Technical Note:

A Rapid Method for Determining Apparent Diffusion Coefficients in Chalk and other Consolidated Porous Media

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Abstract:
The development of a method for the determination of the apparent diffusion coefficient, D_A, for chloride in saturated Chalk cores is described. The method is rapid compared with other approaches, taking typically less than 24 hours for a single determination. Cylindrical Chalk cores approximately 25 mm high by 25 mm in diameter, which are routinely used in porosity and permeability measurements and which had been pre-equilibrated with a 200 mg/L chloride solution, were sealed at both ends and attached to a slowly rotating spindle suspended in a reservoir. A chloride ion selective electrode (ISE) connected to a data logger was used to record chloride diffusion out of the core. D_A was estimated by analysing the change in chloride concentration in the reservoir with time. Diffusion coefficients were estimated for six Chalk samples from a range of Chalk lithologies. Sample porosities for these Chalks ranged from 32-48% and gas permeabilities from 0.3-8.2 $\times 10^{-9}$ m^2. The D_A was found to vary from 3.1-8.7 $\times 10^{-10}$ m^2/s, a similar range to that observed by others. A bromide ISE was also used on one sample and found to give a similar D_A to that obtained for chloride. This approach, which combines a rigorous mathematical model of diffusion with a relatively simple practical method, could easily be adapted for other ions and for other consolidated porous media.

1. INTRODUCTION

1.1 Background

The Chalk is the major aquifer in the UK accounting for 70% of groundwater used and 33% of the total water used in England and Wales (UK Groundwater Forum, 2003). The mechanisms of movement of water and solutes through the Chalk are complex, although the nature of the overall groundwater flow regime has been well documented (Foster and Milton, 1974; Price, 1987).

The Chalk is a soft microporous fractured limestone and can be conceptualised as having three components of porosity and permeability: (i) the Chalk has high intergranular porosity (25–45%) (Bloomfield et al., 1995) but only low intergranular permeability since the pore-neck sizes are typically less than 1 µm (Price et al., 1976); (ii) primary fractures that have low porosity (0.1-1%) but which can, depending on frequency, increase the hydraulic conductivity by two or three orders of magnitude (MacDonald and Allen, 2001), and (iii) secondary fractures that result from the solution and enlargement of primary fractures and which can account for the bulk of the flow in the saturated zone (Price et al., 1982).

The major physical processes controlling the movement of solutes in the secondary fractures are generally assumed to be advection and dispersion, whereas in the matrix these processes are assumed to be insignificant. However, movement of solutes can take place in the matrix by diffusion.

Diffusion in solution is the process whereby ionic or molecular constituents move from an area of high concentration (strictly activity) to an area of low concentration (strictly activity) under the influence of the random kinetic motion of the constituent molecules or ions. Diffusion occurs without any bulk water movement. If the solution is flowing, diffusion is a mechanism (along with mechanical dispersion) that can cause the mixing of ionic and molecular constituents. Diffusion ceases only when there is no longer a concentration gradient, i.e. it continues until there is a uniform concentration everywhere.

The rate of diffusion is of great importance for pollution studies. For example, although the dominant flow in the Chalk is through secondary fractures, contaminants in the fracture water can diffuse into the relatively immobile matrix water. The matrix will, therefore, partially attenuate a contaminant plume. The effectiveness of this depends, amongst other factors, on fracture aperture, spacing and geometry (Barker and Foster, 1981). However, once the contaminant plume has passed through the fractures, the concentration gradient will reverse so that the matrix porewater contaminants will diffuse out from the matrix and into the fracture water. This effect prolongs the remediation of contaminated Chalk (Fretwell et al., 2005).

There have been many studies to determine diffusion coefficients in sediments. Van Rees et al. (1991) compared laboratory techniques based on three approaches: (i) diffusion from a spiked reservoir into sediment; (ii) diffusion from a spiked sediment into a reservoir, and (iii) diffusion from a spiked sediment into an unspiked sediment: (i) above is the most straightforward in practice. A study by Myrand et al. (1992) used such an approach to study the diffusion of a range of volatile organic compounds through clay with experiments lasting up to 30 days. The study by Hill (1984) adopted a slightly different approach. He measured the diffusion of a range of anions from a reservoir, across a Chalk disk, and into another reservoir. These experiments lasted approximately 40 days. Feenstra et al (1984) used a similar approach to Hill (1984) and determined diffusion coefficients for chloride by fixing sandstone discs between a two compartment diffusion cell. Measurements were made periodically during the seven day duration of the tests using an ion-selective electrode. Barone et al (1992a) used a similar design of diffusion cell to obtain diffusion coefficients for a range of organic compounds through clay plugs. In the cells a source solution was allowed to diffuse through the plug of test material and into a collector solution for a period of 14 days. During this time samples were taken from both the source and collector reservoirs. Similar approaches have been used more recently by Polak et al. (2002) and Witthüser et al. (2003).

