Energy-Related Methods: Psychrometers

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INTRODUCTION

The measurement of the direction and magnitude of contaminant migration in the subsurface is often hampered by the heterogeneous and complex nature of most geologic media. An alternative to direct measurement of subsurface migration routes and rates in the unsaturated zone is to indirectly determine water flow using the direction and magnitude of the hydraulic gradient and the hydraulic conductivity of the medium. The direction and magnitude of fluid flow is governed by the tensorial form of Darcy's law:

\[ q = -K(\psi) \nabla H \]

where

- \( q \) = fluid flux vector, m/s;
- \( K(\psi) \) = suction-dependent hydraulic conductivity tensor, m/s;
- \( \nabla H \) = hydraulic gradient, dimensionless;
- \( H \) = total hydraulic head, m;
- \( z \) = elevation head, m;
- \( \psi \) = matric suction head, m; and
- \( \phi \) = osmotic potential head, m.

The estimation of the hydraulic gradient requires knowledge of the distribution of the matric suction and the osmotic potential. The hydraulic conductivity tensor function can be determined in the laboratory using core segments extracted from the site of interest, or from field-scale permeability tests using water or air (see, e.g.,...
Chapter 28 by Evans and Rasmussen in this book). Because the hydraulic conductivity tensor is a strongly nonlinear function of the matric suction, it is important to know the ambient matric suction so that the appropriate value of hydraulic conductivity can be determined for the site.

An important tool for estimating the fluid potential, and hence the flow gradient, is the psychrometer. This device measures the potential of the water vapor present in the subsurface atmosphere. If the potential of the water vapor is equal to the potential of the pore fluid, then the psychrometer provides a means for identifying the pore fluid potential. An additional use of the thermocouple psychrometer is the determination of the moisture characteristic curve for fluid potentials greater than those readily attained using porous plates, approximately 5 bars. The fluid potential of field-collected samples is estimated by allowing samples to equilibrate at specified water contents, thus extending the characteristic curve to conditions much drier than normally obtained from pressure extraction vessels.

THEORY OF PSYCHROMETRIC OPERATION

Psychrometers measure the vapor-phase water activity in the subsurface atmosphere surrounding the sensor. The water activity is related to the relative humidity and the vapor pressure by:

$$a = h / 100 = p / p_o$$

(2)

where

- $a$ = water vapor activity, dimensionless;
- $h$ = relative humidity, percent;
- $p$ = ambient water vapor pressure, kPa; and
- $p_o$ = maximum (saturated) water vapor pressure at ambient temperature, kPa.

The saturated vapor pressure, $p_o$, is a function of the ambient temperature, $T$ (K), and can be approximated using:

$$p_o = \exp(19.017 - 5327/T)$$

(3)

For water vapor in equilibrium with the liquid phase, the water activity is related to the fluid pressure by:

$$\Psi = (p R T / M) \log(a)$$

(4)

where

- $\Psi$ = fluid potential, J-m$^{-3}$;
- $p$ = density of water, 998.21 kg-m$^{-3}$ at 20°C;
- $R$ = ideal gas constant, 8.314510 J-K$^{-1}$mol$^{-1}$;
- $T$ = ambient temperature, K; and
- $M$ = molecular weight of water, 18.05128 g-mol$^{-1}$.

The fluid potential calculated using Equation 4 is generally used to estimate the matric suction of the liquid water present in pores. The fluid potential in the pores may also include, however, the osmotic potential associated with solutes dissolved in the pore fluid. It is important to note that osmotic potentials may be significant when elevated solute concentrations are present. The pore fluid chemistry can be used, if necessary, to estimate the magnitude of the osmotic potential.

The dew-point temperature, $T_o$, is the temperature at which the ambient atmosphere must be chilled in order for water to condense (i.e., for $p_o = p$). An approximate expression for the dew-point temperature is:

$$T_o = [1 - (\log(a)/5327)]^{-1}$$

(5a)

The dew-point depression, $\Delta T_d$, is the difference between the ambient and dew-point temperatures, or approximately:

$$\Delta T_d = (T - T_o) = T [1 - (1 - T \log(a)/5327)]^{-1}$$

(5b)

Table 21.1 presents the relationship between relative humidity, dew-point depression temperatures, and matric suction for an ambient temperature of 20°C (273 K).

