3.2.3 Thermocouple Psychrometry

BRIAN J. ANDRASKI, *U.S. Geological Survey, Carson City, Nevada*

BRIDGET R. SCANLON, *University of Texas, Austin, Texas*

3.2.3.1 Principles

Thermocouple psychrometry is a technique that infers the water potential of the liquid phase of a sample from measurements within the vapor phase that is in equilibrium with the sample. The theoretical relation between water potential of the liquid phase and relative humidity of the vapor phase is given by the Kelvin equation

$$\psi = \text{energy/volume} = (RT/V_w)\ \ln(p/p_o) \qquad [3.2.3\text{–}1]$$

where ψ is water potential (sum of matric and osmotic potential, MPa), R is the universal gas constant (8.314×10^{-6} MJ mol^{-1} K^{-1}), T is temperature (K), V_w is molar volume of water (1.8×10^{-5} m^3 mol^{-1}), and p/p_o is relative humidity expressed as a fraction where p is actual vapor pressure of air in equilibrium with the liquid phase (MPa) and p_o is saturation vapor pressure (MPa) at T.

Difficulties with the technique arise from two main sources. The first stems from the fact that relative humidity in the soil gas phase changes only a small amount within the typical range of interest. For example, at 25°C a water potential of −1.5 MPa corresponds with a relative humidity of about 0.99, and a water potential of −8 MPa corresponds with a relative humidity of about 0.94. The −1.5 MPa value is often associated with the permanent wilting point of agronomic plants, and the −8 MPa value generally corresponds with the lower limit of water extraction for many desert plants. Thus, most measurements of interest to studies of soil–plant–water relations and unsaturated-zone hydrology lie in the narrow relative humidity range from 0.94 to 1.0. The second main source of difficulty arises from the fact that temperature differences in the sensor–sample system may lead to large errors in the determination of water potential. For example, error analysis by Campbell (1979) indicated that at ambient temperatures ≤30°C, a temperature difference of 1°C between the sensor and the sample can introduce an error of >10 MPa. Accordingly, proper sensor design and measurement procedures are critical to ensuring the reliability of the technique.

Thermocouple psychrometry is often used as a collective term for both psychrometric (wet-bulb temperature depression) and hygrometric (dew-point temperature depression) measurements for determining water potential. The psychrometric technique is most widely used. Both techniques are based on measuring the temperature of a wet thermocouple junction that is located in an air cavity adjacent to or nearly surrounded by the sample to be measured. The principle that allows thermocouples to be used for measurements of temperature is the Seebeck effect—a complete electrical circuit formed by two dissimilar metals forms a thermocouple; if the measuring and reference junctions in that circuit are at different temperatures, a current will flow, resulting in a voltage difference that is dependent on the temperature difference between the junctions (details on thermocouple thermometry are given in Section 5.1.1). In thermocouple psychrometry, the temperature depression of the sensing (wet) junction that is measured relative to the reference (dry) junction varies as a function of the relative humidity of air surrounding the sensing junction. Although theoretically water potential can be calculated directly from such measurements, in practice thermocouple psychrometers are calibrated empirically using solutions of known water potential.

Two types of sensors have evolved for determining soil water potential by thermocouple psychrometry: (i) the wet-loop type described by Richards and Ogata (1958) and (ii) the Peltier type first described by Spanner (1951). The wet-loop sensor is only used with the psychrometric measurement technique, whereas the Peltier sensor can be used with both the psychrometric and the hygrometric measurement techniques. The primary difference between these two sensors is the manner by which water is applied to the sensing junction. The wet-loop sensor is wetted by mechanically placing a drop of water on a small silver ring or ceramic bead that is at the sensing junction. The Peltier sensor, which is more widely used, utilizes a thermoelectric principle, the Peltier effect, to apply water to the sensing junction. By adding a small power source to the Seebeck thermocouple circuit, a Peltier cooling current of sufficient magnitude and duration is applied to cool the sensing junction below the dew-point temperature, resulting in condensation of water from the air onto that junction. During Peltier cooling of the sensing junction, an equal amount of heat energy is absorbed at the reference junctions (Joule heating) and must be dissipated at these more massive junctions. A limitation of the Peltier effect is the degree of cooling that can be achieved before Joule heating begins to predominate (Spanner, 1951). The effects of Joule heating vary not only with the magnitude and duration of the cooling current, but also with the water potential itself. Such heating appears to be most problematic at higher water potentials (Millar, 1971a; Slack & Riggle, 1980).

The upper and lower limits of thermocouple psychrometry measurements are strongly dependent on sensor design and measurement protocol. For example, water adsorption on chamber walls or heating of reference junctions during Peltier cooling can result in inaccurate readings (Wiebe et al., 1971). Depending on such factors and the resolution of the voltmeter used, the upper measurement limit is about −0.03 to −0.2 MPa. The lower limit of water potential measurements with wet-loop sensors is about −300 MPa. In contrast to Peltier sensors, the larger drop of water mechanically placed on the sensing junction of a wet-loop sensor allows for more stable readings for a longer time following water application. The lower limit of routine measurements made with Peltier sensors is about −8 MPa. At water potentials less than this value, the dew-point temperature is likely to be more than 0.6°C below the ambient temperature and the efficiency of the Peltier effect using conventional thermocouples and cooling currents is no longer great enough to condense sufficient water on the sensing junction to achieve stable readings.

Following water application, the psychrometric technique measures the wet-bulb temperature depression of the sensing junction as water on that junction evaporates into the air. The difference in temperature between the sensing and the reference junctions upsets the null output in the Seebeck circuit and generates a microvolt output that is registered by the voltmeter. The actual temperature the sensing junction attains depends on factors that influence heat flow to and vapor flow from it. Rawlins (1966) and Peck (1968) developed the basic heat and mass flow theory to explain the temperature (Klute & Richards, 1962) and pressure dependence (Richards et al., 1964) of thermocouple psychrometers. For a given wet-bulb temperature depression, heat flow to the sensing junction is controlled by the dimensions of the psychrometer chamber, the sensing junction, and the thermocouple wires, as well as by the thermal conductivity of the thermocouple wires and the air separating the junction from the chamber wall. If the radius of the chamber does not exceed a few centimeters, heat and vapor flow by convection are negligible compared with conduction for the temperature depressions that normally occur in soil psychrometers. Cooling at the sensing junction is proportional to the product of the evaporation rate and the latent heat of vaporization. Although the evaporation rate is primarily a function of the relative humidity of the chamber, it also varies with the diffusivity of water in air, which decreases with atmospheric pressure. The latent heat of vaporization, thermal conductivity, and water vapor diffusivity of air all increase with increasing temperature. Pressure and temperature effects on the psychrometric measurement may be summarized using the conventional psychrometer equation written in terms of relative humidity (Campbell, 1979)

$$p/p_o = 1 - [(s + \gamma^*)/p_o]\Delta T \qquad [3.2.3\text{–}2]$$

where s is the slope of the saturation vapor-pressure curve, γ^* is apparent psychrometer constant (product of the thermodynamic psychrometer constant and the ratio of vapor-transfer to heat-transfer resistance), and ΔT is wet-bulb temperature depression. The term $[(s + \gamma^*)/p_o]$ determines the psychrometer sensitivity. Temperature dependence comes mainly from the temperature dependence of s and p_o, and pressure dependence comes mainly from the effect of pressure on γ^*; if pressure doubles, γ^* doubles (Rawlins & Campbell, 1986).

The hygrometric measurement technique was first introduced by Neumann and Thurtell (1972) and modified by Campbell et al. (1973). The basic principle is that, if held at the dew-point temperature, a wet thermocouple junction will neither lose water through evaporation nor gain water through condensation. Vapor pressure is regulated by controlling the applied Peltier cooling current to maintain the temperature of the water on the sensing junction at the dew point. Thus, heat flow to the sensing junction from the surrounding air is exactly offset by adjustments in the applied cooling current, so no water evaporates or condenses and measurements can be made without disturbing the vapor equilibrium in the chamber. This eliminates most of the temperature-dependent parameters that influence the psychrometric measurement, and because no water-vapor diffusion occurs, the pressure dependence of the measurement is also eliminated. The fact that dew-point temperature depression is greater than wet-bulb temperature depression increases the sensitivity of the hygrometric technique over that of the psychrometric technique. Theoretical considerations show hygrometric sensitivity to be 7.5 μV MPa^{-1} at 25°C; this value is about 1.7 times greater than psychrometric sensitivity (Campbell et al., 1973). In principle, the hygrometric technique offers advantages over the psychrometric technique. In practice, however, the same errors that limit the accuracy of the psychrometric technique also limit the accuracy of the hygrometric technique (G.S. Campbell, personal communication, 1999).

The microvolt output from a thermocouple psychrometer is very sensitive to fluctuations of environmental temperature. Early work was done under laboratory conditions where temperature was controlled to within ± 0.001°C to allow water potential to be inferred within an accuracy of 0.01 MPa. Work by Spanner (1951), Rawlins (1966), Dalton and Rawlins (1968), and Peck (1968, 1969) provided the theoretical foundation to improve the accuracy and reliability of thermocouple psychrometers. In an analysis aimed at developing techniques to extend thermocouple psychrometry to the field, Rawlins and Dalton (1967) identified the primary ways in which temperature fluctuations can affect measurement of water potential: (i) through temperature dependence of the water potential–relative humidity relation, (ii) through temperature dependence of the sensor microvolt output–relative humidity relation, and (iii) through temperature changes and gradients that can cause relative humidity and temperature differences in the sensor–soil system. The temperature dependence of water potential can be accounted for by recording ambient temperature within the sample chamber. The temperature dependence of the microvolt output can be adequately controlled by adopting suitable calibration procedures. The errors caused by temperature gradients in the sensor–soil system are the most difficult to control and are equally problematic with psychrometric and hygrometric measurement techniques. However, Rawlins and Dalton (1967) constructed and tested an in situ Peltier sensor that was found to be relatively insensitive to soil temperature changes as great as 4°C d^{-1}. Their work demonstrated that, with a suitable sensor design, it was possible to reduce the need for exact temperature control and it opened the door for application of thermocouple psychrometry to measurements of water potential in the field. Detailed analyses of the temperature-induced errors that can affect in situ psychrometric and hygrometric measurements are reported by Rawlins and Dalton (1967), Campbell et al. (1973), Brown and Bartos (1982), and Savage et al. (1983).

3.2.3.2 Equipment

Instruments for determination of water potential by thermocouple psychrometry have been developed for use in the laboratory under controlled conditions and for in situ use in glasshouse and field experiments. The following discussion summarizes results of experimental work that has contributed to the design of various instruments and provides examples of some typical equipment. In addition to the individual papers cited below, further details and discussion of the design and construction of sensors and the electronics used in thermocouple psychrometry may be found in Wiebe et al. (1971), Brown and van Haveren (1972), Savage and Cass (1984), Rawlins and Campbell (1986), and Boyer (1995). Commercial sources of equipment are given in Section 3.2.3.5.

