cover glued in place. This was held in position by three small lugs glued to the outside surface of the cover. The two abutting edges were accurately machined, and a good seal was generally possible by applying petroleum jelly to one of them.

Where a site was open to direct sunlight, an inverted white plastic flower-pot was placed over the apparatus to minimize solar heating.

The temperature of the soil within the chamber was monitored using dip-wells. These were test tubes sunk 10 cm into the ground, filled to the ground surface with anti-freeze, and closed with corks. The ground temperature was measured immediately before and immediately after each respirometry session using an electronic thermometer. (See Appendix 4.)

7. UNCERTAINTIES

The field environment is less well controlled than the laboratory, and there are a number of possible sources of error that are difficult to quantify. They include:

1   Doubts about the origin of the CO_2. Since the pipe sections have only limited penetration into the soil and are open at the bottom, one cannot assume that CO_2 entering the chamber from below is necessarily coming from the region vertically beneath it. If the absorption of CO_2 should result in even slight depletion of soil CO_2, a lateral partial-pressure gradient will be established and cause sideways diffusion into the sampling region. Loss of pressure in the chamber due to CO_2 absorption may also lead to abnormal gas flow. The CO_2 catchment area is therefore vague.

2   If the respirometer pipe is loose in the ground, there is a possibility of CO_2 depletion by diffusion from the soil to the air through the gap around the pipe. CO_2 within the catchment may then reach the surface outside the chamber.

3   Allowances for the mean residence time of a CO_2 molecule assume still air. In fact, under field conditions, the air may be disturbed by thermal effects due to local solar heating, or by a pumping action due to the movement of tree roots under windy conditions.

4   The installation of a pipe inevitably results in a number of fine roots being severed. Live roots are then replaced by dying roots.

5   CO_2 may come from geological sources at depth.

The nett effect of these various hypothetical processes is probably insignificant when dealing with a very active litter layer wholly within the respirometer. Situations in which this is not so would be less suited to this particular technique.

8. CONCLUSIONS

The method is very satisfactory for experimental work in the laboratory. If precautions are taken to avoid enclosing air with an abnormal CO_2 content, and measurements are made at controlled temperatures, it is quick and accurate. It is less satisfactory for in situ experiments, which involve a number of unknown variables.

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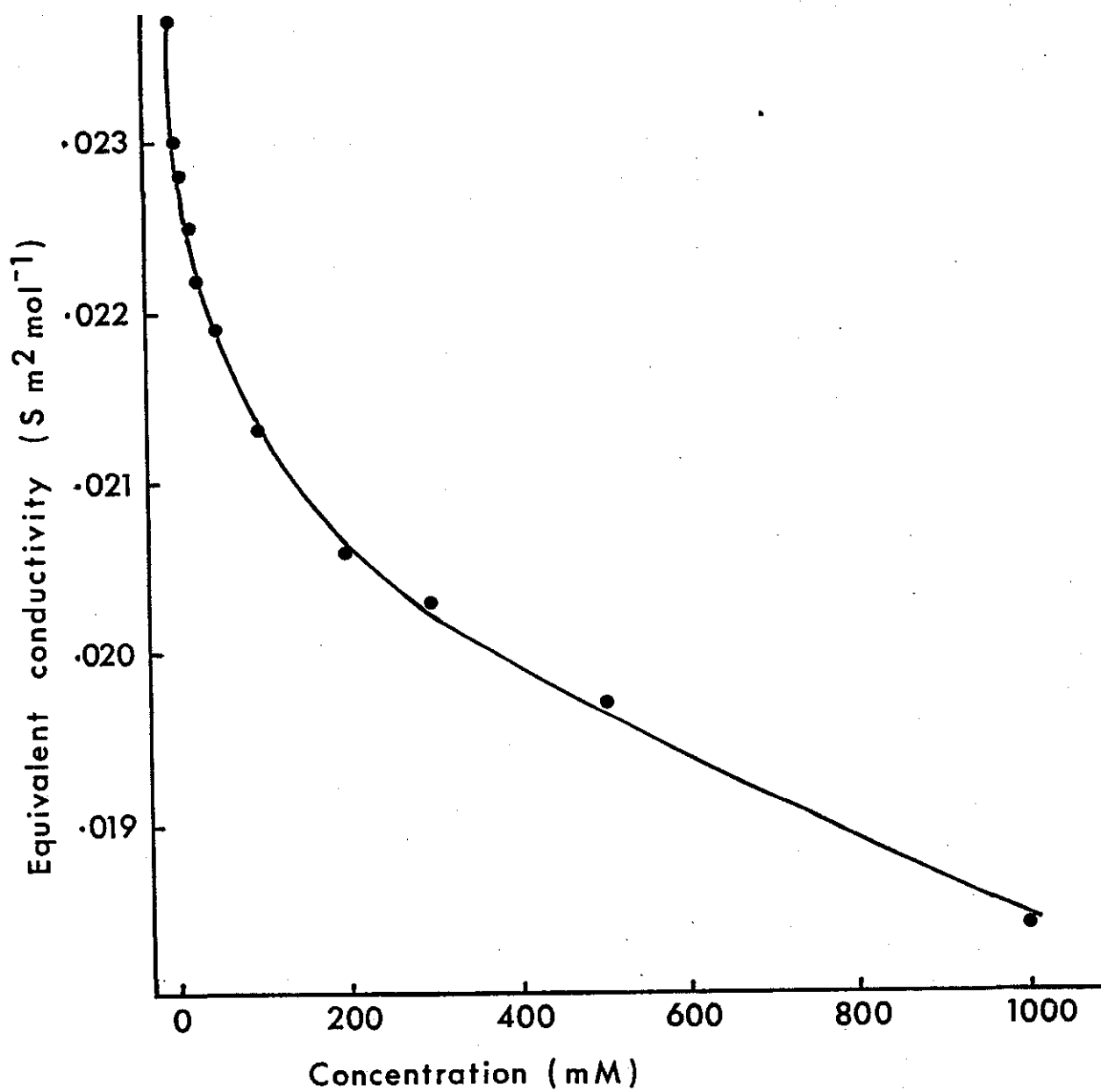
Fig. 1. Equivalent conductivity of KOH at 18°C in relation to
concentration; plotted values were derived from Landolt-Börnstein
(1960).

