A thermodielectric analyzer to measure the freezing and moisture characteristic of porous media

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[1] The freezing and moisture characteristics of porous media are difficult to measure. We have designed an instrument to measure the freezing characteristic of a porous medium in the range −20 to 0°C. Because of the similarity between the freezing characteristic and the moisture characteristic, the data obtained can be used to infer the moisture characteristic from about −30 to −23,600 J kg⁻¹. Temperatures and unfrozen water contents are measured with a thermistor and a spiral-shaped transmission line connected to an oscillator, respectively. Temperatures are converted to water potential using the Clapeyron equation. Experimental results obtained with the freezing technique were compared with vapor pressure methods. The four test media used, a silt loam soil, a silty-clay loam, a clay, and a sandstone, showed good agreement between freezing and standard methods. The freezing technique described here has a water potential resolution of about −11 J kg⁻¹. An entire characteristic can be determined within 24 hours.

INDEX TERMS: 1823 Hydrology: Frozen ground; 1866 Hydrology: Soil moisture; 1875 Hydrology: Unsaturated zone; 1894 Hydrology: Instruments and techniques; KEYWORDS: frozen soil, soil freezing characteristic, soil moisture characteristic, water retention, TDR, instrumentation


1. Introduction

[2] One of the most relevant hydraulic properties of the vadose zone in terms of flow and transport is the relation between the water content and the energy status of the water, i.e., the water potential. This relation, known as the water retention function or the moisture characteristic, is difficult to measure experimentally. The experimental methods currently used to determine the moisture characteristic include hanging water columns, pressure plates, thermocouple psychrometers, and water activity meters [Campbell and Gee, 1986; Campbell, 1988]. Each of these methods can only measure a limited range of water potentials, and no single instrument is able to measure a complete soil moisture characteristic.

[3] The determination of a moisture characteristic is time consuming, particularly because at large negative potentials the hydraulic conductivity of the sample becomes very small, requiring extensive equilibration times. Due to the lack of equilibration at large negative potentials, measurements made with pressure plates are susceptible to errors, particularly at potentials below −500 J kg⁻¹ [Campbell, 1988]. Madsen et al. [1986] found that, at the same sample water content, the water potential determined by thermocouple psychrometers was always higher than the water potential determined with the pressure plate. A similar observation was reported by Peck and Rabbidge [1969] for a loamy soil, where the soil moisture characteristics measured with a pressure plate apparatus showed consistently lower water potentials than the characteristics determined with an osmotic tensiometer. The main reasons for these discrepancies are lack of thermodynamic equilibrium and partial interruption of the continuous water phase during pressure plate measurements [Madsen et al., 1986; Campbell, 1988].

[4] The freezing point depression of liquid water in a porous medium may provide an alternative way to determine the moisture characteristic. It has long been recognized that soils lower the freezing point of water. Early studies have shown that the freezing point depression of water in soils depended on the moisture content and the soil type, and it was suggested that the wilting point of soils could be determined by measuring the freezing point depression [Bouyoucos and McCool, 1916]. Freezing point measurements at the permanent wilting point have subsequently been made by several investigators [e.g., Bodman and Day, 1943; Blair et al., 1950]. It was experimentally demonstrated that the freezing point depression in porous media depends on the water potential [Scholfield and Botelho da Costa, 1938; Day, 1942; Cannel and Gardner, 1959]. When soil water freezes, the water closest to the soil particles remains in liquid form. The reason soil water can remain unfrozen at temperature well below freezing point, is that the energy status of water is lowered by the forces (adsorptive and capillary) exerted by the soil, resulting in a decrease of the freezing point of soil water.
The simultaneous measurement of temperature and unfrozen water content, over a wide range of temperatures, allows the experimental determination of the freezing characteristic. The freezing characteristic can be related to the moisture characteristic by calculating the water potential of the frozen soil from soil temperature using the Clapeyron equation [Koopmans and Miller, 1966; Miller, 1980]. Good agreement was found between moisture characteristics obtained from freezing characteristics and independent measurements with pressure plates in the range of 0 to \(-400\) J kg\(^{-1}\) [Koopmans and Miller, 1966]. In a field study, the moisture characteristic obtained from the freezing characteristic was in good agreement with the one determined with field installed water potential and water content sensors [Spaans and Baker, 1996].

