3.3.2.8.e Comments

The use of simultaneous measurements of temperature and liquid water content in frozen soil to estimate the dry ($\psi < -100$ J kg^{-1}) portion of the moisture characteristic has been demonstrated, and there may soon be commercially available equipment to simplify its application. It offers some potentially powerful advantages for either laboratory determination on small samples or in situ field measurements. However, high accuracy is required in both the temperature and the liquid water content measurements. The latter is still not a trivial measurement and needs additional research. Furthermore, theoretical uncertainty remains regarding the temperature (or water potential) range over which the fraction of capillary water can be considered an insignificant component of the total soil water content.

3.3.2.9 Miscellaneous Methods

JOHN R. NIMMO AND KARI A. WINFIELD, *U.S. Geological Survey,
Menlo Park, California*

For some purposes the most widely used methods of measuring water retention may be unsuitable or undesirable. For applications under arid conditions, where vapor and liquid flow are both important, a method that covers extremely dry conditions is required. When retention properties of porous rocks are of interest, alternative methods can better accommodate their particular features. Yet other applications, for example, where macropore flow is important, may require a more detailed representation of the retention curve than the common step-equilibration methods can provide. This section briefly describes alternative methods that may serve in cases like these.

3.3.2.9.a Controlled Vapor Pressure—Description and Principles

In this method a small soil sample is placed in a closed chamber that also contains an open vessel with a free salt or acid solution. At equilibrium the soil water attains the same total potential as the water vapor in the free phase, which in turn is in equilibrium with the free solution. The total soil water potential is the sum of the matric and the osmotic potential. For a free solution surface at 15°C, Koorevaar et al. (1983) presented the following form of the Kelvin equation:

$$\ln(p/p_o) = 7.5 \times 10^{-9}(-\Pi) \qquad [3.3.2–14]$$

where p is the water vapor pressure (Pa), p_o is the saturated water vapor pressure (Pa) (p/p_o is the relative humidity), and $\Pi = RTc$ is the osmotic pressure (Pa) of the solution, with R being the molar gas constant, T the temperature (K), and c the ionic concentration. Table 3.2.3–1 lists osmotic pressures associated with solutions of practical use. Equation [3.3.2–14] allows the relative humidity to be calculated for known osmotic pressures of the free solution present in the closed chamber. For equal potentials of the soil water and the water vapor, Eq. [3.3.2–14] becomes:

$$\ln(p/p_o) = 7.5 \times 10^{-5}(h_m - h_o) \qquad [3.3.2–15]$$

where h_m (m) and h_o (m) are the matric head and the osmotic head of the soil solution, respectively. Assuming $h_o = 0$, the matric head of the soil water can be calculated. Different h_m values can be obtained by controlling the concentrations of the free solution. Repeating the equilibration and determining the water content at the different h_m values associated with various solutions yields a number of points on the water retention curve. The advantage of the method is that it gives retention data in the very dry range. A disadvantage of this method is that it only applies when h_o of the soil water is negligible or when it is at least approximately known. Probably the main impediment to its widespread use is that the method is slow, sometimes requiring 2 to 3 mo at a single step. It was more commonly used in earlier eras, for example, by Thomas (1928) and Robins (1952).

3.3.2.9.b Measured Vapor Pressure—Description and Principles

For determination of dry-range water retention, a more recently favored type of vapor pressure method adjusts the water state without precisely controlling it, for example, by a transient evaporation technique. The water is not in equilibrium with a standard solution, so both θ and h_m must be measured. Gee et al. (1992) used this method with a chilled-mirror humidity sensor to measure h_m. Alternatively, a psychrometer (Section 3.2.3) or other methods described in Section 3.2 could be used. Again, Eq. [3.3.2–15] applies, though only for the purpose of measuring h_m after the potential equilibrates throughout the sample at each step.

Several techniques are possible for adjusting the water state between steps. Suction may be applied through a membrane, but this is usually impractical for dry-range water retention. Evaporation in open air is feasible; heaters or fans can accelerate the process. Ideally the arrangement of heaters and fans should be balanced so that applied heat compensates for evaporative cooling to better maintain isothermal conditions. Osmotic extraction is possible but experimentally complex. For some applications, centrifugation may be practical for the water extraction (Section 3.6.1.1.b). For measuring water content, sample weighing is the preferred method in most cases.