Table 1. Ionic conductivity as a function of temperature (°C)

| Ion	Ionic conductivity $(S\ m^2\ mol^{-1}\ x\ 10^{-3})$
K^+	$0.1327 \times (T + 30.42)$
Na^+	$0.0930 \times (T + 28.11)$
OH^-	$0.3697 \times (T + 28.76)$
$\frac{1}{2}CO_3^{2-}$	$0.1424 \times (T + 25.10)$
$OH^- - \frac{1}{2}CO_3^{2-}$	$0.2273 \times (T + 31.05)$
Cl^-	$0.1412 \times (T + 28.79)$

Note: Values are derived from data quoted in Landolt-Bornstein (1960).
Regressions were calculated by ourselves. Estimates based on the
calculated regressions are accurate in the range 0-25°C to about $2\frac{1}{2}$
significant figures.

Table 2. Coefficients for converting conductivity change

to uptake of carbon

Conc. of KOH (mM)	Uptake of carbon (μg 1^{-1}) equivalent to a conductivity change of 1μS/cm	
	18°C	25°C
0.5	53	55
1	59	51
2.5	54	47
5	53	46
10	52	45
25	51	44
50	50	43
100	49	43

Appendix 1. Calculation of errors due to conductivity being measured at non-reference temperatures.

The reaction of potassium hydroxide with carbon dioxide in its simplest form is

$$KOH + \tfrac{1}{2} CO_2 \rightleftharpoons \tfrac{1}{2} K_2CO_3 + \tfrac{1}{2} H_2O$$
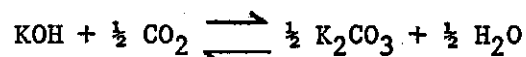
but because the concentration of K^+ is constant, the nett change in ionic terms is

$$\tfrac{1}{2} CO_2 + OH^- \rightleftharpoons \tfrac{1}{2} CO_3^{2-} + \tfrac{1}{2} H_2O$$
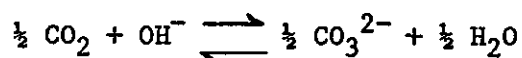
Now if the conductivities of K^+, OH^- and $\tfrac{1}{2} CO_3^{2-}$ ions are K_1, K_2 and K_3, and their ionic proportions in a solution are C_1, C_2 and C_3, the conductivity change due to a 1°C temperature change is given by

$$\delta c = \frac{K_1 \delta C_1 + K_2 \delta C_2 + K_3 \delta C_3}{K_1 C_1 + K_2 C_2 + K_3 C_3}$$