The freezing characteristic by itself is important to describe water and heat flow in frozen porous media [Stähli et al., 1999]. Experimental measurements of the freezing characteristic have not yet been developed. Laboratory conditions, allowing more precise measurement of sample temperature and water content, can overcome limitations encountered in field studies, such as temperature fluctuations, uncertainty of the bulk density and water content measurement, or incomplete freezing of the soil. The purpose of this study was (1) to develop a laboratory method to measure the freezing characteristic of a porous medium, (2) to infer the resulting moisture characteristic, and (3) to compare the moisture characteristic obtained in (2) with data obtained from dew point measurements.

2. Theory

2.1. Clapeyron Equation

The Clapeyron equation describes the equilibrium between two phases of the same substance at a given pressure, and can be written in terms of potential units, energy per mass, as [Lewis and Randall, 1961; Spaans and Baker, 1996]:

\[
d\Psi_{\text{tot,1}} - d\Psi_{\text{tot,i}} = \frac{\lambda}{T} dT \tag{1}
\]

where \(\Psi_{\text{tot,1}}\) and \(\Psi_{\text{tot,i}}\) are total water potentials for the liquid and ice phases (J kg\(^{-1}\)), respectively, \(T\) is the temperature (K), and \(\lambda\) is the latent heat of fusion of water (333.7 kJ kg\(^{-1}\) at 273.15 K). The integral form of (1) is:

\[
\Psi_{\text{tot,1}} - \Psi_{\text{tot,i}} = \int_{T_i}^{T} \frac{\lambda}{T} dT \tag{2}
\]

where the integration is made from the reference point \((T_0 = 273.15\) K, \(\Psi_0 = 1\) atm) to an arbitrary point \((T; \Psi_{\text{tot,1}}, \Psi_{\text{tot,i}})\).

The total water potential (or pressure) both for liquid water and ice is given by the sum of matric potential (\(\Psi_m\)) and solute or osmotic potential (\(\Psi_s\)). Note that we express the Clapeyron equation on a mass rather than on a mole basis, which is convenient for application to soil water potentials.

Salt have a very low solubility in ice, and therefore tend to be excluded from the ice phase when an electrolyte solution freezes [Petrenko and Whitworth, 1999, pp. 98–112]. Assuming solutes are quantitatively expelled from the ice phase when water freezes, the total potential for ice is equal to its matric potential (i.e., \(\Psi_s = 0\)). When liquid water and ice coexists, and if ice is assumed to be at atmospheric pressure (\(\Psi_{\text{tot,i}} = 0\)), then (2) gives the water potential of the liquid phase from temperature only. The latent heat of fusion of water is temperature-dependent, and Spaans and Baker [1996] obtained the following regression equation \((R^2 = 0.99)\) from data published in the work of List [1951]:

\[
\lambda(T) = -712.38 + 5.545T - 6.28 \times 10^{-3}T^2 \tag{3}
\]

Combining (2) and (3), the water potential of the liquid phase can be written as [Spaans and Baker, 1996]

\[
\Psi_m = -712.38 \ln \frac{T}{T_0} + 5.545(T - T_0) - 3.14 \times 10^{-3}(T^2 - T_0^2) - \Psi_s \tag{4}
\]

where \(\Psi_m\) and \(\Psi_s\) are in kJ kg\(^{-1}\) and \(T\) is in K. Equation (4) gives the total water potential from temperature only. The equation is nearly linear with a slope, \(d\Psi_m/dT\), of 1.18 kJ kg\(^{-1}\) K\(^{-1}\).

2.2. On the Similarity Between Moisture and Freezing Characteristic

The determination of the moisture characteristic from knowledge of the freezing characteristic is based on the hypothesis that similar information is contained in the two properties. Koopmans and Miller [1966] postulated that because of the difference between the surface tensions of water-air (\(\gamma_{wa}\)) and water-ice (\(\gamma_{wi}\)) interfaces, a direct relationship between the moisture characteristic and the freezing characteristic can be drawn only for adsorbed water. The reason is that, according to Miller [1980], the adsorptive component acts solely on the mineral-water interface, making the phase on the other side of the water film irrelevant in determining the magnitude of the adsorptive forces. The capillary component is, instead, affected by the surface tension of the water-air and water-ice interfaces. Koopmans and Miller [1966] reported a value of 2.2 for the ratio \(\gamma_{wa}/\gamma_{wi}\). Since soils represent a mixture of capillary and adsorbed forces, the rule of similarity would apply only in the dry region of the curve (at large negative potentials), where only adsorptive forces determine the magnitude of the moisture characteristic. In the wet range of the curve (less negative potentials), the rule of similarity could not be applied a priori, unless corrections for capillary forces are introduced in the wet range of the moisture characteristic.