In a different series of experiments Barone et al (1992b) determined diffusion coefficients for diffusion out of chloride rich mudstones into a reservoir of distilled water. These tests were run for up to 34 days after which time the sample was sectioned and the chloride porewater concentration profile measured. Van der Kamp et al (1996) and Novakowski and van der Kamp (1996) use a radial diffusion method to determine effective diffusion coefficients. The diffusion cell comprised a cylindrical sample of saturated porous material encased in a rigid impermeable tube, with rigid impermeable seals at top and bottom. A hole was drilled along the axis of the sample to create a central reservoir for the test solution. Samples were taken from the reservoir for chemical analysis over a period of at least 40 days. The change in concentration of solutes in the reservoir enabled the determination of the effective diffusion coefficient. Sophisticated tomographic procedures have also been recently used to monitor diffusion in aquifer materials (Betson et al., 2005).

In this paper we present a method for determining the apparent diffusion coefficient for chloride in consolidated porous media. Using an ion selective electrode we measure the change in concentration with time in an aqueous reservoir surrounding a cylindrical core plug that has been pre-equilibrated with a chloride solution. As chloride diffuses out of the core the concentration in the reservoir increases. This new method is both experimentally rapid, taking less than 24 hours, and is simple to carry out with relatively unsophisticated equipment.

1.2 Diffusion Coefficients

Diffusion obeys Fick's first and second laws and is described by a diffusion coefficient. There are several different types of diffusion coefficient. The first major distinction is the phase or phases involved: gas, liquid and solid. The second distinction defines the type of medium involved: self-diffusion (one molecule amongst similar ones), tracer diffusion (a minor constituent within a major one), or interdiffusion (diffusion between two or more different reservoirs). With ions, there is also the issue of whether local charge neutrality is maintained or not. There is therefore significant room for confusion over the meaning of the term *diffusion coefficient.* Several related parameters are in common use reflecting the different types of diffusion and the precise meaning of the term being used is often not clear. A brief summary of the various definitions is given below for the case when surface diffusion is negligible and the concentration is low so that diffusion is independent of concentration and the activity coefficient is close to one.

Fick's first law applied to the diffusion of a solute in water (or any other solvent) relates the diffusive flux, J_{Diff}, directly to the gradient of the concentration, c. For one-dimensional transport in the x direction for steady state diffusion:

$$J_{Diff} = -D_T \frac{dc}{dx} \tag{1}$$

where D_T is normally termed the '**tracer'** (or free-water) diffusion coefficient. (The term 'self-diffusion' applies only to the diffusion of solutes in the presence of identical solutes, but is often erroneously used to refer to free-water diffusion).

The above equation also applies to a saturated porous medium, but a smaller diffusion coefficient, D_E, must be used because of the impediment to transport caused by the matrix. The terms '**effective**' and '**intrinsic**' have been used to describe the coefficient, D_E.

Another value, the '**apparent**' diffusion coefficient, D_A, arises when time-dependent diffusion in a porous medium is described by Fick's second law:

$$\frac{\partial c}{\partial t} = D_A \frac{\partial^2 c}{\partial x^2} \tag{2}$$

Our usage is closer to that used in fields such as chemical engineering than the common usage in the environmental science literature. In order to avoid ambiguity with definitions, it is advisable to ensure that the appropriate diffusion equation is closely associated with diffusion coefficient data, e.g. as a footnote.