So that if, for example, a KOH solution is 50% carbonated, giving ionic proportions of 1:0.5:0.5, and the conductivities refer to 25°C, then using the values in Table 1

$$\delta c = \frac{(0.1327 + 0.3697 \times 0.5 + 0.1424 \times 0.5) \times 100\%}{(0.1327 \times 55.42 + 0.3697 \times 0.5 \times 53.76 + 0.1424 \times 0.5 \times 50.10)}$$

$$= 1.864\% \text{ per } °C$$

Similarly for uncarbonated KOH

$$\delta c = \frac{0.1327 + 0.3697}{0.1327 \times 55.42 + 0.3697 \times 53.76} \times 100\%$$
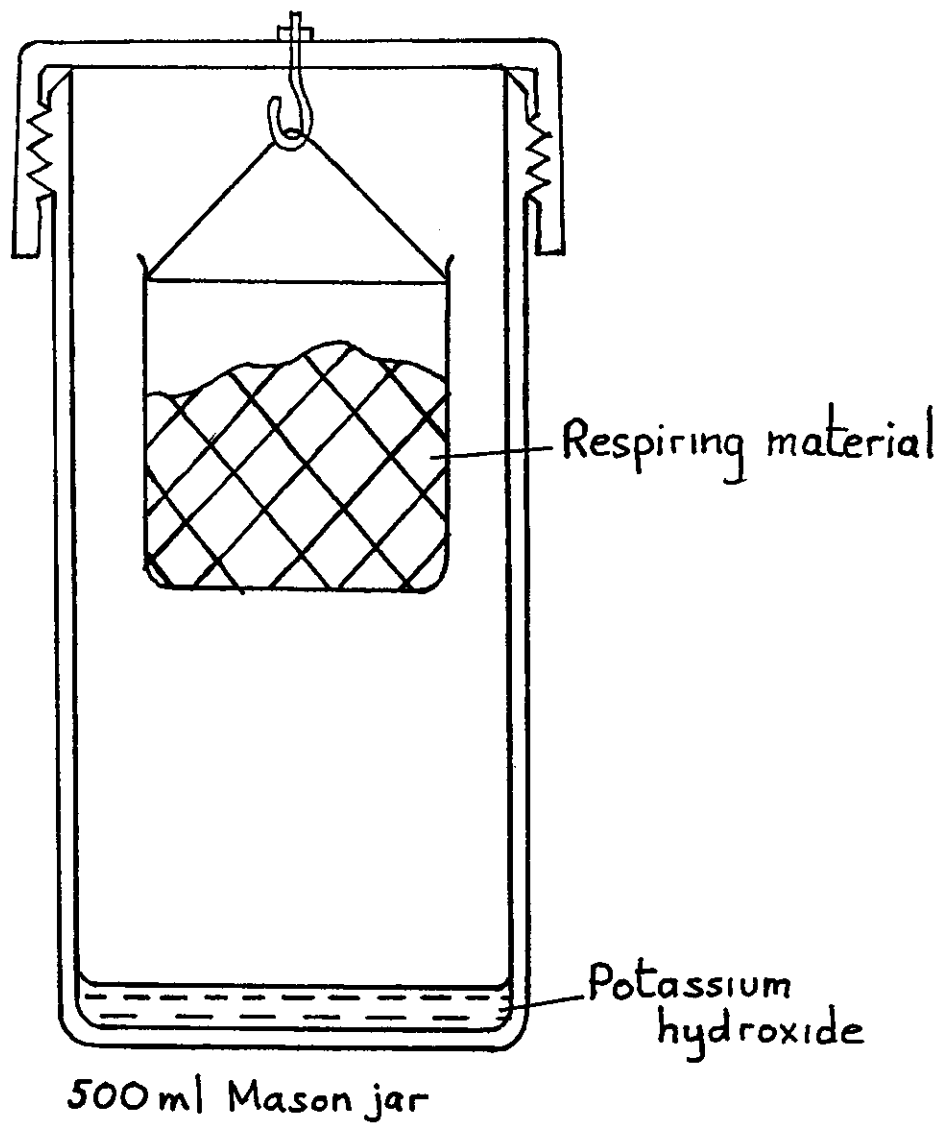
$$= 1.845 \% \text{ per } °C$$