It is difficult to determine at which potential capillary and adsorbed water dominate in the porous medium. Field data reported by Spaans and Baker [1996] indicate good
agreement between moisture and freezing characteristic using (4) for potentials more negative than about $-40$ to $-50$ J kg$^{-1}$.

3. Materials and Methods

3.1. Thermodielectric Analyzer

[12] The measurement of the freezing characteristic of a porous medium is based on the precise measurement of temperature and liquid water content below 0°C. In this study, temperature was measured with a high precision thermistor, and the liquid water content with a transmission line operated as Transmission Line Oscillator (TLO).

[13] A schematic of the thermodielectric analyzer is shown in Figure 1. The porous medium to be measured was completely water saturated and placed into a cylindrical sample holder of 2.06-cm radius and 0.8-cm height, made out of aluminum. Temperature was controlled by two Peltier coolers. The aluminum material is an alloy (6061-T6) consisting of 97.9% Al, 0.62% Si, 0.28% Cu, 1.0% Mg and 0.2% Cr, which has a thermal conductivity of 167 W m$^{-1}$ K$^{-1}$ at 25°C and a specific heat capacity of 396 J kg$^{-1}$ K$^{-1}$ [Sharma, 2000]. Two thermistors were inserted into the aluminum block to measure the block and sample temperatures. A transmission line was placed on the surface of the aluminum block to measure sample water content. A transmission line was placed on the surface of the aluminum block to measure sample water content. The sample cell was covered with insulating material (Styrodur, BASF Inc., Ludwigshafen, Germany) that has low thermal conductivity and gas diffusivity to minimize heat exchange with the ambient and to seal the sample against air or vapor exchange. The heat produced on the hot side of the Peltier coolers was removed by a heat sink equipped with a fan. A copper plate between Peltier coolers and the heat sink ensured an optimal heat conductivity. The Peltier coolers, the thermistors, and the transmission line water content sensor, were controlled by a data logger. All measurements were made in a temperature-controlled room at 5 ± 0.1°C.

3.2. Temperature Measurement

[14] Temperature was measured with two negative-temperature coefficient thermistors (NTC) (Models T101D03-DA and T320D103-CA, CornerStone Sensor, Inc., Vista, CA). The model T320D103-CA was placed inside the freezing unit to control the temperature variations, while the T101D03-DA, the smaller of the two thermistors, was placed directly underneath the transmission line to measure the sample temperature. The NTC thermistors have a precision of 0.005 K, an accuracy of ±1%, and a temperature sensitivity of their resistance of $-3$ to $-6\%$ per Kelvin, which is 10 times greater than the sensitivity of other temperature sensors, such as platinum resistance elements or thermocouples. The operating temperature ranges from $-58$ to 302°C, and the dissipation constant is 1.00 mW°C$^{-1}$ in air. The resistance versus temperature characteristic (also known as R/T curve) of the NTC thermistor forms the basis for its use as a temperature sensor. The value of a thermistor is typically referenced at 25°C and a table listing temperature and resistance was provided by the manufacturer. The thermistor calibrations made by the manufacturer were NIST (National Institute of Standards and Technology) traceable. In addition, we tested the calibration by measuring the melting points of deionized water and KCl standard solutions of known melting point, and found that the calibration curve was accurate to <0.005 K.