While D_T, D_E and D_A are perhaps best regarded as empirical parameters, their interrelations are often expressed in terms of other parameters of porous medium: a thorough treatment is provided by Ohlsson and Neretnieks (1995) and by Grathwohl (1998). For example we could write, $D_E = D_T\ \phi_t\ \delta/\tau^2$ where ϕ_t is the transport porosity, δ is the constrictivity, and τ is the tortuosity. When there is linear sorption, characterized by a distribution coefficient K_d and density ρ, some authors would write $D_A = D_E\ /\ (\phi + \rho K_d\ )$ where and ϕ is the accessible (or 'storage') porosity. (The two porosities, ϕ and ϕ_t , can differ significantly due to the presence of dead-end pores.) The consideration of surface diffusion and nonlinear sorption result in more complex relationships

1.3 Mathematical Model

We make the following assumptions about the behaviour of the diffusion cell:

1. Diffusion in the core is described by Fick's laws with a constant diffusion coefficient;
2. Diffusive exchange takes place only across the cylindrical surface of the core, the planar end surfaces being sealed;
3. The water in the vessel outside the core is well mixed;
4. Measurements of concentration in the vessel water are made passively (i.e. without affecting the concentration or volume of solution);
5. The water within the matrix of the core is immobile;
6. Sorption is negligible.

These assumptions lead to the following equation for the variation of concentration, $c_c(r,t)$, at a radial distance r from the axis of the core at time t:

$$\frac{\partial c_c}{\partial t} = \frac{D_A}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_c}{\partial r} \right) \tag{3}$$

where D_A is the apparent diffusion coefficient. This equation is an example of Fick's second law. The following equation describes the rate of change on concentration, $c_V(t)$ in the vessel:

$$V\frac{\partial c_V}{\partial t} = 2\pi RLD_E\frac{\partial c_c}{\partial r}\bigg|_R \tag{4}$$

where V is the annular volume, R is the core radius, L is the core length, and D_E is the effective diffusion coefficient. The last term is essentially Fick's first law.

The initial conditions are that the concentration is constant both in the vessel:

$$c_V(0) = c_{V0} \tag{5}$$

and in the core pore water

$$c_c(x,0) = c_{c0}\,. \tag{6}$$

Finally, there is the boundary condition of equal concentrations at the face of the rock core:

$$c_c(0,t) = c_V(t) \tag{7}$$

The solution of the above five equations is readily obtained as the Laplace transform with respect to time of the external solution concentration in the vessel:

$$c_V(t) = c_{c0} + (c_{V0} - c_{c0})\,\mathrm{f}\left(\frac{t}{t_c}, \sigma\right) \tag{8}$$

where the function *f* represents the pore water concentration relative to the difference between the initial concentrations and declines from f(0,σ)=1 to f(∞,σ)=1/(1+σ) in an infinitely long experiment This function has a Laplace transform:

$$\bar{\mathrm{f}}(p,\sigma) = \int_0^\infty e^{-p\tau}\,\mathrm{f}(\tau,\sigma)\,d\tau = \frac{1}{p\left[1 + \sigma\,\mathrm{B}\left(\sqrt{p}\right)\right]} \tag{9}$$

where

$$t_c = \frac{R^2}{4D_A} \tag{10}$$

$$\sigma = \frac{\pi R^2 L D_E / D_A}{V} \tag{11}$$

and

$$\mathrm{B}(x) = \frac{\mathrm{I}_1(2x)}{x\,\mathrm{I}_0(2x)} \tag{12}$$

where I_0 and I_1 are modified Bessel functions.

The dimensionless quantity σ can be interpreted as the ratio of water volumes in the core and vessel since the ratio D_E/D_A should equal the accessible porosity, ϕ, assuming negligible sorption. The time t_c represents the characteristic time for diffusion across the core.

The function B(x) was described by Barker (1985a, 1985b) in general terms. In particular, it is readily shown that the above solution can be translated to the solution for other 'core' geometries by: (a) replacing the function B(x) with an expression appropriate to the particular geometry; (b) defining t_c in more general terms as b^2/D_A where *b* is the ratio of core volume to surface area in contact with the vessel water, and (c) retaining σ as the ratio of vessel to pore water volumes.

For small times the following approximation is obtained

$$\mathrm{f}(\tau,\sigma) \approx 1 - 2\sigma\sqrt{\frac{\tau}{\pi}} = 1 - 2\sqrt{\frac{t}{\pi t_V}} \tag{13}$$

where

$$t_V = t_c / \sigma^2 \tag{14}$$

This new characteristic time, t_V, is of the order of magnitude of the time for diffusion into a matrix volume equal to that of the water in the vessel. This approximation provides a simple method of data analysis if required.

2. METHOD

Our apparatus was designed to use the Chalk plugs commonly used for determining porosity and permeability. In principle, our technique can be used to measure the diffusion coefficient of any solute, but here we describe its use only for chloride and bromide ions.