Psychrometers are a generic class of instruments used to measure the relative humidity that employ a dry bulb thermometer to measure the ambient temperature, and a second, wet bulb thermometer to measure the lower temperature associated with an evaporating fluid. For most subsurface applications, the ambient water vapor pressure will be near the saturation vapor pressure, i.e., the relative humidity will generally be greater than 99% and the dew-point depression will be less than 0.2°C. Most liquid-filled thermometers lack sufficient precision to provide measurements within ±0.1°C, much less the precision ±0.001°C required for matric suction measurements near 1 bar. Thermocouple psychrometers are used instead to measure the small temperature depressions associated with relative humidities in the subsurface.

<table>
<thead>
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<th>Relative Humidity (%)</th>
<th>Dew-Point Depression (°C)</th>
<th>Matric Suction (bars)</th>
</tr>
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<td>100</td>
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<td>0</td>
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TYPES OF THERMOCOUPLE PSYCHROMETERS

Thermocouple psychrometers employ a bimetallic junction (e.g., copper-constantan or chromel-constantan), known as a thermocouple. Figure 21.1 illustrates the primary components of the thermocouple junction. The junction produces an electric current that is related to the junction temperature. This coupled heat-current phenomenon is known as the Peltier effect. The junction temperature can be found by measuring the current generated by the thermocouple junction, or, conversely, the temperature of the junction can be changed by inducing a current through the junction.

Thermocouple psychrometers use either the "wet-bulb" or "dew-point" methods to determine the water activity of the atmosphere surrounding the junction. Both methods use a thermocouple to measure the ambient temperature. The wet-bulb psychrometer measures the temperature of a "wet" junction (i.e., a junction covered with water), while the dew-point psychrometer measures the temperature at which saturated vapor pressure equals the ambient vapor pressure.

Wet-Bulb Psychrometry

The wet-bulb temperature is determined either by placing a small drop of water on a copper-constantan thermocouple junction (Richards method), or by cooling the thermocouple using the Peltier effect until water condenses on it (Spanner method). Cooling of the thermocouple is monitored as the water evaporates. For both methods, the drop in temperature on the wet-bulb (i.e., the wet-bulb depression) varies with the rate of evaporation. The evaporation rate, in turn, increases as the water activity surrounding the thermocouple decreases.

The equilibrium temperature attained by the wet bulb depends on factors that influence heat flow toward the junction and vapor flow away from the junction. Heat fluxes to the wet junction result from conduction through the connecting wires, from radiation to the bulb from the walls of the sample chamber, and from conductive and convective heat gain from the surrounding air. These heat fluxes are controlled by the dimensions of the sample chamber and thermocouple components. Cooling at the wet junction is proportional to the product of the latent heat of vaporization and the evaporation rate, a function of the water activity within the chamber and the diffusivity of water in air. These factors generally increase with temperature. The diffusivity of water in air also decreases with atmospheric pressure.

![Figure 21.1. Schematic diagram of Peltier junction and psychrometer chamber.](image)

The effects of temperature and pressure are incorporated using the conventional psychrometer equation (Campbell, 1979):

$$ a = 1 - \Delta T (s + g) / p_0 $$

where

- $s$ = slope of the saturation vapor pressure curve, Pa·K⁻¹;
- $g$ = psychrometer constant, Pa·K⁻¹; and
- $\Delta T = $ wet-bulb depression, K.

The psychrometer constant, $g$, varies with atmospheric pressure and is relatively insensitive to temperature changes. The slope of the saturation vapor pressure curve, $s$, and the saturated vapor pressure of water, $p_0$, are significantly affected by temperature changes.

Dew-Point Psychrometry

An improved psychrometer technique uses a feedback loop to control the Peltier cooling rate, thereby maintaining the temperature of the measuring junction at the dew point (i.e., the temperature at which the ambient vapor pressure equals the saturated vapor pressure, $p = p_0$). When held at the dew-point temperature, a wet thermocouple junction neither loses water through evaporation nor gains water through condensation because heat flow to the wet junction from its surroundings is exactly offset by adjustments in the cooling current. The measurement is independent of the rate of heat flow to the wet junction and, thus, no water vapor diffusion occurs. This method eliminates most of the temperature and pressure dependence associated with wet-bulb measurements. The lowest matric suction that can be reliably measured in the laboratory using this device is approximately 1 bar under ideal conditions, with a lower limit of approximately 3 to 5 bars for field applications.