3.2.3.2.a Sample-Chamber Sensors

Sample-chamber sensors are typically used for laboratory measurements of soil water potential. Various chamber-wall materials and chamber–thermocouple–sample geometries have been used since the original chambers of Spanner (1951) and Richards and Ogata (1958). Experiments by Millar (1971b) showed that the time required for samples to reach equilibrium with chamber air varied with both of these factors. Chambers made of brass and stainless steel adsorbed less water and equilibrated more rapidly than chambers made of materials such as polyethylene and Teflon (DuPont, Wilmington, DE)[1]. Chamber geometries that decreased the exposed-wall surface area relative to the sample-surface area also reduced the equilibration time.

Millar (1971b) constructed a stainless-steel sample chamber for measuring water potential within a soil core. A Peltier sensor was placed within a central hole bored into the soil core, the chamber was sealed, and the entire sample chamber was immersed in a controlled water bath so that temperature fluctuations were <0.001°C. Stainless steel was selected for use in the chamber because it is much more resistant than brass to oxidation or corrosion and is easy to clean. The geometry of this apparatus approaches that of an ideal thermocouple psychrometer by nearly surrounding the sensing junction with the soil sample.

Laboratory measurements of soil water potential using sample chambers are more routinely made using small, disturbed samples. A sample chamber commercially available from Wescor, Inc. is shown in Fig. 3.2.3–1. This chamber allows single samples contained in metal sample holders to be inserted into position for measurement without disassembling the apparatus. When the sample is in place, the metal thermocouple mount is pressed against the sample holder and the measurement chamber is sealed with an O-ring by turning the cap screw. This unit does not permit the sensing junction to protrude into a cavity within the soil, but rather the sensing junction is placed just above the sample. The metal-to-metal contact and thermal shielding provided by the aluminum housing give adequate thermal stability for measurements to be made in the laboratory without a controlled-temperature water bath. Additional insulation is required if ambient temperature changes are rapid. This sample chamber uses a Peltier sensor that can be used in either the psychrometric or hygrometric mode depending on the type of measuring equipment used. The measurement range is from about −0.05 to −8 MPa nominally, but with capability to −300 MPa using special psychrometric techniques (Wiebe, 1981; Wescor, Inc. 1998).

A sample changer that is capable of measuring water potential successively on up to 10 samples and is commercially available from Decagon Devices, Inc. is shown in Fig. 3.2.3–2. This unit is a modification of that originally described by Campbell et al. (1966). Samples contained in stainless-steel cups are rotated to a single thermocouple and a lever–piston arrangement raises the cup up against the metal thermocouple mount and seals the chamber for each measurement. When measuring water potential of soils, samples contained within the cups are packed with a device that produces a conical depression in the sample for the thermocou-

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[1] Use of trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey or the University of Texas at Austin.

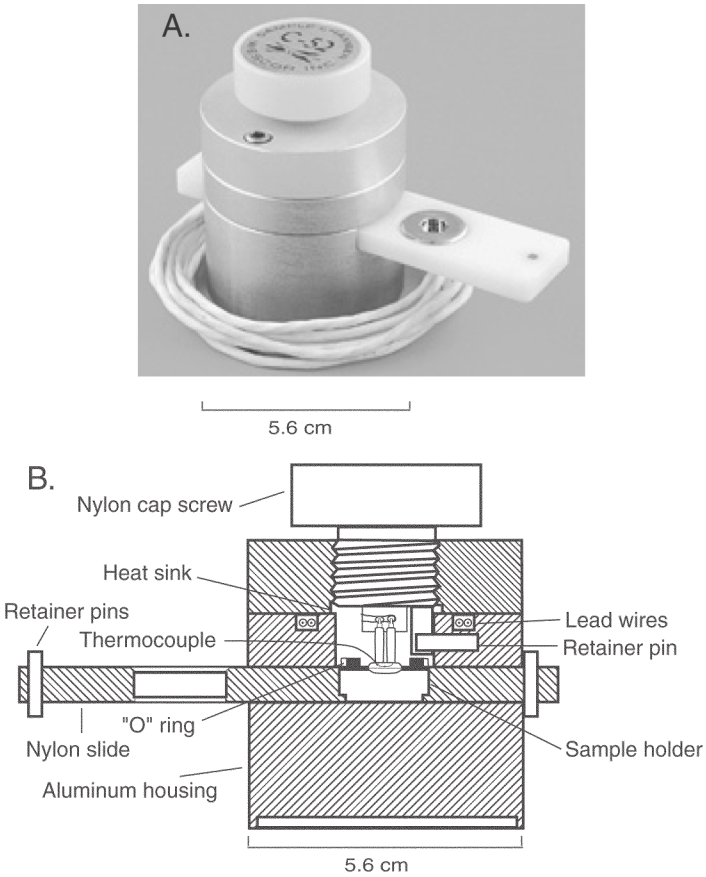

Fig. 3.2.3–1. (A) Photograph and (B) schematic of sample chamber (Model C-52, Wescor, Inc., Logan, UT) for measurement of water potential on single samples held in a shallow metal sample holder. Measurements can be made using either the psychrometric or hygrometric technique. (Schematic modified from Wescor, Inc., 1981).

ple and increases the sample surface area relative to that of a flat surface. The sample changer permits rapid measurements and direct comparison of samples with calibration standards. The sample changer can be fitted with either a Peltier sensor or a modified wet-loop sensor on which the silver loop (Richards & Ogata, 1958) has been replaced by a small ceramic bead. The bead is wetted by dipping it into water contained in one of the sample cups. A thermistor measures ambient temperature of the unit. The massive aluminum housing provides sufficient thermal stability for most applications, although use of a housing blanket or other insulation is beneficial if room temperature changes are rapid or extremely precise measurements are needed. The upper limit of the measurement range is –0.03 MPa (Decagon Devices, Inc., 1998) and the lower limit may be extended to about –300 MPa when the unit is fitted with the wet-loop sensor (Rawlins & Campbell, 1986).

Fig. 3.2.3–2. Photograph of sample changer (Tru-Psi Sensor, Decagon Devices, Inc., Pullman, WA) capable of measuring water potential successively on up to 10 samples that are held in metal cups. Measurements can be made using either a Peltier-type sensor or a modified wet-loop type sensor. A housing blanket can be placed over the unit for additional thermal stability if room temperature changes are rapid or extremely precise measurements are needed.

3.2.3.2.b In Situ Sensors

In situ sensors are used for laboratory, glasshouse, and field measurements of soil water potential. The basic components of these instruments consist of lead wires that pass into the body of a sensor and, in turn, attach to several thermocouple junctions; the sensing junction is enclosed within a protective housing that maintains an air cavity in the soil and permits heat and vapor transfer between the sensor cavity and the soil. Intensive experimental research on the effect of sensor design on temperature-gradient errors was done by Wiebe et al. (1977), Campbell (1979), and Wiebe and Brown (1979).

Most in situ sensors now used have the same basic circuitry and use Peltier cooling to remotely wet the sensing junction. Examples of typical three-lead-wire sensors developed for in situ use are illustrated in Fig. 3.2.3–3. The sensing junction is formed by welding chromel and constantan wires. A short distance back from the sensing junction these wires may be attached to lead wires (Fig. 3.2.3–3A) or gold-plated pins (Fig. 3.2.3–3B) of larger diameter to form two reference junctions. The ambient temperature of the sensor is determined using a copper–constantan junction formed by one of the copper lead wires (designated as electrically nega-

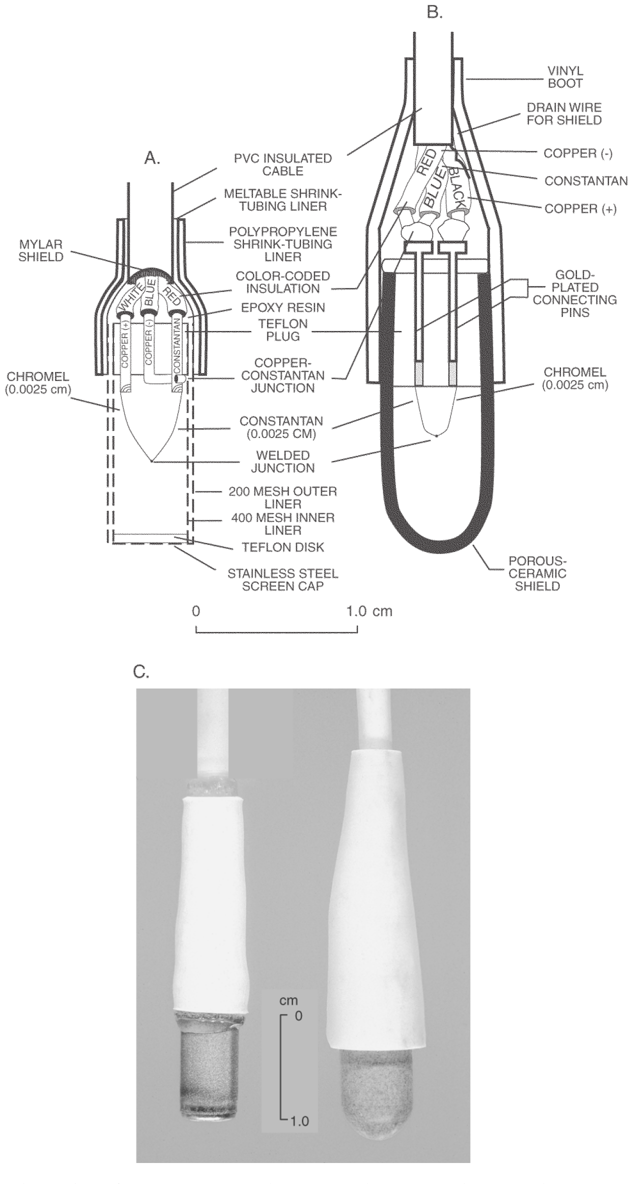

Fig. 3.2.3–3. Schematics of (A) screen-caged sensor and (B) ceramic-cupped sensor. (C) Photograph of commercially available sensors. (Schematic of screen-caged sensor modified from Brown & Collins, 1980; schematic of ceramic-cupped sensor modified from Wescor, Inc. 1984, P55 Series Psychrometers; photograph shows a screen-caged Model 74 sensor, J.R.D. Merrill Speciality Equip., Logan, UT, and a ceramic-cupped Model PCT-55 sensor, Wescor, Inc., Logan, UT).

tive) and the constantan lead wire. An alternative double-loop sensor design (Hsieh & Hungate, 1970) places the sensing and reference junctions at the same level inside the protective housing. The double-loop sensor can reduce errors resulting from heat conduction along the lead wires, but such a design does not eliminate temperature gradients within the sensor (Wiebe et al., 1977).