The apparatus (Fig.1) consists of a reaction vessel, maintained at 25.0 ± 0.1°C by a circulating water bath with the temperature controlled by a solid-state thermostat and heater. A chloride (Model Orion 9317, Thermo Electron Corporation) (or bromide, Model Orion 9635, Thermo Electron Corporation) ion selective electrode (ISE) and double junction reference electrode (Model Ref 451, Radiometer Analytical), both interfaced to a PC-based data logger, were suspended in the vessel. This enabled the continuous monitoring of chloride ion activities (or concentrations). The calomel reference electrode was separated from the reaction vessel by a pumped salt bridge containing 0.01M KNO_3 in order to avoid cross-contamination. An approximately 25 mm × 25 mm diameter cylindrical Chalk plug was suspended within the vessel and driven by a small electric motor. The Chalk plug was attached to the motor by specially-made plastic connectors attached with a non-reactive adhesive. This also formed a complete seal. Such seals were applied to both end surfaces. The relatively small changes in concentration involved mean that the apparatus is best suited to monitoring diffusion out of a core rather than diffusion into it.

As most UK groundwaters are relatively dilute electrolyte solutions – conductivities are typically in the range 500-1500 µS/cm (Edmunds et al., 1989) indicating ionic strengths of approximately 10-20 mmol/L) – variations in ionic strength were assumed to have no significant effect on the apparent diffusion coefficient.

2.1 Core Saturation

All samples were taken from a single borehole drilled in the south of England into the Chalk aquifer. Basic aquifer properties of the tested samples are given in Table 1.

Chalk-saturated water and calibration standards were prepared and stored in a room maintained at 23°. The use of Chalk-saturated water minimised any subsequent dissolution of the Chalk matrix. The difference in temperature between this temperature and the temperature of the experiment (25.0°C) had a minimal impact on the estimated diffusion coefficients. The equilibrated solution was filtered through a 0.45 µm filter to exclude any large particles.

Small-diameter cores were cut and then dried in an oven at 60°C for approximately 1 week. The core was placed in a desiccator and evacuated for 2 days. The sample was then saturated (as the vacuum was released) with a 200 mg/L chloride solution and allowed to equilibrate for 5-6 days before being finally weighed to ensure saturation.

2.2 Electrode Calibration

KCl calibration solutions were prepared in decade intervals ranging from 10^{-1}-10^{-4} molar using Chalk-saturated water. This 'matrix matching' ensured that readings from the chloride ISE could be converted directly to concentrations. Calibration solutions were placed in a 50 ml reaction vessel maintained at 25.0°C. Each solution was placed in the reaction vessel in turn, mV responses being noted after the electrode had stabilized (<0.02 mV/min). Further details of the data logging equipment are given in Kinniburgh et al. (1995).

2.3 Experimental Method

After calibration of the electrode, the reaction vessel was filled with sufficient Chalk-saturated distilled water to just cover the electrodes when the Chalk plug was placed in the vessel. This normally required ~26 ml although this varied depending on the precise size of the core. The greater the ratio of matrix pore volume to exterior solution volume, the greater and the more rapid the monitored increase in concentration. The Chalk plug was removed from the chloride solution in which it had been equilibrating and excess water carefully removed with a dry tissue. The Chalk was then suspended in a reservoir by a rod to a stirrer and allowed to rotate slowly. The electrode response was then monitored. The data logger was configured to take a reading every 30 seconds for the first hour and every minute thereafter. The experiment was deemed to have ended when the measured concentration was within 70% of the theoretical maximum concentration. This generally took approximately 20 hours and never exceeded 30 hours.

At the end of the experiment, the calibration solutions were again measured in order to determine the amount (if any) of electrode drift that had occurred during the experiment. The short experiment times generally resulted in minimal electrode drift, generally <0.5mV between pairs of calibration solutions at the experiment start and end and with no systematic increase or decrease in response for any given experiment . Experiments were carried out on duplicate cores, that is, two cores taken adjacently from the same chalk block in an attempt to minimise the effects of any natural heterogeneity.

The use of ISE's to monitor solute concentrations in the exterior solution has the advantage that no sample needs to be removed from the reaction vessel for analysis. This simplifies the subsequent data analysis.