[15] A full-bridge circuit was used to obtain high accuracy resistance measurements. The full-bridge output voltage ($V_{\text{out}}$) is given by [e.g., Campbell Scientific, 1985]

$$V_{\text{out}} = V_{\text{in}} \left( \frac{R_2}{R_3 + R_4} \right)$$

\[5\]
where $R_s$ is the resistance of the sensor (10,000 $\Omega$ at 25°C), which is a function of temperature, $R_1$, $R_2$ and $R_3$ are fixed resistors (35,700 $\Omega$) and $V_{in}$ is the input voltage (500 mV). From (5) we can calculate the resistance $R_s$ by measuring $V_{out}$. The normalized output voltage was used to obtain the calibration curve between voltage and temperature (Figure 2)

$$T = -1.736 - 77.320\kappa + 14.334\kappa^2 - 80.536\kappa^3 + 85.084\kappa^4 - 639.191\kappa^5$$

where $T$ is the temperature in °C, $\kappa = V_{out}/V_{in}$, and the coefficient of determination is $R^2 = 1.00$.

### 3.3. Control Algorithm and Data Logger Program

The sample temperature was controlled by using two Peltier Coolers (Model 2SC055 045-127-63, Melcor Inc., Trenton, NJ) assembled in series and connected to a CR10X data logger (Campbell Scientific Inc., Logan UT). The data logger controls the current from the power supply to the coolers through the circuit shown in Figure 1. A Proportional Integration Differentiation (PID) algorithm was used as a controller. The input voltage (mV) was controlled by the difference between the measured temperature and the target temperature ($T_t - T_{target}$) and the rate of change of the temperature ($dT/dt$) between temperature at time $t$ and $t + 1$ [Murrill, 1991]:

$$V_{t+1} = V_t + K_g \left(K_p \frac{dT}{dt} + (T_t - T_{target}) \right)$$

where $V_{t+1}$ is voltage (mV) at time $t + 1$, $V_t$ is the voltage (mV) at time $t$, $T_t$ is the temperature (K) at time $t$, $T_{target}$ is the target temperature (K), $K_p$ is a gain factor, and $K_s$ is the time delay between the current input and the temperature response. The gain factor, $K_p$, was set to 0.1, and the time delay, $K_s$, was set to 100 s by manual optimization. A nine-point Savitzky-Golay filter [Press et al., 1992], was used to compute the derivative. The most recent nine temperatures values were used for each computation. The convergence criteria for the PID were set as $|T_t - T_{target}| < 0.005$ K and $|dT/dt| < 0.001$ K s$^{-1}$. Figure 3 shows an example of the temperature convergence to a target of $-9.00$°C. The PID algorithm was explicitly calibrated to avoid oscillations around the target temperature, which would cause melting and re-freezing of water, and result in hysteresis. During a measurement sequence, the sample temperature is initially decreased from 5°C (ambient temperature) to $-20$°C in about 19 minutes (Figure 4). The sample is allowed to equilibrate at $-20$°C for 78 minutes, then the temperature is increased at increments of 0.1°C (corresponding to 120 J kg$^{-1}$ potential increments), given by the temperature convergence criteria described earlier. Above $-1$°C, the temperatures were increased in increments of 0.01°C (corresponding to 12 J kg$^{-1}$ potential increments) to obtain a better resolution of the freezing characteristic. This was done because the freezing characteristic is usually very steep close to 0°C, i.e., there is a large change in liquid water content in this region. This rapid initial cooling minimizes thermally induced water movement toward the cold plate. It has been shown that water flow in frozen soil is strongly affected by temperature gradients, and thermally induced water flow is reduced when temperature decreases at high rate because the formation of ice occurs in situ at a higher rate than the migration of water toward the freezing front [Cary et al., 1979].

### 3.4. Water Content Measurement

Water content of the sample was inferred by measuring the relative dielectric permittivity using a transmis-
Figure 5. Magnified view of the transmission line used to measure relative dielectric permittivity. The spacing between the two conductors is 0.508 mm, the width of the conductors is 0.508 mm, and the total length of each conductor is 38 cm. The overall diameter of the spiral is 29 mm.

Discussion line. The transmission line used in this study was designed to measure the relative dielectric permittivity without the need to insert the sensor into the sample. The soil sample was placed directly on the surface of the transmission line. The transmission line was constructed by etching a spiral copper circuit into a copper-clad Duroid substrate (Figure 5). The Duroid (RT 6002, Rogers Corporation, Microwave Material Division, Chandler, AZ) has excellent thermal stability and a low relative dielectric permittivity. These properties make the material well suited for high frequency application such as TDR.