The internal body of the in situ sensors often is constructed from a Teflon plug and the sensing junction is protected by either a stainless-steel screen cage or a porous-ceramic cup (Fig. 3.2.3–3). The pore size of protective housings on commercial sensors is about 25 μm for screen cages and 3 μm for ceramic cups; the 3-μm pore size corresponds with an air-entry pressure of about 0.1 MPa. The evaporation surface for screen-caged units is at the screen and soil–water interface, whereas the evaporation surface for ceramic-cupped units is at the interior of the ceramic surface. Equilibration time for screen-caged sensors is faster than that for ceramic-cupped sensors. The ceramic cup acts as a continuation of the soil-pore system, and ideally, it should be in liquid equilibrium with the soil water. Equilibration time for ceramic-cup sensors will be slowed to a greater degree under conditions when liquid contact is lost between soil particles and the ceramic. Such conditions can be aggravated in dry soils, coarse-textured soils, and fine-textured soils with appreciable shrink–swell capacity. However, if changes in water potential are sufficiently slow, loss of contact may not be a problem because vapor flow alone will eventually bring the ceramic and the air enclosed by it into equilibrium with the soil water potential (Brown, 1970). Salt adsorption by ceramic may preclude its use in saline soils where the osmotic component of water potential is either large or changing rapidly (McAneney et al., 1979). Brunini and Thurtell (1982) overcame the salt adsorption problem by replacing the ceramic with a porous silver membrane.

Other sensor designs include a stainless-steel body with a stainless-steel screen end window (some commercial models were evaluated by Wiebe et al., 1977), a brass body fitted with various end- and side-window configurations constructed of porous ceramic (Campbell, 1979), and a copper body fitted with either a porous-ceramic tip (McAneney et al., 1979) or porous silver-membrane side windows (Brunini & Thurtell, 1982). For the latter two designs, a 1.5-MPa air-entry pressure was chosen for the porous materials so they would not desaturate across the water potential range of interest for agricultural studies. From available information, it appears that low-thermal-conductivity material for the body and a cylindrical stainless-steel screen cage provide the optimum combination for most routine water-potential measurements. Major advancements in development of in situ sensors since the 1980s have been limited by existing materials, but refinements to minimize their temperature sensitivity may be possible through further trial-and-error methods, or through a careful theoretical analysis of heat and vapor flow through and around the sensor.

Recently, Loskot et al. (1994) described a six-wire Peltier sensor that was developed for application in deep unsaturated-zone boreholes (up to 800 m) where environmental temperature gradients are minimal. This screen-caged sensor consists of a wet-bulb (chromel–constantan) sensing junction and a separate dry-bulb (copper-constantan) sensing junction. Two reference junctions are formed where the chromel and constantan wires of the wet-bulb sensing junction are soldered to separate, paired, copper lead wires. This is in contrast to the circuitry of the standard design (Fig. 3.2.3–3A and 3.2.3–3B) where the wet-bulb and dry-bulb junctions share common lead wires. Loskot et al. (1994) used the six-wire configuration to read the wet bulb as a four-wire resistor during current excitation to track any change in the resistance of the wet bulb with time. This information can be used to detect irregularities that call for recalibration or abandonment of a sensor.

3.2.3.2.c Electronics

The sequence of steps used in making psychrometric (wet-bulb temperature depression) measurements with Peltier sensors includes: (i) measuring ambient temperature of the sensor, (ii) measuring the voltage when the sensing and reference junctions are dry (referred to as the *zero-offset* voltage (Wiebe et al., 1977)), (iii) passing Peltier current through the fine-wire thermocouple in the direction to cause cooling of the sensing junction to condense water on it, and (iv) measuring the voltage that is spontaneously generated by wet-bulb depression (temperature difference between the sensing and reference junctions) as condensed water evaporates from the sensing junction. Use of the wet-loop sensor also relies on voltage measurements of wet-bulb temperature depression. The zero-offset voltage is an indicator of temperature gradients in the sensor circuit, but its interpretation and use have been the subject of debate (Wiebe et al., 1977; Campbell, 1979; Brown & Bartos, 1982; Brown & Chambers, 1987; Savage et al., 1987). The microvolt output measured during the evaporative part of the measurement sequence is typically adjusted using the zero-offset voltage, and the resultant value is used in water potential determinations. One such adjustment is simple algebraic subtraction of the zero-offset voltage if it falls within an acceptable user-defined range of values. There appears to be no consensus as to what value of zero offset results in an unacceptable water potential determination. Some manufacturers suggest that the magnitude of zero offsets should be <3 μV for meaningful water potential measurements (Wescor, 1979). In practice, many workers accept in situ water potential measurements if the magnitude of the zero offset is <1 or 2 μV. Another approach is to apply a calibration model that mathematically adjusts for the zero offset across a wide range of values (e.g., from –60 to +60 μV; Brown & Bartos, 1982). Brown and Bartos (1982) chose the ± 60-μV range because the microvolt output generated by a chromel–constantan thermocouple is about 60 $\mu V\ ^{\circ}C^{-1}$; thus, a zero-offset of 60 μV implies a temperature difference of about 1°C between the sensing and reference junctions.

Requirements for the electronic recording and switching circuitry to accomplish psychrometric measurements are outlined in detail by Wiebe et al. (1971). The resolution of some commercially available readout systems is about ± 0.05 μV. Some control systems have an optional "heat" function that reverses the Peltier current to heat and dry the sensing junction prior to cooling. However, water driven off the sensing junction may condense on the interior chamber wall and cause erroneously high water potentials if there has been insufficient time to allow this water to equilibrate throughout the sample volume (Wiebe, 1984). Automated switching and recording systems have been developed to reduce the time and labor requirements for making manual water potential measurements. More recently, commercially available instruments have been developed with the capability to control and measure several sample chambers or sample changers in the laboratory. Psychrometer–data logger systems are increasingly being used to measure in situ water potentials. These systems permit frequent measurement of water potential at the same location, and some systems are capable of measuring as many as 140 individual sensors. Data loggers can be powered by alternating- or direct-current sources and may include telephone or radio-frequency communications hardware and software for remote programming and data acquisition. Figure 3.2.3–4 shows an example of a psychrometer–data logger measurement and control system with 80 Peltier-type sensor leads attached.

The hygrometric (dew-point temperature depression) measurement technique uses adjustments in the applied Peltier-cooling current to exactly balance heat flow to the sensing junction so that microvolt output readings can be taken at the dew-point temperature. In the original design (Neumann & Thurtell, 1972), measurements required a Peltier sensor with a two-thermocouple (four-wire) configuration and a common sensing junction that was made by crossing and welding chromel and constantan wires. A current was passed through one thermocouple to cool the sensing junction by the Peltier effect, while the other thermocouple si-

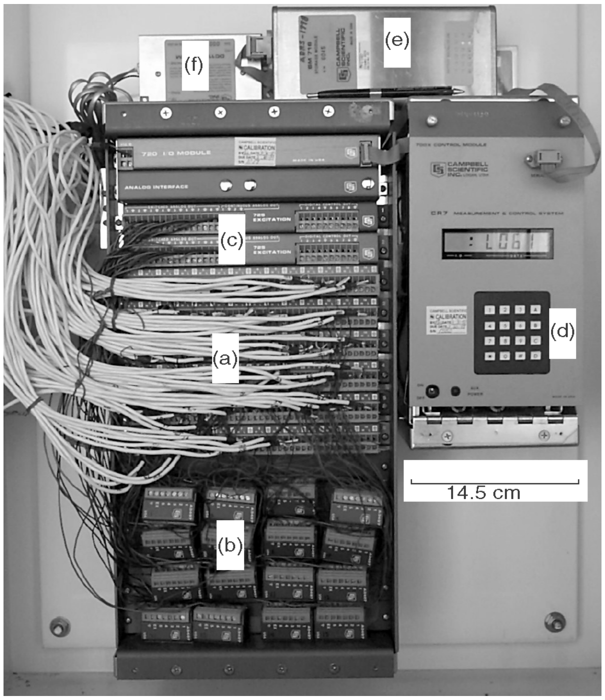

Fig. 3.2.3–4. Photograph of psychrometer–data logger measurement and control system (Model CR-7, Campbell Sci. Inc., Logan, UT) showing 80 Peltier-type sensor leads (J.R.D. Merrill Speciality Equipment, Logan, UT) attached. Lower case letters identify lead wires and input cards (a), cooling current interfaces (b), excitation cards (c), numeric keypad (d), data storage module (e), and telephone modem (f) for remote programming and data acquisition. This unit was placed within an environmental enclosure that was housed within an insulated instrument shelter. A protective aluminum panel that covers the input–output module and all lead-wire connections for increased thermal stability was removed for the photograph.

multaneously measured the dew-point temperature depression of the junction. This procedure required that measurements be made first with the thermocouples exposed to dry air and then with the thermocouples exposed to a calibration solution or unknown sample. A modification of the Neumann and Thurtell (1972) hygrometric technique by Campbell et al. (1973) makes water potential determinations possible in a single operation and with standard two- or three-wire Peltier sensors commonly used in sample chambers and in situ sensors. This dew-point meter, which is commercially available from Wescor, Inc., is capable of making measurements in both the hygrometric and psychrometric modes. When operating the meter in the hygrometric mode, the sequence of steps includes (i) measuring ambient temperature of the sensor, (ii) zeroing the meter, (iii) passing Peltier current through the fine-wire thermocouple in the direction to cause cooling of the sensing junction to condense water on it, and (iv) switching the meter to hygrometric mode in which a time-share circuit is used to automatically modulate the cooling-duty cycle and measure the voltage as condensed water evaporates and the sensing junction converges upward to the dew-point temperature. The microvolt output quantifies the dew-point temperature depression and is used in water potential determinations. This method requires that the electronic gain of the duty-cycle control circuitry be matched to the cooling coefficient (π) of the thermocouple being used. Proper setting of π is essential since it ensures the energy-balance condition that will converge the sensing junction to the dew-point temperature (Wescor, Inc., 1979). While the dew-point meter provides a convenient and portable unit for water potential measurements, the hygrometric technique is susceptible to errors caused by temperature drifts of the reference junctions as well as to the other errors that limit the accuracy of the psychrometric technique. In practice, accuracy of the hygrometric and psychrometric techniques is comparable. For example, Nnyamah and Black (1977) compared water potentials measured in the field using the hygrometric and psychrometric techniques and found that, over the observed range of about −1.3 to −0.3 MPa, agreement between the two techniques was linear ($r = 0.99$) and values were within ± 0.03 MPa.