2.4 Calculation of D_A

The apparent diffusion coefficient (D_A) was estimated by fitting the measured chloride data to Eqn (8). The optimization was carried out using a derivative-free nonlinear least squares algorithm based on Powell's VA05 algorithm from the HSL Archive (HSL Archive, 2005). This uses a hybrid approach based on a combination of Newton's method, steepest descent and the Marquadt-Levenberg algorithm. Input parameters for the model were the concentration of the saturating solution, the core dimensions in terms of radius and length and the core porosity. Only D_A was adjusted for best fit. Optimisation was most effective when based on fitting log D_A rather than D_A directly.

Equation (13) can be used as an alternative method of analysis to check the results obtained with the least-squares analysis. A plot of concentration against the square root of time has a slope given by

$$s = -\frac{2}{\sqrt{\pi t_V}} \tag{15}$$

Note that once t_V has been estimated, the apparent diffusion coefficient can be obtained from:

$$D_A = \frac{1}{t_V}\left(\frac{V}{2\pi RL\, D_E / D_A}\right)^2 = -\left(\frac{\pi s V}{4RL\phi}\right)^2 \tag{16}$$

uation (11) can be used

3. RESULTS

Fig. 2 shows a typical set of results with the fitted curve shown based on Eqn (4) and the estimated D_A. The line marked at 43.9 mg/L is the theoretical maximum concentration that can be achieved when both solutions (i.e. the matrix pore water and the external solution in the annulus) are fully mixed. The fitted curve asymptotically approaches this value. All model fits gave an R^2 of greater than 0.99. Such good fits give confidence that normal Fickian diffusion is occurring.

The results (Table 2) are similar to those found by Hill (1984), although our data have been obtained in a much shorter timescale compared with Hill (1 day compared with 40 days). Hill (1984) found a clear linear relationship between log ϕ and D_A and a similar relationship is observed here even if the samples with the highest D_A fall off the linear trend. A much better positive correlation is observed between gas permeability and D_A. In this case the whole data set can be well described by by a second order polynomial with an R^2 greater than 0.99.

A similar experiment to that described above was also carried out on sample 6 using a bromide ISE. D_A for bromide of 3.5 × 10-10 m^2/s was found compared with an average of 3.4×10^{-10} m^2/s for chloride. The literature tracer diffusion coefficient for chloride is 0.199×10^{-10} m^2/s and that for bromide 0.202×10^{-10} m^2/s (Robinson and Stokes, 1968) and so the lack of a significant difference in our estimated D_A's is not surprising. The difference in molecular size between the chloride and bromide ions (181 pm compared with 196 pm) therefore has no observable effect on D_A.

Residual errors are very small although in the example shown (Fig. 2) the residuals clearly show a systematic trend. This either indicates a shortcoming in the model or a systematic error in one of the experimental or model parameters. We found that other experimental runs did not always show this trend. Four possible sources of error are: (i) random and systematic errors in the measurement of chloride by an ISE; (ii) the assumed porosity; (iii) the assumed initial chloride concentration (based on a gravimetric method of preparation), and (iv) the measured dimensions of the Chalk plug.

Model simulations show that a 2% absolute error in porosity measurement (i.e. 49% porosity against 50%) can alter the calculated diffusion coefficient by approximately 5%. A 2% error in measuring the core radius (for cores of this size ± 0.2mm) also leads to a 5% change in the calculated D_A. A 1% error in measuring the initial concentration (i.e. 198 mg/L chloride as opposed to 200 mg/L) leads to a 3% change in the calculated D_A. Cumulatively these errors are less than the error between duplicates (Table 2), which are still in themselves, reasonable and fit for purpose.

The random error is minimised in the procedure by the large number of observations while the systematic error (drift) is minimised by the short duration of the experiments. The 70% of maximum concentration threshold chosen provides a good compromise which ensures that sufficient data are collected while keeping the overall experimental time, and the electrode drift, to a minimum.

4. CONCLUSIONS

A method has been developed that enables the rapid determination of the apparent diffusion coefficient of a solute, D_A, in Chalk rock. D_A ranged from $3.1–8.7 \times 10^{-10}$ m^2/s in six Chalk samples which varied in porosity from 32-48% and whose gas permeability ranged from $0.3\text{-}8.2 \times 10^{-9}$ m^2.