A transmission line oscillator (TLO) [Campbell and Anderson, 1998] was connected to the spiral waveguide. The TLO adjusts its period (or frequency) as function of the relative dielectric permittivity of the transmission line. In this study, an open reflection oscillator with balanced sensor was calibrated at 5 ± 0.1°C, and the oscillation period (ns) of the TLO by [Campbell and Anderson, 1998]

\[ t_s = \frac{L\sqrt{\epsilon}}{c} \]  

where \( L \) (m) is the physical probe length, \( \epsilon \) is the dielectric permittivity of the medium and \( c \) is the speed of light in a vacuum \((2.977 \times 10^8 \text{ m s}^{-1})\). The travel time \( t_s \) is related to the oscillation period \( P \) (ns) of the TLO.

\[ t_s = \frac{P}{4} t_{pd} + t_c \]  

where \( t_{pd} \) (ns) is the propagation delay of the amplifier and \( t_c \) (ns) is the charging time for stray capacitance. The sum \( t_{pd} + t_c \), needed to solve (9), was obtained by measuring the travel time with a cable tester (Model 1502C, Tektronix Inc, Beaverton, OR) and the oscillation period \( P \) for the same sample. Using (8) and (9), we can then calculate the dielectric permittivity from measurement of the oscillation period \( P \).

A mixing model was used to calculate the volumetric water content from the dielectric permittivity [Roth et al., 1990; Seyfried and Murdock, 1996]

\[ \epsilon_w = \epsilon_m + \alpha \epsilon_a + (1 - \alpha)\epsilon_a + \theta_i \epsilon_i \]  

where \( \epsilon_m \) is the composite dielectric permittivity, \( \epsilon_a, \epsilon_a, \epsilon_m, \) and \( \epsilon_i \) are the dielectric permittivities for soil matrix, air, liquid water, and ice, respectively, \( \alpha \) is a geometric factor, \( \theta_i \) is volumetric liquid water content \((\text{m}^3\text{m}^{-3})\), \( a \) is the volumetric air content \((\text{m}^3\text{m}^{-3})\), \( \phi \) is the soil porosity, and \( \theta_i \) is the volumetric ice content \((\text{m}^3\text{m}^{-3})\). Since the TLO sensor was calibrated at 5 ± 0.1°C, where no ice phase is present, (10), which was used for the calibrations, can be written as [Roth et al., 1990]

\[ \theta_i = \frac{\epsilon_w - (1 - \phi)\epsilon_a - \phi\epsilon_i}{\epsilon_w - \epsilon_a} \]  

Table 1. Selected Properties of Soils and Sediments

<table>
<thead>
<tr>
<th>Name</th>
<th>Sand, %</th>
<th>Silt, %</th>
<th>Clay, %</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Bluff</td>
<td>17.9</td>
<td>36.5</td>
<td>45.6</td>
<td>0.51</td>
</tr>
<tr>
<td>Salkum</td>
<td>11.9</td>
<td>59.7</td>
<td>28.4</td>
<td>0.49</td>
</tr>
<tr>
<td>Walla Walla</td>
<td>8.3</td>
<td>78.4</td>
<td>13.3</td>
<td>0.38</td>
</tr>
<tr>
<td>Sandstone</td>
<td>na⁰</td>
<td>na</td>
<td>na</td>
<td>0.12</td>
</tr>
</tbody>
</table>

⁰Particle sizes measured by sieving and light scattering methods. Textural classes are according to USDA classification.

⁰Here na indicates not available, entire sample is rock material.
The permittivities $\varepsilon_w$ and $\varepsilon_a$ were measured by taking the arithmetic mean of 10 measurements in air and deionized water. The values for $\alpha$ and $\varepsilon_s$ were then obtained by least squares optimization [Marquardt, 1963] of (11) to the measured calibration data (Figure 6). The values of the exponent $\alpha$ found in this study, were consistent with theoretical values for the mixing model used and other data obtained with soils [Roth et al., 1990].