3.2.3.3 Procedures

In addition to understanding the theoretical principles of thermocouple psychrometry, application of the method requires attention to operational details and precautions to ensure accuracy of the data collected. These include care in cleaning and handling, careful calibration, adequate temperature and vapor-pressure equilibration, proper sample loading and/or installation of in situ sensors, and proper interpretation of the microvolt output data. Although many precautions for laboratory and in situ applications are similar, each use has specific requirements. This section describes basic procedures required to avoid unnecessary errors. For further details, the reader is encouraged to refer to the citations provided, and when using commercially available equipment, the user should become very familiar with instrument manuals.

3.2.3.3.a Cleaning and Handling

Meticulous cleaning and thorough drying of sample chambers and in situ sensors before calibration and use are essential to instrument performance. Contaminants, such as salts, can act as vapor sinks by absorbing moisture and, if present on the thermocouple junction, can affect cooling, evaporation, and the microvolt output. Introduced contamination sources may originate from the manufacturing process, handling, calibration, or from elements in the surrounding soil (e.g., salts, volatile-organic or acidic compounds). Daniel et. al. (1981) found problems with corrosion of in situ sensors were severe with acidic ($pH < 4$) soils, but corrosion was not a problem with a basic ($pH = 8.8$) soil. Aside from elements in the surrounding soil, the most serious and likely source of introduced contamination is the salt solutions used in calibration.

New sample chambers and thermocouples should be cleaned before and after the first calibration and use, and subsequent checks for contamination should be routinely made thereafter. In most cases, sample chambers and thermocouples can be cleaned with distilled or deionized water. Most of the excess water can be removed by shaking and residual droplets can be eliminated with short blasts of pressurized air to ensure that water is removed before it can evaporate and leave any residue. If there is a heavy concentration of salt or other contaminants, thermocouples may be cleaned with a mild detergent or boiling water, as well as a 10% ammonia solution. If grease is a problem, reagent grade acetone may be used. In all cases, the final steps should include several rinses with distilled water and removal of excess water. Extreme caution must be exercised to avoid damaging the thermocouple and to avoid scratching the thermocouple mount and chamber surfaces.

In situ sensors should be cleaned before and after calibration and use. The pore size of the protective housings on in situ sensors prevents most contaminants, such as soil particles, from entering the sensor cavity. The most serious contamination occurs if dissolved contaminants migrate through or accumulate on the protective housing. Ceramic-cupped units are likely to be more problematic than screen-caged units because the mode of operation for ceramic can move dissolved contaminants to the interior surface of the cup. Screen-caged sensors usually can be cleaned inside and out without disassembly. A wash bottle is used to spray distilled water onto and directly through the screen; oil and grease can be removed and initial drying can be accomplished in a similar manner using an aerosol cleaner–degreaser and pressurized air, respectively. Complete drying can be ensured by placing the sensor in a forced-air oven at 40°C for at least 2 to 4 h or by allowing it to air-dry overnight. If light residues appear on screen-caged or ceramic housings, an initial soaking of assembled sensors with distilled water may be sufficient to dissolve the residues and allow them to be rinsed away. Heavy salt accumulations, however, may require that the sensor be disassembled for cleaning. If traces of rust appear on detachable screen cages, they can be removed by soaking the cages for 5 min in a 10:1 mixture of water and hydrochloric acid (Savage et al., 1987). If acetone is used as a cleaning agent, care should be taken to avoid contact with vinyl components or protective plastic coatings that may be used to protect the thermocouple from corrosion.

In situ sensors need to be handled with care. Sensors should be stored in sealed containers or plastic bags to keep them free of dust and other contaminants. The protective housings are fragile; screen-cages can be easily crushed and ceramic housings can be cracked. Damage to the protective housing can cause shorts in the microvolt signal and immediate loss of data, or it can enhance the possibility of corrosion of the thermocouple, which in turn, can cause a slow temporal drift in microvolt output; such temporal drift can be especially problematic when collecting time-series data in the field.

3.2.3.3.b Calibration, Signal Generation, and Signal Interpretation

Correct calibration of sensors for psychrometric and hygrometric determinations of water potential for laboratory and in situ use is extremely important because the accuracy of all subsequent measurements and interpretations will be based on these data. It is important that the calibration conditions duplicate, as closely as possible, the conditions that will exist during actual measurements and that the calibration-measurement protocol be consistent with that used for actual measurements. In general, the variability in microvolt-output characteristics among individual sensors necessitates that each sensor be calibrated separately. This section first describes factors that need to be considered when developing protocol for calibration and for generation and interpretation of the microvolt-output signal. The section then outlines procedures for calibration of sample chambers and in situ sensors.

A range of NaCl or KCl solutions of known osmotic potential is typically used to establish the relation between water potential and microvolt output. Careful preparation of calibration solutions is mandatory, and detailed procedures and precautions are provided by Wiebe et al. (1971) and Brown and Van Haveren (1972). Once calibration solutions are prepared, steps should be taken to prevent changes in concentration that result from evaporation or from cross-contamination of drop-bottles used to transfer solutions to calibration chambers.

Calibration solutions are chosen to cover the anticipated range of water potentials to be measured, and if measurements are to be made at different temperatures, calibration temperatures are chosen to cover the expected temperature range. Recognizing the possible contamination problems that can occur as a result of calibration, it is advisable not to use high molality solutions unless they are essential to covering the anticipated range of actual measurements. Osmotic potentials for NaCl solutions across a range of concentrations and temperatures are given in Table 3.2.3–1; distilled-deionized water can be used for a 0-MPa solution. Solutions of KCl that cover a narrower range of osmotic potentials (about –0.2 to –4.7 MPa) at temperatures from 0 to 40°C are given by Campbell and Gardner (1971). For extremely low water potential applications, the reader is referred to Campbell and Wilson (1972) for LiCl solutions with water potentials ranging from –5 to –100 MPa at 25°C and to Greenspan (1977) for humidities of saturated salt solutions with water potentials as low as –300 MPa.

The anticipated range of water potentials to be measured influences the number of calibration solutions and measurement protocol used. Typical calibration data for hygrometric and psychrometric measurements with Peltier sensors are shown in Fig. 3.2.3–5. The water potential–microvolt output relation for hygrometric and psychrometric measurements is approximately linear between 0 and about –3.5 MPa, but is not linear across the entire measurement range of 0 to –8 MPa. Thus, for routine measurements across the entire range, a minimum of four calibration solutions are typically selected to characterize each sensor's response to changes

Table 3.2.3–1. Water potentials of sodium chloride (NaCl) solution at temperatures from 0 to 40°C.†

	Temperature								
Molality	0°C	5°C	10°C	15°C	20°C	25° C	30°C	35°C	40°C
	Mpa								
0.05	–0.214	–0.218	–0.222	–0.226	–0.230	–0.234	–0.238	–0.242	–0.245
0.1	–0.423	–0.431	–0.439	–0.447	–0.454	–0.462	–0.470	–0.477	–0.485
0.2	–0.836	–0.852	–0.868	–0.884	–0.900	–0.915	–0.930	–0.946	–0.961
0.3	–1.247	–1.272	–1.297	–1.321	–1.344	–1.368	–1.391	–1.415	–1.437
0.4	–1.658	–1.693	–1.727	–1.759	–1.791	–1.823	–1.855	–1.886	–1.917
0.5	–2.070	–2.115	–2.158	–2.200	–2.241	–2.281	–2.322	–2.362	–2.402
0.6	–2.484	–2.539	–2.593	–2.644	–2.694	–2.744	–2.794	–2.843	–2.891
0.7	–2.901	–2.967	–3.030	–3.091	–3.151	–3.210	–3.270	–3.328	–3.385
0.8	–3.320	–3.398	–3.472	–3.543	–3.612	–3.682	–3.751	–3.818	–3.885
0.9	–3.743	–3.832	–3.917	–3.998	–4.079	–4.158	–4.237	–4.314	–4.390
1.0	–4.169	–4.270	–4.366	–4.459	–4.550	–4.640	–4.729	–4.815	–4.901
1.1	–4.599	–4.713	–4.820	–4.924	–5.026	–5.127	–5.226	–5.322	–5.418
1.2	–5.032	–5.160	–5.278	–5.394	–5.507	–5.620	–5.730	–5.835	–5.941
1.3	–5.470	–5.611	–5.742	–5.869	–5.994	–6.119	–6.239	–6.354	–6.471
1.4	–5.912	–6.068	–6.210	–6.350	–6.487	–6.623	–6.754	–6.880	–7.006
1.5	–6.359	–6.529	–6.684	–6.837	–6.986	–7.134	–7.276	–7.411	–7.548
1.6	–6.811	–6.996	–7.163	–7.330	–7.491	–7.652	–7.805	–7.950	–8.097
1.7	–7.260	–7.460	–7.640	–7.820	–8.000	–8.170	–8.330	–8.490	–8.650
1.8	–7.730	–7.940	–8.130	–8.330	–8.520	–8.700	–8.880	–9.040	–9.210
1.9	–8.190	–8.430	–8.630	–8.840	–9.040	–9.240	–9.430	–9.600	–9.780
2.0	–8.670	–8.920	–9.130	–9.360	–9.570	–9.780	–9.980	–10.16	–10.35

† Adapted from Lang, 1967.

in water potential at a given temperature. When using the psychrometric method with Peltier sensors, the anticipated range of water potentials to be measured can also influence selection of the optimum cooling current, the cooling-current duration, and following cessation of cooling, the characteristic microvolt output used to estimate the corresponding water potential. The magnitude of the cooling current must be sufficient to depress the temperature of the sensing junction below the dew-point temperature of the surrounding atmosphere. The duration of the cooling current must be sufficiently long to attain what is theoretically assumed to be a thin

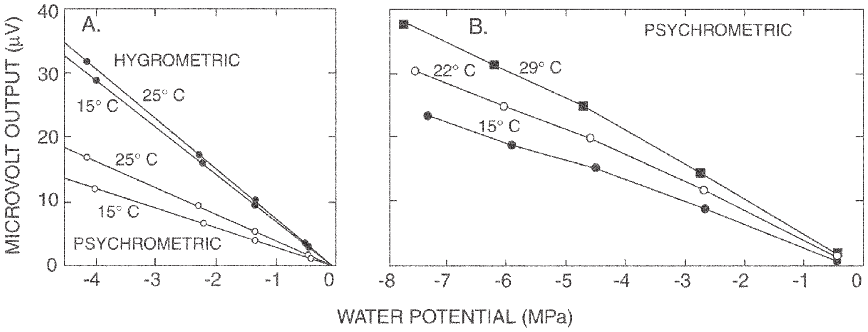

Fig. 3.2.3–5. Typical Peltier-type sensor calibration data for (A) hygrometric and psychrometric measurements made between –4.5 and 0 MPa and at two temperatures and for (B) psychrometric measurements made between –8 and 0 MPa and at three temperatures. (Fig. 5A modified from Nnyamah & Black, 1977; Fig. 5B modified from Fischer, 1992.)