After water extraction at each step, the sample must be sealed up for a time to establish equilibrium conditions. The equilibration required is entirely within the sample, not between the sample and an outside solution. As a result this method is faster than those based on vapor pressure control.

Small samples, on the order of a few grams, are generally required because some types of instrumentation limit sample size. Even when this is not the case, small samples will equilibrate faster, and the unavoidable use of whole-sample averages for θ and h_m is more appropriate for smaller samples. If many small replicate samples are available, there is more experimental flexibility for such options as simultaneous replicate measurements or simultaneous determination of several points on the retention curve. Large samples must be divided carefully to assure adequate representation of the whole (Section 1.4).

3.3.2.9.c Controlled Osmotic Pressure—Description and Principles

An alternative technique uses osmotic equilibration with an osmotic membrane separating a solution, usually polyethylene glycol in water, from direct con-

tact with the soil (Zur, 1966; Pritchard, 1969; Waldron & Manbeian, 1970). After the soil water equilibrates with the osmotic solution, and assuming the matric potential of the osmotic solution equals zero, it follows that

$$h_{\text{m-soil}} + h_{\text{o-soil}} = h_{\text{o-solution}} \qquad [3.3.2\text{--}16]$$

Therefore, as with the controlled vapor pressure method, if the osmotic head of the soil water ($h_{\text{o-soil}}$) is known, the known osmotic head of the free solution ($h_{\text{o-solution}}$) yields a value for the matric head in the soil ($h_{\text{m-soil}}$). Weighing the sample provides data to determine the water content, and repetition with different solutions gives a number of points on the retention curve.

Membranes for this method can be made of commercially available dialysis materials, typically in the form of tubing. Because polyethylene glycol molecules are large, this sort of membrane can permit most of the molecules normally present in soil solution to pass through, so that the equilibration is actually with the matric head rather than the total head of the soil water. In effect, the $h_{\text{o-soil}}$ term of Eq. [3.3.2–16] is then zero, which eliminates the problem of an unknown osmotic head of the soil solution, as may arise with the vapor-equilibration method.

This method works at matric head values closer to zero than vapor-based methods. It is typically employed for matric head values of less than −100 m; the range is not as extreme as that of vapor equilibration, but drier than is usually practical with most other methods.

Osmotic extraction is likely to be prohibitively slow for all but the smallest samples (a few grams or less). Another limiting factor is that the dialysis membranes to be used for this purpose are fragile and vulnerable to microbiological degradation. There is little published information on this method since about 1970. Since then, however, there have been substantial technological advances in osmotic membranes for dialysis, as well as for desalinization, tensiometry, and other applications. These advanced membranes might be advantageous for measuring water retention.

3.3.2.9.d Comments on Vapor-and Osmotic-Based Methods

For the dry range of a retention curve there are not many alternatives to these types of methods. Because the measured vapor pressure method does not require the sample to equilibrate with an imposed standard, this method is faster and hence more widely used than the controlled vapor pressure method. Instead, the measured vapor pressure method has the more easily satisfied requirement that the sample come to a state where its average θ and h_{m}, as measured by the chosen techniques, both represent a single water state in the sample. The method gains speed at the expense of foreknowledge of the precise h_{m} values at which retention will be measured. The osmotic pressure method is also practical in its time requirements. It avoids the problem of unknown soil osmotic pressure, and is generally applicable over a somewhat wetter range than the vapor methods.

Typically, small samples are used in these methods in order to minimize equilibration times. Small samples are particularly sensitive to perturbations of θ or h_{m} during weighing or other operations, so caution in handling is necessary. Prepara-

tion procedures normally destroy the soil structure of small samples. The resulting alteration of properties, however, is likely to be less problematic for the dry portions of the curve, where adsorbed water that coats particle surfaces in thin films is more important than water in filled pores. Vapor and osmotic phenomena are particularly sensitive to temperature variations. Some degree of protection from air temperature fluctuations, and also from fluctuations in radiant heating from ordinary light (Robins, 1952), is usually necessary in the application of these methods.