Chilled-Mirror Psychrometry

The chilled-mirror psychrometer improves the accuracy of the water activity measurement by employing a mirror that is chilled to near the dew-point temperature. Slight changes in the temperature of the mirror surface results in condensation on the surface of the mirror when the mirror surface drops to the dew-point temperature. The induced condensation causes a change in the light reflection properties of the surface. Monitoring of the change in light reflection from the mirror can then be used to determine the dew-point temperature in the laboratory from 1.5 to over 2500 bars.

USGS Four-Wire Current Psychrometer

While psychrometers are normally installed near the ground surface at depths of less than a few meters, psychrometers have been installed to a depth of over 350 m in deep unsaturated volcanic rocks (Montazer et al., 1988). A new method suitable for monitoring in deep unsaturated media (up to 600 m) has been developed by Merrill Instruments and J.P. Rousseau of the U.S. Geological Survey, Denver. The device uses a 4-wire thermocouple psychrometer in current mode rather than in the voltage
Suction values between 0.5 to 80 bars.

PSYCHROMETER CALIBRATION

Regular calibration of thermocouple psychrometers is necessary due to the possibility of corrosion of the metals used to create the thermocouple junction. Another reason for regular calibration is the possible accumulation of soluble salts on the junction which affects the measured wet-bulb and dew-point temperatures.

Psychrometers can be calibrated using a salt solution of known water activity. The salt solutions are used to create an osmotic potential which maintains a prescribed water vapor activity in the atmosphere above the salt solution. One possible design for the calibration chamber uses a closed, thermally-insulated chamber partially filled with a reference solution. The psychrometers to be calibrated are placed in the air space above the solution (Figure 21.2), ensuring that the salt solution does not come into direct contact with the psychrometer or psychrometer cable. Sufficient time should be allowed for the contents of the chamber to come into thermal equilibrium, e.g., overnight for a 100 mL solution placed in a 500-mL chamber (Rhodes, 1993).

Two methods using osmotic potentials are used for establishing the known water activities. The first method employs salt solutions (e.g., NaCl or KCl) of variable concentrations to impose a range of calibration points. Table 21.2 presents a list of NaCl and KCl salt solutions and their associated relative humidities and matric suctions. The osmotic potential associated with various solutions can be calculated using Raoult’s law and Kelvin’s law (Rasmussen and Evans, 1986):

\[
a = \frac{55.556}{55.556 + O}
\]  

(7a)

and

\[
\phi = \frac{RT}{V} \log_e(a)
\]

(7b)

where O is the solute osmolality, obtained from standard handbooks of chemistry and physics. Because the osmotic potential, \(\phi\), is a function of temperature, calibration values should be recalculated if the reference solution varies from 20°C.

A significant problem associated with the use of this technique lies in the inability to maintain a constant salt solution concentration. Evaporation of the salt solution may cause an unacceptable increase in the salt concentration, and, hence, osmotic potential, while condensation may cause a decrease in the salt solution concentration.

Saturated salt solutions are used to avoid the problems associated with changing salt solution concentrations (Rhodes, 1993). In this method, a surplus of salt is added to a volume of water so that if evaporation or condensation were to occur, then salt would precipitate or dissolve to maintain a constant concentration. Table 21.3 presents a list of selected salts, with the relative humidities and water potentials given by their saturated solutions at 20°C.

For both methods, the psychrometer(s) are placed in at least two, and preferably four, different salt solutions that represent the range of matric suctions at the site of interest. After allowing for the temperature and vapor pressure within the chamber to equilibrate, readings of psychrometer output are obtained, and the psychrometers are moved to another chamber which contains a different fluid potential. The psychrometer reading and chamber temperature should be recorded for each solution once the reading becomes steady. Once the calibration data have been collected, the observed readings should be compared to the theoretical values specified by the manufacturer. If the psychrometer departs from the theoretical value beyond the

![Figure 21.2. Chamber for psychrometer calibration using salt solutions.](image-url)
FIELD INSTALLATION OF PSYCHROMETERS

It is extremely important that only the smallest possible installation hole surrounding the psychrometer be used. A small installation hole with minimal backfilling should be used to minimize disturbance to the geologic medium surrounding the probe. The hole should be backfilled with a silica flour or native geologic media to minimize void spaces. Clays of low permeability should not be used as backfill material for two reasons. First, clays require long times to equilibrate with the ambient matric suction. Second, clays may be of such low permeability that they prevent equilibration of water vapor between the psychrometer and the surrounding porous medium. For these reasons, sealing materials such as grouts and bentonite clays should be avoided during borehole completion to minimize absorption or release of water in the region surrounding the monitoring interval.