film of water surrounding the sensing junction (Peck, 1968), but has microscopically been observed to be a uniform coating of closely spaced droplets of water (Wiebe, 1984). For water potential measurements in wet to dry soil, respective cooling currents reported in the literature generally range from 3 to 8 mA for cooling durations that range from 10 to 60 s. The apparent discrepancies in the literature regarding the specific combination chosen for cooling current magnitude and duration are due, in part, to differences in the thermocouples used, but are also due to what the various authors considered optimum performance for their specific application. Optimum cooling currents may be estimated from models (Dalton & Rawlins, 1968; Peck, 1968) or determined experimentally. Model calculations suggest that the optimum cooling current for 0.0025-cm-diam. wire is typically 3 to 5 mA. For Wescor sensors, a special welding process produces a larger thermocouple junction, which in turn, increases the optimum current for most rapid cooling to about 8 mA (R.D. Briscoe, personal communication, 1999). For wet environments, however, a current of this magnitude can cause undesirable transients resulting from Joule heating of the wires. Slack and Riggle (1980) worked with Wescor sensors and found a cooling current of 3 mA applied for 15 s was optimum for measurements within a water potential range of −0.5 to −2.2 MPa. Brown and Bartos (1982) worked with sensors of the Brown and Collins (1980) design and found a cooling current of 5 mA applied for 30 s was optimum for most measurements across the full (0 to −8 MPa) water potential range. They observed that a shorter cooling time decreased precision of water potential estimates and resulted in greater variability among the sensors, and a longer cooling time did not offer any strong advantages over the 30-s cooling time. For very dry applications, Millar (1971a, b) found that cooling currents of about 8 to 9 mA applied for 60 s optimally extended the measurement range of his sensor to −13 MPa. At high water potentials, however, this cooling current caused undesirable Joule heating of the wires. Millar advised that if a maximum range of measurements is desired, calibrations should be made at more than one combination of cooling current magnitude and duration.

One of the most difficult and confusing aspects of successful psychrometric measurements with Peltier sensors is the interpretation of the microvolt output following cessation of Peltier cooling (Savage & Wiebe, 1987; Brown & Oosterhuis, 1992). Figure 3.2.3–6 illustrates typical microvolt outputs that were generated using an automated psychrometer–data logger system for water potentials ranging from wet (−0.91 MPa) to dry (−7.08 MPa). Following condensation, the microvolt output reaches a plateau region, and then decreases as water on the sensing junction evaporates back into the air; eventually the microvolt outputs for all water potentials decrease to the reference voltage level as the temperature of the sensing junction returns to ambient. Ideally, the characteristic microvolt output of concern should be recorded at the plateau where the change in microvolt output with time equals zero because the plateau represents the wet-bulb temperature of the sensor when the evaporation of water from the sensing junction reaches a steady state with the relative humidity of air in the sensor chamber. If the sample water potential is high, or if the Peltier cooling has been sufficiently long, the plateau can persist for many seconds and is easy to determine. With dry samples or short cooling times, however, the plateau becomes increasingly transient and determination of the characteristic microvolt output that corresponds with the plateau can be quite subjec-

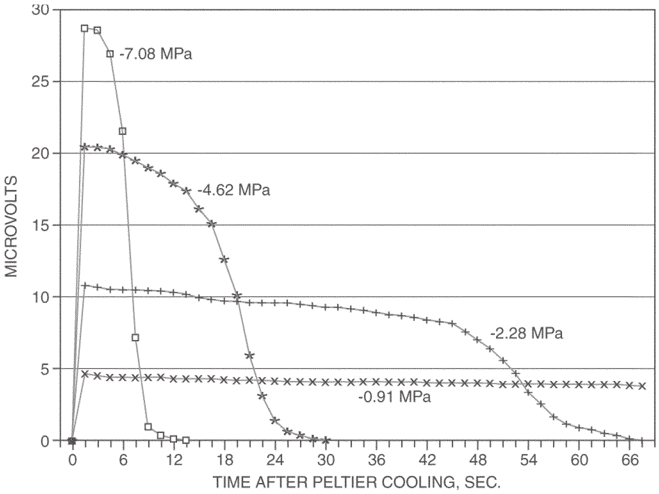

Fig. 3.2.3–6. Typical microvolt output of Peltier-type sensors measured with a psychrometer–data logger for four water potentials at 25°C using a 5 mA cooling current for 15 s. (Modified from Brown & Oosterhuis, 1992.)

tive. At high water potentials, it is not uncommon to observe an initially large microvolt-output value immediately after Peltier cooling is terminated, which is then followed by a rapid decline to the plateau region (not shown in Fig. 3.2.3–6); this transient spike results from the temperature differential generated between the sensing and reference junctions during the Peltier-cooling phase of the measurement sequence. The microvolt-output value(s) associated with this transient spike should not be used as a measure of the characteristic microvolt output of concern (see, for example, Merrill & Rawlins, 1972; Slack & Riggle, 1980). Finally, the shape of the microvolt-output curve can also be influenced by contaminants. The output from a dirty thermocouple is usually less, has a narrower plateau, and is more unstable than that for a clean sensor. Caution must also be used when working in a soil environment where volatile-organic compounds are present. If the concentrations of such compounds are sufficient to approach their vapor-phase saturation pressure, they may condense on the measuring junction and change the shape and interpretation of the microvolt-output curve.

Various methods have been used to estimate the plateau voltage. One common method consists of manually reading and recording the greatest steady microvolt output displayed by a microvolt meter or by an output trace from a strip-chart recorder. Automated systems are also available that allow time-series data for full microvolt-output curves to be recorded and then downloaded to a computer for analysis and interpretation. Time-series measurements during the first 30 s following cessation of cooling can provide sufficient data to define the plateau voltage between 0 and −8 MPa (R.W. Brown, written communication, 1990). When using automated systems that allow for measurement and control of numerous sensors, it can be desirable to reduce the recorded output for each sensor from a time-series of values to a single, characteristic microvolt-output value. In addition to reducing the quantity of raw data collected, measurement and recording of a single value can be important to minimizing the time required when repeated measurements are to be made with numerous sensors. For example, the automated psychrometer–data logger system shown in Fig. 3.2.3–4 required 9 min to complete the measurement and control cycle for 80 sensors using a 30-s Peltier-cooling duration and measuring a single wet-bulb output 2.4 s after Peltier cooling. The time required to complete the cycle would approximately double if the same system were used to measure a series of wet-bulb outputs for each sensor during the first 30 s following cessation of cooling.

Savage and Wiebe (1987) evaluated several procedures for determining the characteristic microvolt output value. These procedures included (i) visual selection of the plateau voltage, (ii) recording the voltage at a preselected time following cooling, and (iii) calculating an "intercept" voltage by extrapolating the voltage plateau back to an intercept value that corresponded with the time when cooling ended. They concluded that the preselected-time and the intercept-voltage procedures can give reproducible estimates of water potential if used with care. For a wet environment, Slack and Riggle (1980) used a preselected time of 6 s. For a desert environment, Fischer (1992) and Andraski (1997) used a preselected time of 2.4 s. However, longer times (5 s) have resulted in ill-defined plateau voltages (Montazer et al., 1988). Kurzmack (1993) developed an intercept-voltage algorithm for use with the six-wire sensor described by Loskot et al. (1994). The algorithm reads values from the microvolt-output curve, identifies a plateau region, and extrapolates a linear regression back to determine the intercept voltage. The algorithm works best when there is a clearly defined plateau region, but when properly conditioned, reasonable results can be achieved even with incomplete or noisy data. The choice and refinement of reliable, automated procedures to reduce the full microvolt-output curve to a single value generally requires trial-and-error testing for the anticipated measurement conditions and the specific instrumentation to be used.

Another factor that influences calibration and measurement protocol is the anticipated range of temperatures to be encountered during actual measurements. The difference in temperature sensitivity between the hygrometric and psychrometric water potential–microvolt output relations is illustrated in Fig. 3.2.3–5A. Temperature dependence can be corrected for by calibrating across a range of temperatures and then interpolating between calibration curves. It is often more convenient, however, to develop a multiple-regression predictive model (Meyn & White, 1972) or to apply a corrective equation (Savage & Cass, 1984; Rawlins & Campbell, 1986) that can be used to calculate water potential for a range of microvolt outputs and temperatures. In addition to these methods, Brown and Bartos (1982) developed a comprehensive psychrometric calibration model to predict water potentials across a range of environmental conditions and measurement protocol. This mathematical model can be applied using calibration data for individual sensors that are measured at a minimum of three water potentials and one temperature within the range of anticipated need. A spreadsheet version is available upon request from the model's senior author (R.W. Brown, personal communication, 1999). For applications requiring large numbers of sensors, individual calibration data can be used to develop a single correction coefficient (Brown & Bartos, 1982) or a common regression equation (Scanlon, 1994; Andraski, 1997) for the entire group. The principal disadvantage of this computationally simpler procedure is that some loss in precision of water potential estimates results because of the variability in microvolt output characteristics among the sensors used. When psychrometric calibrations are done using four to five salt solutions and three temperatures, common regression equations are often of the form

$$\psi = \beta_0 + \beta_1 V + \beta_2 V T_c \qquad [3.2.3\text{–}3]$$

where β_0, β_1, and β_2 are empirically determined constants, V is microvolt output (μV), and T_c is temperature (°C). The coefficients of multiple determination and standard errors of estimate are typically 0.99 and 0.2 MPa, respectively. To determine the appropriate temperature-correction procedure for a given situation, one must evaluate the best combination of desired predictability, computation time, and calibration time required.

Although the hygrometric calibration relation is relatively insensitive to temperature (Fig. 3.2.3–5A), the accuracy of the Campbell et al. (1973) technique is critically dependent on the correct setting of the thermocouple cooling coefficient (π), which is temperature dependent and can vary markedly from sensor to sensor. The optimal π value may be determined empirically across a range of temperatures (Savage et al., 1981), or when using Wescor sensors, a single calibration value may be corrected for temperature using an equation supplied by the manufacturer (Wescor, Inc., 1979).