So that if a CO_2 assay is based on conductivity differences between exposed and unexposed solutions (blanks), the error would be

$$1.864 - 1.845 = 0.019 \text{ \% per } °C$$

Provided therefore, that blanks and treatments are at the same temperature, departures from the reference temperature (25°C in this case) will usually have a negligible effect on the final result.
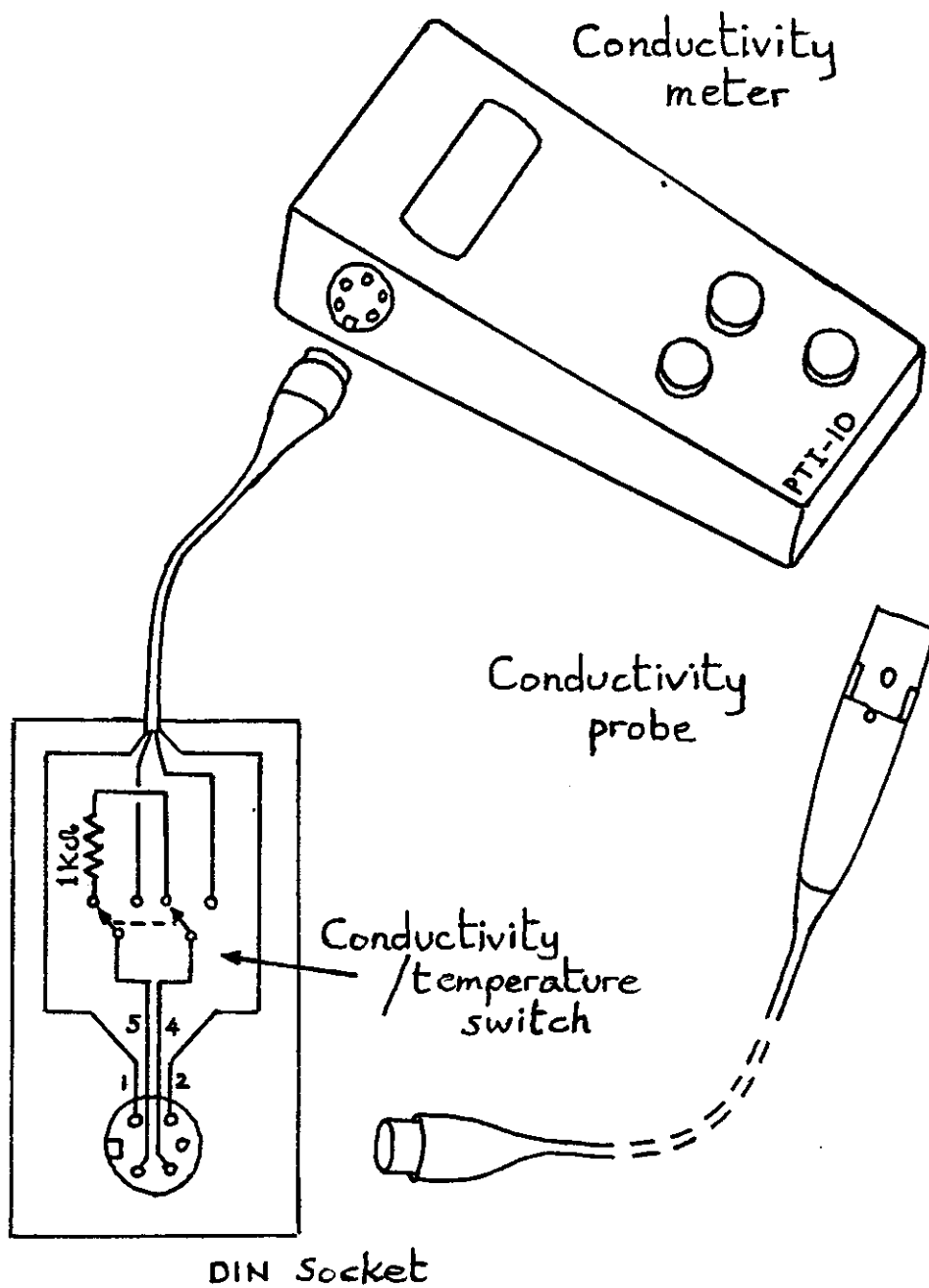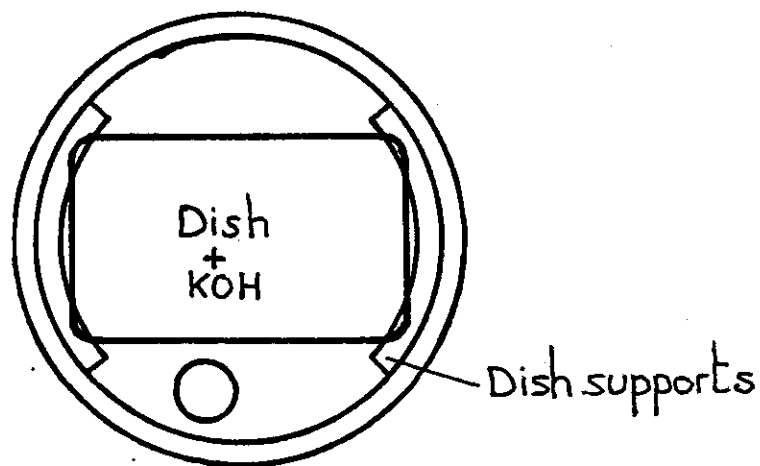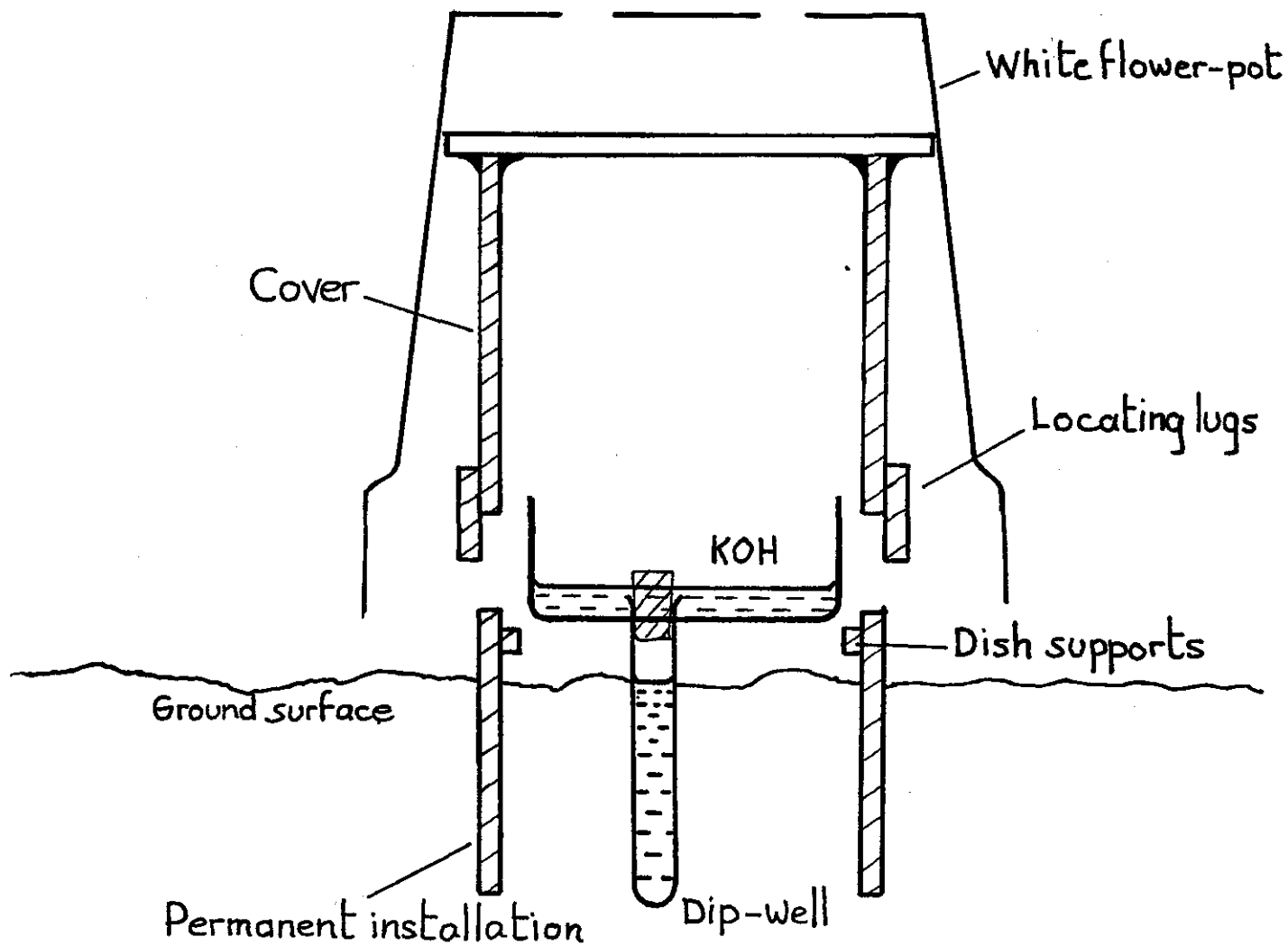
Appendix 2   The conductivity meter adapted for temperature measurement

Respiring material

Potassium hydroxide

500 ml Mason jar

Scale approx ¾

Appendix 3   A laboratory respirometer

White flower-pot

Cover

Locating lugs

KOH

Dish supports

Ground surface

Permanent installation

Dip-well

Dish
+
KOH

Dish supports

Scale approx   1/3

Appendix 4 Apparatus for *in·situ* respirometry