Figure 21.3A demonstrates one possible field installation strategy. A small diameter hole is placed vertically to the desired depth. A drilling method should be used that does not employ water or air (e.g., a percussion tool or auger may be suitable). Psychrometers should be emplaced in duplicate pairs for the purpose of evaluating the magnitude of instrument drift. A large weight can be attached to the thermocouple leads near the psychrometer pairs to help lower the probes to the desired depth, and to provide a large thermal mass to minimize thermal transients. The hole is then backfilled with a silica flour moistened to reproduce the anticipated matric suction at the site of interest.

Another possible field installation strategy is to use inflatable packers. In this application, a monitoring interval is flanked by two packers to isolate the zone of interest (Figure 21.3B). The packers are expanded to seal the interval using compressed gas lines connected to a compressor or bottled gas on the surface. Because the expanding gas cools adiabatically when the packers are inflated, a large thermal perturbation will be observed and must be allowed to dissipate prior to obtaining a reliable reading. The advantage of using inflatable packers lies in the ability to reposition the psychrometers so that greater spatial coverage can be obtained using the same instruments.

INTERPRETATION OF PSYCHROMETER MEASUREMENTS

As described above, psychrometric measurements can be made using either: (a) the dew-point method, (b) the wet-bulb method, or (c) a combination of both. Figure 21.4 presents representative outputs for a sample at 25 bars and 32.8°C. It can be noted that the output reading in micromvolts shows a more pronounced deflection using the dew-point method than for the wet-bulb method. The deflection to a stable micromvolts reading is the value used to calculate the matric suction.

For some observations, however, no clear deflection is observed. Instead, a more gradual drift in reading is observed over time. This drift is especially apparent in the wet-bulb method, and when the dry-bulb technique is used near the upper or lower limit of its range. Under these conditions, utilization of both techniques provides redundant estimates of matric suction, along with an indication of measurement accuracy. In general, better accuracy is indicated if both techniques provide consistent matric suction estimates.

Figure 21.5 presents results of laboratory psychrometric readings for 105 rock core segments obtained from the Apache Leap Tuff Site in central Arizona (Rasmussen et al., 1990). The cylindrical core segments (measuring 1 cm in length and 1 cm in diameter) were collected at known water potentials. The thermocouple psychrometer using a backfill extends into the monitoring interval. The advantage of using inflatable packers lies in the ability to reposition the psychrometers so that greater spatial coverage can be obtained using the same instruments.

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Laboratory moisture characteristic (drying) curves for 105 core segments from the Apache Leap Tuff Site, central Arizona. Extraction and psychrometer curves show all observations (O,X) and mean (lines).

LABORATORY PSYCHROMETER DATA

Figure 21.5. Laboratory moisture characteristic (drying) curves for 105 core segments from the Apache Leap Tuff Site, central Arizona. Extraction and psychrometer curves show all observations (O,X) and mean (lines).

cm in diameter) were first saturated in a sterile, deionized solution containing 0.001 M CaSO₄. The segments were then allowed to dry on a precision balance to reach a target relative saturation (between 70 and 10% saturation in 10% increments). The segments were then transferred to a psychrometer chamber, allowed to equilibrate, and the matric suction was determined. Also shown for comparison are moisture characteristic curves (drying curves) obtained for 105 cores using an extractor vessel technique. A reasonably good agreement can be observed by extrapolating between the two sets of data.

An interesting field application of thermocouple psychrometers was conducted at Kartchner Caverns in southern Arizona. Relative humidities very near saturation within the cave were monitored to determine the magnitude and direction of water vapor movement resulting from the enlargement of the cave entrance. Figure 21.6 presents the interpreted matric suction within the cave atmosphere. It is apparent from the figure that the two stations closest to the entrance are significantly drier than more distant stations. If it can be assumed that vapor flux within the more remote sections of the cave is small and that the cave atmosphere is in equilibrium with the subsurface media surrounding the cave, then the matric suction of the rock surrounding the cave can be estimated to be approximately 5 bars. No apparent trend can be discerned in the cave matric potential beyond the first two stations.