Sample-Chamber Calibration. Laboratory sample chambers are calibrated using precut filter paper disks or strips thoroughly wetted with calibration solution so the saturated vapor pressure within the chamber reflects the osmotic potential of the solution. Disks are used in shallow sample holders such as those shown in Fig. 3.2.3–1, and strips are cut and rolled to line the wall of deeper sample cups such as those shown in Fig. 3.2.3–2. The filter paper method reduces the potential for accidental splashes of calibration solution and minimizes the exposed wall area of sample cups that could serve as a source or sink for vapor adsorption. Filter paper disks may be stacked, if needed, to better simulate the height of an actual soil sample. Filter paper should be no closer than 1 mm from the upper edge of the wall. If the filter paper extends to the top of the wall, solution may move up the filter paper and contaminate the thermocouple assembly. Once in place, a drop-bottle is used to wet the filter paper with calibration solution. When using sample cups, several drops of solution are added to cover the bottom of the cup. This method does not give the exact chamber geometry obtained with soil samples, but it is adequate to give accurate calibrations (Wiebe et al., 1971). Rapid cooling of sample containers should be prevented to avoid condensation from the sample onto chamber walls.

Once a calibration solution is loaded into a sample chamber, vapor and thermal equilibrium must be achieved before making a measurement. The metal housings of commonly used sample chambers and changers generally provide sufficient thermal shielding for most laboratory applications, but the operator should avoid unnecessary handling of metal components that could result in heat exchange. The time required for temperature and vapor-pressure equilibrium will vary and can best be judged through experience with the device used and with similar samples. As a general guide, when using a single-sample chamber unit such as that shown in Fig. 3.2.3–1, routine measurements can be made within about 2 to 3 min after the calibration sample is loaded. For low water potential applications, however, Wiebe (1981) made measurements within 10 s after the sample was loaded. This procedure required special precautions to ensure thermal equilibrium; these included use of additional insulation and replacement of the standard nylon sample slide with one made of aluminum. When using a 10-sample chamber such as that shown in Fig. 3.2.3–2, each sample contributes to temperature equilibrium, which is generally reached within 15 to 30 min after the calibration samples are loaded. Upon reaching thermal equilibrium, sequential measurements can usually be made following a 2- to 3-min vapor-equilibrium period for each individual calibration sample. Jones et al. (1990) found that measurement uncertainty of this unit could usually be reduced by taking readings at a 3-min rather than 2-min time interval.

In Situ Sensor Calibration. In situ sensors are typically calibrated by direct immersion into a small container of calibration solution or by suspension of the sensor in a calibration chamber lined with a strip of filter paper that is just saturated with calibration solution. The immersion method has often been selected because (i) this calibration configuration best approximates sensor–soil geometry in the field and (ii) the pore size of typical screen-cage and ceramic-cup housings is sufficiently small to prevent liquid from entering the air-filled sensor cavity (Briscoe, 1984). Brown and Collins (1980) completely immersed screen-caged sensors to a depth of 0.2 m in NaCl solutions and no solution penetrated the screen cage. However, the immersion method is often criticized because it can enhance the migration of salts into the housing. These salts are difficult to remove, and their retention decreases the apparent water potential within the sensor cavity and leads to corrosion of the sensor. To reduce problems experienced with the immersion method, Wheeler et al. (1972) wetted ceramic-cupped sensors by splashing calibration solution onto them with a vibrating bath. Screen-caged sensors are typically calibrated by placing the sensor, filter paper, and calibration solution in a stainless-steel calibration chamber like that illustrated in Fig. 3.2.3–7. A similar calibration-chamber configuration may be obtained using small test tubes that are fitted with rubber stoppers through which the lead wires extend. The desire is to just saturate the filter paper with calibration solution delivered using a drop bottle. Excess solution should be allowed to drip out of the inverted calibration chamber following application, and care should be taken to avoid having solution come in contact with the sensor. Although the vibrating-bath and calibration-chamber techniques do not simulate the exact geometry when a sensor is buried in the soil, the error introduced is generally assumed to be negligible. For measurements in crystalline rock, however, Schneebeli et al. (1995) constructed calibration chambers from porous Teflon blocks into which a cavity was drilled to simulate the dimensions of rock cavities used for actual measurements.

Once calibration solutions and in situ sensors are loaded into individual calibration chambers, the entire assembly and a ≥0.3-m length of coiled lead wire are submerged in an isothermal water bath. Because the sensors equilibrate through a vapor gap, temperature gradients must be minimized; a temperature difference of 0.01°C between the sensor and calibration solution will result in a measurement error

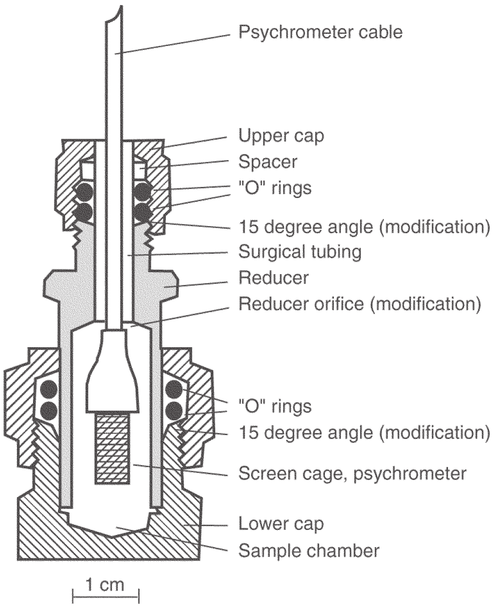

Fig. 3.2.3–7. Schematic of stainless-steel calibration chamber and in-situ sensor. (Modified from Brown & Collins, 1980.)

of 0.08 MPa. Thus, water baths with a temperature stability of ± 0.01°C or better are typically used. Rapid heat transfer between the calibration chamber and water bath allows temperature equilibrium to be achieved in about 30 min. Vapor-pressure equilibrium occurs more slowly, requiring 2 to 6 h before a calibration measurement can be made. Vapor-pressure equilibrium may be assumed when two reproducible water potential measurements are read 1 h apart (Brown & Bartos, 1982). Other options for creating an isothermal environment include the use of aluminum blocks, foam boxes, and incubators. If the calibration assembly is warmer than the water bath into which it is placed, water can condense inside the chamber and greatly slow down the vapor-pressure equilibrium process. Condensation problems can be avoided by cooling the calibration components (sensor, chamber, solution) below the water bath temperature before the solution is loaded and the calibration assembly is placed into the water bath. If calibration for a given salt solution is to be done at different temperatures, the operator should start with the lowest temperature and sequentially increase the water bath temperature after each set of readings. When working with several sensors, greater convenience and reproducibility are achieved by calibrating the sensors simultaneously. Preliminary evaluation of microvolt outputs can identify operational problems that might occur during calibration (e.g., when calibrating at water potentials <0 MPa, a 0-μV output often corresponds with water leakage into a calibration chamber). After completing measurements for a given calibration solution (at different temperatures), the chamber should be opened and inspected for leakage. The calibration components are then disassembled, cleaned, dried, and reassembled as necessary for the next set of calibration measurements, including any repeat measurements that are needed.

3.2.3.3.c Sample Handling and Laboratory Measurement

Many of the precautions described for calibration of sample chambers apply to measurement of soil samples, and the sample handling and measurement procedures should be performed as similarly as possible. Because of the expense and difficulties of installing and monitoring in situ sensors in the field, information on spatial variability of water potentials is often based on laboratory measurements of soil samples collected from various locations and depths (Scanlon et al., 1997). If soil-probe or borehole-core samples are collected for determination of water-potential gradient profiles, desired core segments should be isolated as soon as possible following sample collection to minimize errors that could result from water redistribution (core sampling methods are discussed in Section 2.1.2). For many applications, negligible differences will arise from measuring water potential at laboratory temperature rather than at the field temperature, or from use of disturbed samples with altered bulk density rather than undisturbed field soil. However, temperature effects may become significant for drier soils, and bulk density effects may become significant for wet or swelling clay soils (Campbell & Gardner, 1971; Mohamed et al., 1992). For dry (less than −0.1 MPa) nonswelling soils, water potential changes little with bulk density. Water loss from samples can result in large measurement error and precautions are required to minimize evaporation from the sample during collection, storage, and transfer to the sample chamber. Coarse-textured and drier soils are most problematic because a large decrease in water potential can occur in response to a small decrease in water content. Field samples should fill sample containers to minimize air space, sample containers should be air-tight to prevent water loss, and rapid cooling of the containers should be prevented to avoid condensation from the sample onto the container walls. In the laboratory, water loss during sample transfer can be reduced if the sample chamber is placed and loaded inside a glove-box in which the humidity is kept high by lining it with wetted blotter paper (Campbell & Wilson, 1972). This method will provide a relative humidity of about 0.6 to 0.7. Since it is difficult to adjust the humidity of the glove-box to approach that of the sample, the user must still work quickly to minimize the exchange of moisture between the sample and the atmosphere. Once a sample is loaded into a sample chamber, time must be allowed for it to reach thermal and vapor-pressure equilibrium before making a measurement. The time required will vary and can best be judged through experience with the device used and with similar samples. As a general guide, soil samples equilibrate more slowly than liquid samples and may require 15 to 30 min or more to fully equilibrate. To the extent possible, consistent equilibration times should be used in any series of measurements. It is good practice to routinely include measurement of calibration solutions along with soil samples. This permits the operator to detect irregularities that call for a change in the calibration curve or for thermocouple cleaning or repair.

The accuracy with which soil water potential is determined using a sample chamber may also be influenced by the type of sensor used to make the measurement. Experiments with Peltier sensors have indicated that the small amount of vapor condensed from the soil sample atmosphere by Peltier cooling has no measurable drying effect on the soil water potential (Campbell & Wilson, 1972). Zollinger et al. (1966) found that the small drop of water placed on a wet-loop type sensor increased water potential readings of dry samples (−5 MPa) by as much as 1.5 MPa, but pointed out that increasing the surface area of the sample would reduce this effect appreciably. More recently, comparisons between water potential measurements made using a wet-loop sensor and a water-activity meter suggested that the error associated with the wet loop's addition of water is relatively small (Gee et al., 1992).

3.2.3.3.d In Situ Sensor Installation and Measurement

Protocol for the installation and measurement of in situ sensors should be followed to duplicate, to the extent possible, the conditions and procedures used during calibration. Although this subsection focuses on field and glasshouse installation and measurement techniques, in situ sensors are also used to make repeated water potential measurements in the laboratory on soil cores and columns. For example, methods for determining water-retention curves using in situ sensors have been described by Mehuys et al. (1975), Riggle and Slack (1980), Daniel (1982), and Madsen et al. (1986). Mehuys et al. (1975) and Daniel (1982) also used in situ sensors in determinations of unsaturated hydraulic conductivity.