For the measurement of the freezing characteristic, the soil samples were first completely saturated and then frozen. The medium in the sample cell thus consists of the solid soil material, liquid, and frozen water; no air phase is present and therefore $a = 0$. Equation (10) can then be written as

$$\theta_{0} = \frac{\varepsilon_w^{0} - \varepsilon_{i}^{0}}{(1 - \phi)\varepsilon_{s}^{a} + \phi \varepsilon_{i}^{a}}$$

The ice phase permittivity $\varepsilon_{i}$ was independently measured in a pure ice phase. The ice phase permittivity shows a temperature dependence $\varepsilon_{i}(T)$, which was accounted for in the mixing model using a fourth-order polynomial (Figure 7)

$$\varepsilon_{i}(T) = 3.32 + 1.21 \times 10^{-2}T + 1.18 \times 10^{-3}T^2 + 5.2 \times T^3 + 8.4 \times 10^{-7}T^4$$

The increase of the ice permittivity with temperature is consistent with previous findings [Hallikainen and Winebrenner, 1992]. The temperature dependence of the liquid phase permittivity $\varepsilon_w$ was accounted for by using the data and the approach presented by Archer and Wang [1990, equations 1 and 3].
a constant temperature reading was observed [Dorsey, 1940].

3.5. Reference Moisture Characteristic

[24] The moisture characteristic obtained with the freezing method should correspond to the main wetting branch of the moisture characteristic because during the thawing of the porous medium the water in the smallest pores and the water closest to the solid surfaces thaws first [Black and Tice, 1989]. The moisture characteristics obtained from the TDA measurements were therefore compared with wetting data measured by standard methods. To determine the moisture characteristics for the samples, a dew point water activity meter (WP-4, Decagon Devices Inc., Pullman, WA) was used. Twelve grams of samples were incrementally wetted by adding known amounts of water by using a pipette. The samples were then covered with parafilm to avoid evaporation, and equilibrated for about 12 hours. We initially tested the length of the equilibration time by measuring the dielectric permittivity of the samples over time, and found that for our soils, the permittivities reached a constant value after about 12 hours.

4. Results and Discussion

4.1. Hysteresis in the Freezing Characteristics

[25] There are at least three possible mechanisms for hysteresis in the freezing characteristics of porous media. (1) Supercooling of water: a liquid does not necessarily freeze at its thermodynamic freezing point when the temperature is reduced, but rather remains liquid in a metastable state, until freezing is induced by nucleation. Pure liquid water can remain unfrozen at considerable temperatures below 0°C [Dorsey, 1940]. (2) Effects of electrolytes: When a soil solution freezes, a major portion of electrolytes will be excluded from the ice phase and remain in the unfrozen liquid phase. The freezing point depression of the solution according to [Robinson and Stokes, 1959]

\[
\Psi_s = -C\gamma RT
\]

where \( C \) is the molal electrolyte concentration, \( \nu \) is the number of moles of ions formed from one mole of electrolyte, \( \gamma \) is the osmotic coefficient, \( R \) is the gas constant (8.31 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature in Kelvin, and \( \Psi_s \) is given in J kg\(^{-1}\). The freezing point depression \( \Theta \) (K) of an electrolyte solution can be calculated by [Harned and Owen, 1958]

\[
-\ln a_w = 9.696 \times 10^{-3}\Theta + 5.1 \times 10^{-6}\Theta^2
\]

Figure 8. Spatial sensitivity of the transmission line oscillator, measured at 5 ± 0.1°C. Dashed line corresponds to water permittivity at 5°C [Weast, 1986].

[26] We have experimentally verified, that supercooling and electrolyte exclusion occurred in our system. Hysteresis due to pore size irregularities, as found by Koopmans and Miller [1966], was not observable because of the pronounced supercooling in our system (Figure 9). The effects of electrolytes are discussed in more detail as follows.

4.2. Effect of Salts on Freezing Curve Analysis

[27] If a solution containing soluble salts is frozen, salts are excluded from the ice phase and remain in the unfrozen liquid phase. For example, when ice forms from seawater, it is almost pure, with the excess salts remaining in the liquid [Petrenko and Whitworth, 1999, p. 290]. The salts lower the osmotic potential of the solution according to [Petrenko and Whitworth, 1999, p. 290]

\[
\Psi_s = -C\gamma RT
\]

where \( C \) is the molal electrolyte concentration, \( \nu \) is the number of moles of ions formed from one mole of electrolyte, \( \gamma \) is the osmotic coefficient, \( R \) is the gas constant (8.31 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature in Kelvin, and \( \Psi_s \) is given in J kg\(^{-1}\). The freezing point depression \( \Theta \) (K) of an electrolyte solution can be calculated by [Harned and Owen, 1958]

\[
-\ln a_w = 9.696 \times 10^{-3}\Theta + 5.1 \times 10^{-6}\Theta^2
\]

where \( a_w \) is the water activity given by \( \ln a_w = -\Psi_{tot}/(RT) \) with \( M_w \) being the molecular mass of water. If the process is reversed and the system is thawed, there is no depression of the phase transition temperature because the ice is a pure phase containing no electrolytes.