3.3.2.9.e Transient Liquid-Phase Methods

Most retention methods proceed in discrete equilibration steps, but not all applications require this. Transient methods, sometimes called *dynamic* or *unsteady* methods, change the water state of the soil in a controlled and continuous way, usually with applied suction. The soil water is not in equilibrium with an established pressure, so these methods require simultaneous measurement of both h_m and θ during the changing conditions. The pairing of these measurements represents a transient retention curve. This curve may differ from curves measured by equilibrium and steady-flow techniques, but it is not well established how great the transient vs. equilibrium retention differences are (Davidson et al., 1966; Topp et al., 1967; Rogers & Klute, 1971). Transient methods are relatively fast because there is no waiting for equilibration, and the sample can be taken through wetting and drying cycles as fast as its properties and the time resolution of the instrumentation will allow.

Most of these methods resemble the experiments of Topp and Miller (1966) and Bomba (1968), who used transient methods to measure both retention and the unsaturated hydraulic conductivity of glass bead samples. Perroux et al. (1982) developed a similar technique for use with natural soils, as did Nimmo and Miller (1986) with an apparatus later improved by Salehzadeh (1990). Section 3.6.2 describes additional inverse methods that are essentially transient in nature.

The design and implementation of transient or dynamic methods is not standardized, so one should consult the original references. The required elements are (i) a means of controlling the applied matric head, ideally according to a preset program; (ii) a point-like h_m measurement, usually made with tensiometers; and (iii) a point-like θ measurement, made, for example, using gamma-ray attenuation (Section 7.2.2.1). The pressure control frequently involves an air tank that is slowly filled or emptied to change its pressure, and that is linked in some way to the soil matric head. Recent innovations include computer-controlled valves to make an easily programmed pressure controller (Zurmühl, 1998). The h_m and θ measurements must be made simultaneously for the same small portion of the sample, so fast-response, high-resolution instruments are essential. For h_m, small tensiometers equipped with solid-state pressure transducers are suitable. For θ, gamma-ray attenuation is generally the best choice. Certain types of time domain reflectometry (TDR) apparatus, such as that of Kelly et al. (1995) or Nissen et al. (1998), may also be suitable.

Once operational, transient methods are a fast way to obtain retention curves, sometimes the fastest practical means. They easily produce large numbers of

closely spaced measured points, giving a high level of resolution that may be useful in assessing the effects of soil structure. They lend themselves to concurrent Darcian unsaturated conductivity (K) measurements (Topp & Miller, 1966) and to the measurement of soil water hysteresis. It is possible to determine both drying and wetting curves, main and scanning, through appropriate implementation of the pressure-control program. For use with fine-textured media or for low θ conditions, transient methods are most suitable for samples in the form of thin slabs. The heterogeneities of undisturbed core samples may be tolerable if the geometry of the regions of h_m and θ measurement is well defined. A significant disadvantage is the need for specialized equipment.

3.3.2.10 Computational Corrections

J. H. DANE, *Auburn University, Auburn, Alabama*

JAN W. HOPMANS, *University of California, Davis, California*

Accurate determination of the matric head–volumetric water content, $h_m(\theta)$, relation is important for modeling soil water movement. Richards' equation, which describes the movement of water in porous media, is solved assuming knowledge of the unsaturated hydraulic properties determined at physical points, also referred to as *macroscopic volume elements*. Because a soil sample has a finite height, the data obtained with some of the methods described above are not applicable at a physical point; that is, the data pertain to an average volumetric water content, $\overline{\theta}$, for the sample as a whole, and the corresponding matric head is defined by

$$\overline{h}_m = (\overline{P}_w - \overline{P}_a)/(\rho_w g) \qquad\qquad [3.3.2\text{--}17]$$
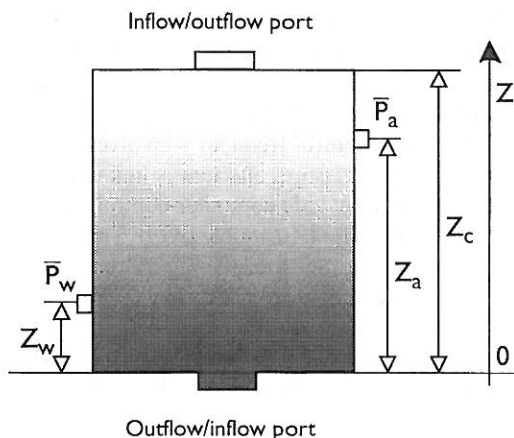

Fig. 3.3.2–10. Simplified pressure cell diagram as used in the correction procedure to obtain physical point retention data from averaged pressure cell data.