In strong contrast to isothermal calibration or controlled laboratory conditions, in situ measurements in field and glasshouse experiments are subject to temperature gradients that, even with the most appropriate sensor designs available, require adoption of additional precautions to reduce the associated measurement errors. Merrill and Rawlins (1972) suggested the important practice of installing sensors horizontally rather than vertically in near-surface soil to minimize temperature-gradient effects on water potential measurements, particularly at depths shallower than 0.4 m. Figure 3.2.3–8 shows the effect of different sensor orientations on diurnal variation in zero-offset values (i.e., psychrometer emf in upper part of figure) and apparent water potentials. The temperature-gradient error implied by the zero-offset values is the reverse direction if the vertical sensor is inverted, or can be nearly eliminated if the sensor is oriented perpendicular to the temperature gradient. More recently, Brown and Chambers (1987) evaluated the effect of reference junction orientation on measurements. They stated that planar orientation of the two reference junctions within horizontally placed sensors did not appear to have a measurable influence on water potential measurements. In addition to the sensor, horizontal placement and burial of a length of lead wire (preferably ≥0.3 m) immediately behind the sensor minimizes heat conduction along the lead wire. For glasshouse experiments where small containers are often used, the lead wire buried behind the sensor may be looped and wrapped several times to create the necessary thermal mass to minimize heat conduction problems, but additional insulation and other precautions are required to decrease the thermal instability of the containers (Savage et al., 1987). To install sensors in near-surface soils, a small pit can be dug and sensors placed into access holes made horizontal to the soil surface. Where soil is cohesive, a steel rod with a diameter matching that of the sensor can be driven or drilled into the pit wall, the rod removed, the sensor placed into the resulting hole, and the hole backfilled to the extent possible to form a seal around the lead wire. Where

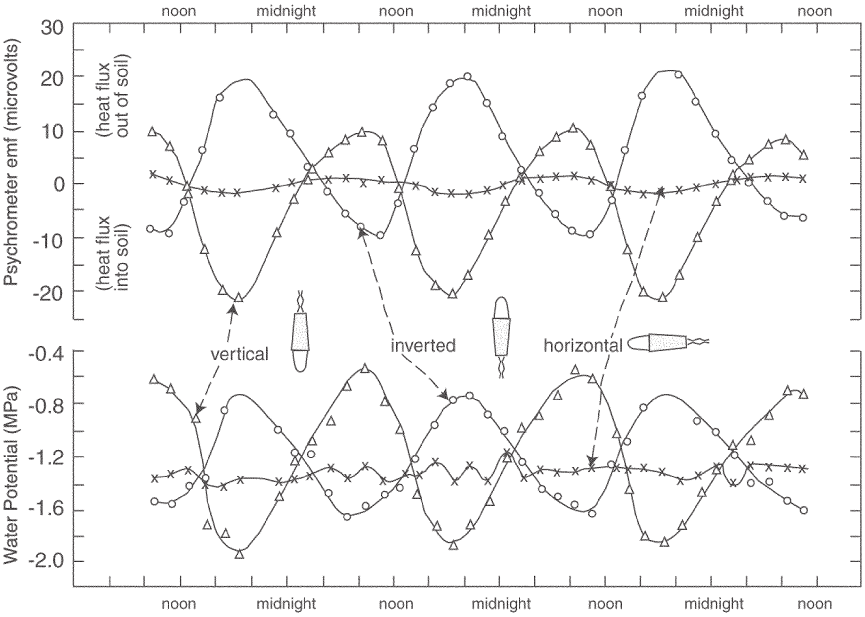

Fig. 3.2.3–8. Diurnal variation in microvolt zero-offset values (i.e., psychrometer emf in upper part of figure) and apparent water potential for ceramic-cup sensors installed in different orientations at a soil depth of 0.25 m. Data shown were collected in the summer with no crop canopy present. Note that zero-offset values were designated positive when the sensing junction was warmer than the reference junctions, and negative when the sensing junction was cooler. (Modified from Merrill & Rawlins, 1972.)

soil is prone to collapse, a small-diameter steel pipe fitted with a removable drive-point insert (e.g., carriage bolt) can be driven into the pit wall, the pipe retracted a short distance to remove the drive point, the sensor inserted to the end of the pipe, and the pipe removed allowing soil to collapse around the sensor and lead wire. Following sensor installation, the access pit should be carefully backfilled with the original soil.

Temperature differences at lead wire–voltmeter connections can contribute to positive or negative zero-offset voltages. Therefore, the lead wire connections should be shielded from air currents and the voltmeter and data logger should be placed in an environmental enclosure well insulated from direct solar radiation. It is also good practice to house lead wires that run from the measurement site to the voltmeter in polyvinyl chloride (PVC) pipe, or similar material, to protect them from exposure to direct sunlight and from rodent damage.

Measurement procedures can be adopted to further minimize thermal-gradient effects on water potential determinations in shallow-soil and glasshouse applications. Based on the zero-offset and apparent water potential data shown in Fig. 3.2.3–8, Merrill and Rawlins (1972) suggested that diurnal temperature-gradient errors could be avoided by making measurements at 12-h intervals to generate daily water-potential values. Zero-offset voltages have often been used to indicate the presence and magnitude of sensor–soil temperature gradients, but some workers have stressed that zero-offsets may not be as reliable an indicator as originally believed (Brown & Chambers, 1987; Savage et al., 1987). Since typical in situ sensors have two reference junctions embedded in a Teflon plug and separated by a few millimeters (Fig. 3.2.3–3A and 3.2.3–3B), it is possible that temperature differences between the two reference junctions may lead to misidentification of the presence or absence of temperature gradients. Thus, it is suggested that measurements of soil temperature and zero-offset be made at several depths and locations over several diurnal periods to determine the period(s) of minimum temperature gradients for the particular site and soil type being studied. Where temperature gradients are of concern, water potential measurements should then be confined to those times.

Application of thermocouple psychrometry to the study of flow and transport processes in deep unsaturated zones has greatly broadened during the last 20 yr. A major problem inherent in measuring water potentials in such settings is that the installation process may markedly affect the natural system, causing the measured data to be an artifact of the installation process rather than a reflection of the natural system. In principle, the diameter of the borehole should be as small as possible, the exposure of borehole walls to drilling fluids and air should be avoided, and the backfilling techniques should stabilize the instrumented column, isolate the monitoring intervals of interest, and minimize vapor-equilibration time between the thermocouple psychrometer and the surrounding native formation.

Various drilling techniques have been used to install thermocouple psychrometers in the deep unsaturated zone. The minimum diameter of the borehole and the minimum degree to which borehole walls are exposed to air will be largely dictated by the nature of the native formation and the desired depth of the installation. Working in relatively stable and shallow sediments, Enfield and Hsieh (1971) used a 7.5-mm-diam. hand auger to install sensors to a depth of 4.4 m, and Scanlon (1994) used a 50-mm-diam. solid-stem-auger rig to install sensors to a depth of 14.3 m. Wetting or drying of the surrounding native formation was expected to be minimal because no drilling fluid was used and because the borehole diameters were small. For deep unconsolidated sediments, Enfield et al. (1973) used a dry core barrel–staggered casing technique to install sensors to a depth of 94 m. The diameter of the individual lengths of staggered casing ranged from 150 to 300 mm. The use of casing reduced the exposure of borehole walls to air and the staggered design reduced the skin-frictional forces encountered during its removal. More recently, pneumatically driven downhole-hammer techniques have become available that simultaneously drill and stabilize the borehole with casing (Hammermeister et al., 1985). Air is injected down the drill pipe and drill cuttings are removed to land surface by blowing them up through the inside of the casing. Hammermeister et al. (1985) found this method to be rapid and equally effective in drilling 150-mm-diam. boreholes in cohesive, noncohesive, and bouldery sediments, and in fractured rock down to depths of 130 m. They also found that the method minimally disturbed the water content of the surrounding formation. This drilling-and-casing technique has been used to install sensors in 150- to 200-mm-diam. boreholes in the upper 50 m of the unsaturated zone (Fischer, 1992; Andraski & Prudic, 1997; Prudic et al., 1997), but other borehole diameters and greater installation depths are possible (D.E. Prudic, B.J. Andraski, and D.A. Stonestrom, unpublished data, 1999). For very deep, stable rock (fractured-tuff) applications, vacuum reverse-air circulation drilling (Whitfield, 1985) was used to drill an uncased borehole that was instrumented to a depth of 387 m (Montazer et al., 1988). The diameter of the instrumented borehole ranged from 445 to 900 mm. With this drilling technique, air is injected down the annulus of a dual drill pipe and a vacuum system is used to circulate the air and remove drill cuttings up through the inner drill pipe, thereby minimizing exposure of the uncased borehole walls to drilling air.

A variety of materials and combinations thereof can be used to backfill deep boreholes instrumented with thermocouple psychrometers. Native sediments and drill cuttings, and nonnative materials such as sand and grout have been used to stabilize the instrumented column. Low-permeability materials such as epoxy, powdered bentonite, bentonite–sand mixtures, and grout have been used to prevent preferential liquid and gas flow down the borehole and to isolate sensors in the monitoring interval of interest. Sensors have been embedded in native sediments and drill cuttings, and in nonnative, high air-permeability materials such as sand, gravel, and polyethylene beads. High air-permeability materials are used because the coupling of the sensor with the formation is through the vapor phase; therefore, a continuous liquid phase is not required. The backfill is usually placed into the borehole using tremie pipes to avoid damage to the sensors and lead wires, and to avoid bridging of the borehole as it is backfilled. When using a cased-hole drilling technique, the casing is incrementally withdrawn to expose the native formation as the borehole is backfilled. The use of native or nonnative backfill materials is usually dictated by the nature of the native formation and the degree to which materials extracted from the borehole are disrupted by the drilling process. When working in relatively easy-to-drill formations, auger drilling and dry core barrel-type techniques can produce native backfill materials that are less disrupted than those produced by other drilling techniques. Native backfill materials that are relatively uniform and coarse textured can generally be placed back in the borehole with some ease and predictability. In contrast, heterogeneous, fine-textured, or rocky sediments, and drill cuttings can be difficult to work with; under such circumstances, nonnative backfill materials are often used because they can be placed into the borehole with greater ease, uniformity, and predictability. If the drilling technique extracts sediments with minimal disruption, water potential differences between the native formation and the resultant backfill can be reduced by quickly transferring and storing extracted sediments in air-tight containers that are labeled for depth and then replacing the stored sediments at their original elevation in the borehole. If sensors are to be embedded in native materials that have been greatly altered by the drilling process or are to be embedded in nonnative materials, water potential differences can be reduced by wetting or drying the backfill to match the ambient water potential. However, accurate determination of the ambient water potential can be difficult and procedures to adjust the water potential of backfill require extreme care. In desert environments where sediment water potentials are often less than −1 MPa, adding too much water can be especially problematic and can result in exceedingly long equilibration times. Thus, the most common procedure in such settings is to place sensors in backfill that is initially drier than the surrounding native formation.