PSYCHROMETRY ERRORS

Accurate determinations of matric suction in the subsurface require an understanding of the potential sources of transient and systematic errors. Errors from the following causes should be considered:

- temperature fluctuations with time,
- temperature gradients,
- vapor pressure gradients, and
- wet junction characteristics.

Laboratory psychrometers are designed to measure the water potential of soil samples by sealing the thermocouple just above or within the sample. One design allows the soil samples to be packed into several stainless steel cups, which are rotated to meet the thermocouple. These are fitted either with a Richards-type junction modified with the addition of a ceramic bead or with a Peltier-type wet junction. Measurements made with this equipment may be significantly affected by temperature fluctuation with time, particularly when the sample is considerably smaller than the dimensions of the chamber. The accuracy is greatest when the sample completely surrounds the junction. The effect of temperature fluctuations can be minimized by enclosing the device in a constant temperature bath or placing the device in contact with a large heat sink to reduce the rate of temperature changes.

Field psychrometers utilize thermocouples protected by cups or bulbs of various sizes, usually ceramic or fine mesh, to provide a protected space within the in situ environment. Field measurements are often subject to thermal gradients. Potential errors due to nonisothermal media can be eliminated if the psychrometer is oriented so that its axis of symmetry is perpendicular to the temperature gradient, or if a
thermal mass (e.g., a weight) is placed near the device to minimize thermal transients.

Thermocouple psychrometer devices are currently available that measure both wet-bulb and dew-point temperatures in the field. Field units should be placed in duplicate to allow multiple devices to be used for verifying accuracy. Also, the devices should be regularly removed and recalibrated to determine whether corrosion or contamination of the bimetallic junction may have occurred. Psychrometers should be placed in such a manner as to assure minimal void space surrounding the device, and backfill material should be minimized by using an installation hole that closely matches the dimensions of the psychrometer. Also, psychrometers protected using ceramic bulbs may require prolonged equilibration times compared to fine mesh psychrometers.

While vapor pressure gradients may be caused by extraneous sources or sinks for water vapor, this problem is rare with Peltier psychrometers and can be reduced if samples are not significantly smaller than their sample chambers. Both laboratory and field psychrometer measurements may be affected by wet junction characteristics. Ideal psychrometer conditions assume free evaporation from a spherical wet junction surface. Yet actual size and shape of the wet area depends upon its wetting characteristics, among other factors, and can be contaminated with use. Such changes can be eliminated by cleaning or recalibrating.

Deviations from ideal psychrometer operating conditions may cause significant loss of psychrometer sensitivity, and substantial errors can be introduced if temperature differences between the reference junction and the liquid phase are not controlled to within ±0.001°C (Rawlins and Campbell, 1986). Thus, there is a critical need to accurately measure temperatures; a small temperature difference error results in a large error in the calculated fluid potential.

Caution should be exercised when interpreting psychrometric readings collected near a site containing volatile liquids. The psychrometric equation assumes that water is the first liquid to condense from the soil atmosphere. For sites where other volatile liquids are present in sufficient quantity to achieve partial pressures near their vapor-phase saturation pressure, the first liquid to condense may be a liquid other than water. For example, if a benzene-saturated site is suspected, and the wet-bulb depression is smaller or the dew-point temperature is higher for the benzene gas than for water, then the benzene may condense prior to water. If this possibility is confirmed, then the vapor pressure of benzene can be determined, but no information about water saturation is possible.

A further complication results when two vapors form an azeotrope upon condensation. An azeotrope is a mixture of liquids whose components do not undergo dilution or concentration as the mixture is distilled. For the previous example using benzene, the condensate may consist of a mixture of benzene and water, with the benzene comprising approximately 90% of the mixture by weight. As the mixture evaporates during a test reading, the concentrations of both components remain constant, altering the psychrometric relationship which assumes the presence of pure water. This binary azeotropic system is further complicated if more than two volatile components are present.

It should be emphasized that the caveats described here do not preclude the use of psychrometers at contaminated sites. While the methods may not provide quantitative evidence regarding fluid potentials, temporal changes in readings can provide crucial information regarding direction and magnitude of migration of water and contaminants.

ADDITIONAL INFORMATION

An excellent, although somewhat dated, summary of thermocouple psychrometry theory and applications can be found in Brown and Van Haveren (1972). Rawlins and Campbell (1986) also provide an excellent overview of thermocouple psychrometry.

REFERENCES