[28] In our TDA system, the sample is cooled at one side by Peltier cooling. During freezing, the water closest to the Peltier coolers will freeze first and electrolytes will be excluded in the remaining liquid phase. The freezing point depression for an electrolyte solution can then be calculated with (15). During thawing, the pure ice phase is undergoing the phase transition and therefore the thawing occurs at 0°C. Measured freezing and thawing phase transition temperatures in pure electrolyte solutions indeed show this hysteresis (Table 2). Since the algorithm of the TDA was designed such that temperature was recorded at discrete values, no

Figure 9. Freezing and thawing characteristics for Walla Walla silt loam soil. The rates of freezing and thawing were identical.
Table 2. Freezing and Thawing Points for KCl Solutions of Different Molality

<table>
<thead>
<tr>
<th>Concentration, mmol kg⁻¹</th>
<th>Theoretical FP, °C</th>
<th>Freezing, °C</th>
<th>Thawing, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>0</td>
<td>[-0.002, -0.025]</td>
<td>[-0.006, -0.031]</td>
</tr>
<tr>
<td>1</td>
<td>-0.0036</td>
<td>[-0.010, -0.003]</td>
<td>[-0.005, -0.022]</td>
</tr>
<tr>
<td>5</td>
<td>-0.0181</td>
<td>[-0.024, -0.006]</td>
<td>[-0.006, -0.045]</td>
</tr>
<tr>
<td>10</td>
<td>-0.0357</td>
<td>[-0.038, -0.033]</td>
<td>[-0.008, -0.009]</td>
</tr>
<tr>
<td>20</td>
<td>-0.0708</td>
<td>[-0.070, -0.040]</td>
<td>[-0.007, -0.008]</td>
</tr>
<tr>
<td>50</td>
<td>-0.1743</td>
<td>[-0.181, -0.141]</td>
<td>[-0.008, -0.031]</td>
</tr>
<tr>
<td>100</td>
<td>-0.3444</td>
<td>[-0.370, -0.301]</td>
<td>[-0.005, -0.062]</td>
</tr>
</tbody>
</table>

*FP is freezing point, calculated with equation 15; osmotic coefficients were taken from Robinson and Stokes [1959, Appendix 8.9].

Values bracket the temperature where the phase transition occurred.

*Deionized water.

precise determination of the phase transition temperature was possible. However, we can measure the two temperatures between which the phase transition occurred.

[29] It has been observed, that when seawater freezes, liquid water with higher salinity can form so-called brine inclusions [e.g., Arcone et al., 1986; Golden et al., 1998]. These brine inclusions will cause more liquid water to be present at a given temperature than in case of the freezing of pure water. It is possible that brine inclusions formed during freezing of our soil samples; however, we have not experimentally determined whether, and to what extent, such brine inclusions have occurred. Inclusion of brine will results in a larger liquid water content at a given temperature as compared if brine inclusions would not occur. Therefore, we would expect that the freezing characteristics would shift toward higher water contents at the same temperature, and consequently the moisture characteristics would as well shift to higher water contents at the same water potential. Our data do not show a clear trend on whether brine inclusions would not occur. Therefore, we would expect that the freezing characteristics would shift toward higher water contents at the same temperature, and consequently the moisture characteristics would as well shift to higher water contents at the same water potential.

[30] The experiments with the porous media were run as thawing measurements (Figure 4). Running the experiments as freezing measurements would yield non-interpretable data because of the supercooling phenomenon. The supercooling generates a pronounced hysteresis in the freezing characteristics, as shown for the Walla Walla silt loam (Figure 9). During freezing water undergoes supercooling down to about -4°C, and as soon as an ice nucleation forms, the supercooled water freezes instantaneously. After freezing occurs, the two branches of the characteristic do not show any marked hysteresis anymore.