Disturbance caused by borehole installation and backfilling techniques can greatly influence the time required for measured water potentials to come into equilibrium with the surrounding native materials. For example, time-series data reported by Scanlon (1994) showed that near-surface measurement of sensors installed in close contact with undisturbed soils equilibrated within 1 d of installation. In contrast, deeper measurements made using sensors embedded in loamy sand backfill in a 50-mm-diam. borehole required about 1 to 2 mo to equilibrate. Much longer equilibration times (>1 yr) have been observed in a 445- to 910-mm-diam. borehole in which sensors were housed within a well screen, which in turn was embedded in coarse sand (Montazer et al., 1988) and in an experimental 600-mm-diam. borehole in which sensors were embedded in polyethylene beads that were placed inside slotted-PVC casing, which in turn was surrounded by coarse sand (Rousseau et al., 1994). In all three borehole installations, measured water potentials increased during the equilibration period and the rate of increase became less as the backfill around the sensor approached the ambient water potential of the formation. The observed increase in water potentials was attributed to water movement from the formation into the initially drier backfill. Knowledge of the hydraulic properties and field water potentials of the backfill and formation at the Scanlon (1994) and Montazer et al. (1988) study sites indicated that liquid fluxes in the backfill were negligible during the equilibration period and that vapor diffusion into the backfill and subsequent adsorption of vapor on solid surfaces probably were the dominant processes by which the backfill equilibrated with the surrounding formation. Based on results of field monitoring and numerical simulations, Montazer (1987) suggested that in situ rock water potential may be measured most effectively by eliminating the use of backfill and isolating sensors in air-filled borehole cavities that are created using inflatable packers. Because a field trial-and-error approach is usually cost prohibitive for the evaluation and development of deep-borehole installation methods, refinements to improve such methods will likely come through a combination of numerical analyses of liquid, vapor, and heat flow to and around the sensor, controlled small-scale experiments, and subsequent field testing.

In addition to temporal drift during the in situ equilibration period, temporal drift in water potential measurements may occur as a result of a shift in sensor calibration with time. For example, early work by Merrill and Rawlins (1972) evaluated changes in the sensitivity of 33 ceramic-cup sensors by recalibrating the units after 8 mo of field use: sensitivity of 45% of the units shifted by <5%, 33% shifted between 5 and 10%, and the remainder shifted by ≥10%. Brown and Johnston (1976) performed a similar experiment with screen-end-window sensors that had been buried in the field for about 3 yr: 86% of the sensors showed an average change in sensitivity of 6%, and the remainder showed no change. Similar to Daniel et al. (1981), these workers indicated that changes in sensor sensitivity may be greatest in acidic soils. Finally, Brown and Collins (1980) evaluated 27 screen-caged sensors, like the one shown in Fig. 3.2.3–3A, and reported a calibration drift of <3% after 1 yr of field exposure.

Because of such findings, methods have been proposed to facilitate periodic removal, recalibration, and replacement of in situ sensors without repeated disruption of the soil or rock matrix. These methods rely on the installation of an access pipe that allows for insertion and removal of a sensor that is either isolated within a screened air cavity at the end of the pipe, or is isolated within a small drilled hole that extends a short distance beyond the end of the access pipe. The methods described by Moore and Caldwell (1972) were proposed for vertical installations, whereas those described by Fischer (1992) and Tumbusch and Prudic (2000) were developed for the installation of sensors placed laterally out from an experimental instrument shaft that extends to a depth of 13.7 m. Photographs of the instrument shaft can be viewed online (U.S. Geological Survey, 1998). In addition, Schneebeli et al. (1995) developed techniques for measuring water potential in crystalline-rock at the end of drill holes that extended 1.6 m into a tunnel wall.

For installations where sensors are not retrievable, replicate units have been used to make a qualitative assessment of the field-measured values. For example, in a multiple-year study, Andraski (1997) reported that 77% of the units remained operable for ≥4.5 yr. Recognizing the variability in electrical-output characteristics among sensors and the potential effects of spatial variability on water potential measurements, the generally good agreement between replicate units provided confidence in the field-measured values: differences typically were ≤0.5 MPa. A general observation, made on the basis of these data and those reported by Scanlon (1994), was that sensors that remained operational during their first 6 mo of field use typically remained operational for monitoring periods that ranged from 20 mo to several years. Similar observations have been made at other desert sites (E.P. Weeks, personal communication, 1996; M.A. Kurzmack, personal communication, 1999). Because performance of a sensor can depend on its design and how it is used, as well as the environmental conditions to which it is exposed, additional experimental work is needed to evaluate the effects of specific installation procedures and field conditions on temporal changes in sensor sensitivity.

3.2.3.3.e Separation of Matric and Osmotic Water-Potential Components

To this point we have focused on measurement of water potential, defined here as the sum of the matric potential and the osmotic potential. In some cases it is important to know the magnitude of each of these two water-potential components. Richards and Ogata (1961) separated the matric and osmotic components by bringing soil samples to a specified matric potential on a pressure membrane and then measuring the water potential with a thermocouple psychrometer. However, several workers have raised questions about the accuracy of pressure-plate measurements made at matric potentials below about –0.5 MPa (e.g., Madsen et al., 1986; Campbell & Mulla, 1990; Jones et al., 1990; Andraski, 1996). For very precise work, Oster et al. (1969) combined psychrometric and pressure measurements into a single apparatus that consisted of a ceramic-cupped (1.5-MPa air-entry pressure) Peltier sensor embedded in soil contained in a pressure vessel. The water potential was measured with the air pressure in the vessel at atmospheric pressure. Incremental increases in air pressure then were applied to the soil sample, and because the inside of the ceramic-cupped sensor was vented to the atmosphere, each increment of air pressure increase raised the matric potential of the water in the ceramic wall by an equal increment. The osmotic potential was obtained when further increases in air pressure did not change the thermocouple psychrometer reading. The matric potential was calculated by subtracting the osmotic potential from the water potential. The standard error of measurement of the water potential components was

0.004 MPa. This represents the practical maximum precision that can be obtained with Peltier sensors under ideal laboratory conditions (Rawlins & Campbell, 1986).

For less precise work, an estimate of osmotic potential can be calculated from the concentration of a solute in soil water according to the van't Hoff equation (Campbell, 1985)

$$\psi_o = -vC\chi RT \qquad [3.2.3\text{–}4]$$

where ψ_o is osmotic potential (MPa), v is number of osmotically active particles per molecule (e.g., 2 for NaCl), C is concentration (mol Mg^{-1}), χ is osmotic coefficient (unitless), and R and T are as defined in Eq. [3.2.3–1]. Osmotic coefficients for common solutes are given by Robinson and Stokes (1959).

Rough correlations exist between osmotic potential and electrical conductivity of the soil solution, so a relatively rapid approximation of the osmotic potential can be obtained either from in situ salinity-sensor measurements (Scholl, 1978) or from electrical conductivity measurements corrected for water content (U.S. Salinity Laboratory Staff, 1954). Osmotic potential of a soil solution can be calculated from the electrical conductivity of a saturation extract by

$$\psi_o = -\text{EC}_e(\theta_s/\theta)0.036 \qquad [3.2.3\text{–}5]$$

where ψ_o is osmotic potential (MPa), EC_e is electrical conductivity of the saturation extract (dS m^{-1}), θ_s/θ is the ratio of saturated and actual water contents ($\text{m}^3\ \text{m}^{-3}$), respectively, and 0.036 is a coefficient (MPa dS^{-1} m) recommended by the U.S. Salinity Laboratory Staff (1954). This relation assumes that the soil solution is an ideal solution, and it ignores anion exclusion and precipitation of solutes with low solubility. Osmotic potentials can also been estimated from electrical conductivity measurements of a saturated soil paste (Roundy, 1984).

3.2.3.4 Comments

Thermocouple psychrometry is a reliable and accurate method for determining water potential (sum of matric and osmotic potential) if proper techniques and precautions are used. The method covers a broad water-potential measurement range of interest to studies of soil–plant–water relations and of unsaturated-zone hydrology, but the method is best suited for measurements in drier soils. Because the method measures conditions in the vapor phase, it does not require a continuous liquid phase and only microscopic quantities of water are involved in the measurement. In addition, the method is versatile and equipment is commercially available for use in laboratory, glasshouse, and field experiments. Essential to the method are careful cleaning, handling, and calibration of instruments, and consistency in measurement technique.

The measurements themselves can be made fairly quickly, often with the use of automated data-acquisition equipment, but sufficient time must be allowed to ensure complete vapor-pressure equilibration, and steps must be taken to detect and prevent temperature-gradient errors. Laboratory measurements made with a sample chamber require only a small sample, which is advantageous when repeated sampling is necessary. However, when working with small samples, precautions are necessary to prevent large errors that can be caused by evaporative loss during sample handling. Some of the limitations of thermocouple psychrometry are calibration dependence, susceptibility to error in environments with rapidly changing temperature, susceptibility to corrosion in acidic environments, a need for sensitive measuring equipment, and a degree of complexity that makes the method somewhat difficult to understand and apply.

Despite the reliability and accuracy of thermocouple psychrometry, the need for close attention to details in cleaning, calibrating, and installing relatively fragile sensors has limited the broad application of the method to field studies of soil water movement. Thus, the operational life span of these instruments is largely unknown, but historically has been anticipated to be relatively short. However, there is evidence from multiple-year studies that in situ sensors can be used reliably for at least 3 to 5 yr. Improvements in the longevity of sensor performance may result from the use of nontraditional installation techniques that place the sensor in an air cavity rather than in direct contact with the soil, and from the use of protective thermojunction coatings such as those now being applied to some commercially available sensors.

3.2.3.5 Commercial Sources

Commercial sources of thermocouple psychrometry equipment and supplies:

3.2.3.5.a Laboratory Sample Chambers

Decagon Devices, Inc., P.O. Box 835, Pullman, WA 99163, www.decagon.com

Wescor, Inc., P.O. Box 361, Logan, UT 84323, www.wescor.com

3.2.3.5.b In Situ Sensors

J.R.D. Merrill Speciality Equipment, 1105 West 2200 South, Logan, UT 64321

Wescor, Inc., P.O. Box 361, Logan, UT 84323, www.wescor.com

3.2.3.5.c Electronic Measurement and Control Equipment

Campbell Scientific, Inc., 815 West 1800 North, Logan, UT 84321, www.campbellsci.com

Decagon Devices, Inc., P.O. Box 835, Pullman, WA 99163, www.decagon.com

Wescor, Inc., P.O. Box 361, Logan, UT 84323, www.wescor.com

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