The approach has been shown to work using both chloride and bromide ISEs, and in its current form could be used for determining diffusion coefficients for any consolidated porous medium and for any solute whose concentration can be accurately monitored *in situ*. The method might also be simplified by removing the ISE and taking 3-4 small (0.5 mL) sub-samples of water from the annulus surrounding the core at key time intervals (e.g. 4, 6, 8 and 16 hours). The outward diffusion of solute would not be so well characterised but a good estimate of the apparent diffusion coefficient could still be obtained with a relatively small effort. This would enable D_A to be determined for almost any ion or indeed a cocktail of possibly competing ions. Such an approach lends itself to 'mass production'.

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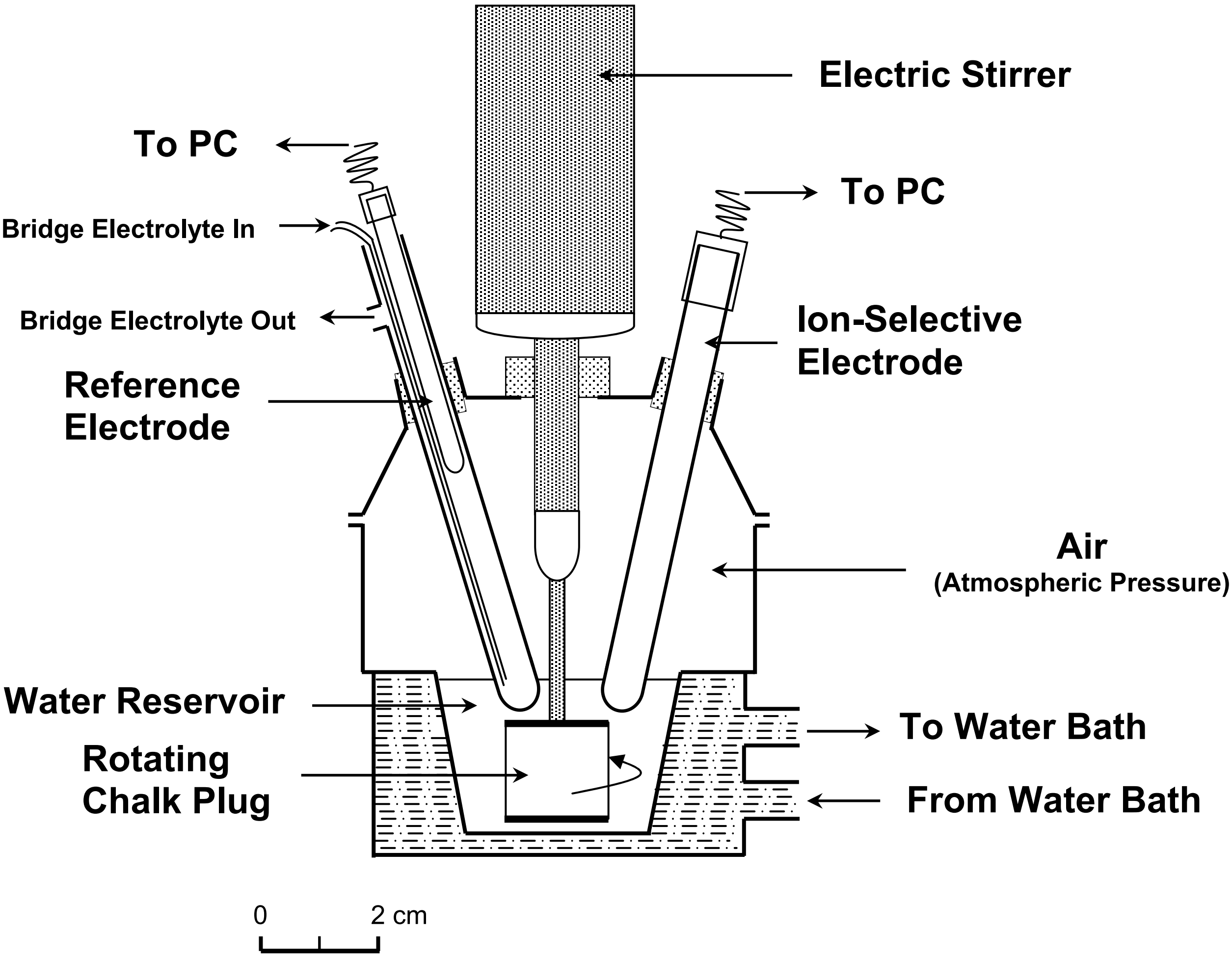

Figure 1. Schematic representation of analytical equipment used to determine diffusion of chloride (or bromide) from consolidated porous plugs.