[31] Soil freezing characteristics using the thawing branch for the four samples are shown in Figure 10. The freezing characteristic for deionized water shows a zero water content from -20 to 0°C. The phase transition occurs between -0.006 and 0.031°C (Table 2). The well-defined step-like form of the freezing characteristic for water is an important quality feature of the instrument. All porous media samples show a change in water content at temperatures well below 0°C, indicating the presence and continuous release of liquid water as the temperature increases. Between -3 and 0°C, the slope of the curve changes at a higher rate compared to lower temperatures. This change in slope corresponds to a change in liquid water content due to the melting of ice in successively larger pores.

[32] The slope of the freezing characteristic is an important feature that represents the different pore size distributions of the samples. For instance, in the range of -20 to -2°C, the Red Bluff clay has a steeper slope than the other samples, indicating a wider pore size distribution typical for clayey soils. The sandstone, on the other hand, shows a more gradual change in the water content measurement in this range, while displaying a steeper slope between -2 to 0°C distribution, indicating melting of increasing amounts of ice in larger pores.

[33] The moisture characteristics obtained from the freezing characteristics show good agreement with the results of the standard methods (Figure 11). The TDA data show little scatter between repetitions, except in the region between 0 and -30 to -50 J kg⁻¹, where issues related to capillary water and measurement resolution confound the analysis. With a temperature measurement accuracy of 0.01 K, the water potential can be resolved to 11 J kg⁻¹. In addition, changes in soil structure due to the ice expansion will preferentially affect the wet region of the soil moisture characteristic, so that the measurements will not be reliable in that region. The three repetitions shown in Figure 11 represent different samples measured, and are not repeated.

Figure 10. Freezing characteristics for deionized water, soil, and sediment samples. The inset shows a magnification of the ordinate.
cycles measured on the same sample. Freeze-thawing cycles in the same material are known to lead to structural changes [e.g., Campbell, 1952], which we wanted to avoid.

5. Conclusions

[34] The method described here offers a novel technique to measure the freezing characteristic and the corresponding moisture characteristic of porous media. As compared with the dew point water activity meter, the freezing method is fast and provides a high degree of resolution for the moisture characteristic.

[35] The water content measurements have been calibrated with a dielectric mixing model at 5°C. No direct calibration was done in the presence of an ice phase. As demonstrated by Spaans and Baker [1995] and Seyfried and Murdock [1996], empirical calibrations made in unfrozen soil might not be applicable to frozen conditions, mainly because the dielectric permittivity of ice is different from air. In our calibrations, we use a mixing model where the dielectric permittivity of ice and water, as well as the temperature dependence of ice and water permittivity, can be accounted for. The calibrations might not reflect the frozen conditions accurately, but for operational purposes, the mixing model calibration seems to be adequate. A disadvantage of our methodology, however, is that a new calibration has to be made for each different soil used.

[36] The freezing characteristics reported here represent thawing curves. We attempted to also measure freezing curves, but problems occurred due to supercooling of water and due to exclusion of electrolytes from the ice phase. Whereas the increasing electrolyte concentration could be accounted for [e.g., Banin and Anderson, 1974], the problem of supercooling is difficult to address. The thawing curves correspond to wetting curves in the soil moisture characteristics; it seems not possible to measure the drying branch of the moisture characteristic with the freezing technique presented here.

[37] The analysis presented in this study did not account for the modified dielectric properties of water close to the solid surfaces (bound water). Or and Wraith [1999] studied the temperature effects on the overall bulk dielectric permittivity by accounting for the release of bound water as a function of temperature. In their study, they assume that bound water undergoes relaxation at frequencies lower than 0.8 to 1 GHz. This bound water has different dielectric properties than bulk water, and is partially invisible in TDR measurement made with a Tektronix cable tester. In this study, we measured the permittivities at frequencies of 30 to 60 MHz, far below the frequencies where we would expect differences in the relaxation frequency between bound and bulk water. However, the complexity of the dielectric behavior of frozen media requires additional investigation to address the possible modification of the dielectric properties of bound water and its effect on the overall freezing characteristic.

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Figure 11. Moisture characteristics for soil and sediment samples. Lines denote TDA measurements, symbols are data obtained with a dew point water activity meter. The three lines in each graph represent three repetitions. Note the different scales of the ordinates.
References


