Permittivity measurement of minerals

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Abstract. An electromagnetic logging tool moves along a borehole to measure continuously the complex dielectric permittivity of the rock formation. Dielectric properties of formation fluids and minerals are required to interpret the log. Methods to measure mineral permittivities are reviewed and experimental results are described for various particulate minerals.

1. Wellbore logging

Early borehole logging tools measured the kHz electrical resistivity \( \rho_i \) of a rock formation of porosity \( \phi \), with oil and brine in its pores, to obtain the oil volume fraction \( f_O \). Log interpretation used Archie’s law \([1]\) \( \rho_n / \rho_i \approx f_O^2 \) (for brine resistivity \( \rho_B \)) to obtain \( f_O = \phi - f_B \). This method could discriminate only between brine (\( \rho_B \approx 1 \text{ ohm m} \)) and oil (\( \rho_o \approx 10^9 \text{ ohm m} \)). Modern electromagnetic well-logging [2] measures the formation permittivity \( \varepsilon \) and conductivity \( \sigma \) in the MHz – GHz range. Permittivity is material-specific, e.g. oil (\( \varepsilon \approx 2 \)), rock minerals (\( \varepsilon \approx 4–16 \)), brine (\( \varepsilon \approx 70 \)). This paper describes a method to measure the permittivity of solid granular minerals required for dielectric log interpretation.

2. Permittivity-matching

Mixtures of dissimilar dielectric materials, such as a liquid-saturated rock or mineral particles suspended in a liquid, have a real permittivity \( \varepsilon(q_1,q_2) \) that depends largely on the mixture’s volumetric composition \( (q_1, q_2, \text{ etc.}) \) and on its dielectric constitution \( (\varepsilon_1, \varepsilon_2, \text{ etc.}) \).

We compare various formulations of \( \varepsilon(q_1,q_2) \), particularly for two-component systems where \( \varepsilon_1 \approx \varepsilon_2 \), and describe the permittivity-matching method to obtain rock mineral permittivity. Subterranean minerals usually are available only in granular form of irregular particle shape so that methods for homogeneous materials cannot be used. Rock formation minerals are largely insulating and we shall assume the permittivity \( \varepsilon_{\text{min}} \) to be real. Simple methods measure the permittivity \( \varepsilon_{\text{min}} \) of a suspension of the mineral with a liquid of known permittivity \( \varepsilon_{\text{liq}} \), and use a mixture rule that describes \( \varepsilon_{\text{min}} \) in terms of \( \varepsilon_{\text{min}}, \varepsilon_{\text{liq}}, \text{ and the respective volume fractions} \) [3]. However, such rules are approximate and various rules will give different \( \varepsilon_{\text{min}} \) from the same experimental data. Here we describe the dielectric matching method where the particle permittivity is obtained from the liquid permittivity which is unaltered by adding suspended particles. This method is independent of particle shape and concentration, and was used to obtain the porosity and water content of soils, sediments, and rocks [4].

2.1. Theory

General theorems exist for a two-component heterogeneous medium having a structural length-scale large compared with molecular dimensions but small compared with the size of the sample. To define effective dielectric parameters of such microscopically-heterogeneous and statistically-homogeneous media the volume-averaged fluxes and fields in the media (assumed isotropic) can be generally related. The effective permittivity \( \varepsilon \) is given by \( \overline{D} = \varepsilon \overline{E} \) in terms of the volume-average flux and field vectors \( \overline{D} \) and \( \overline{E} \). Statistical continuum theory \([5,6]\) gives the permittivity \( \varepsilon \) of a loss-free dielectric as

\[
\varepsilon = \overline{\varepsilon} - \left( \frac{\varepsilon(r) - \overline{\varepsilon}}{3\varepsilon} \right)
\]

for weak fluctuations of \( \varepsilon(r) \) about the volume average permittivity \( \overline{\varepsilon} \), i.e. \( \varepsilon(r) - \overline{\varepsilon} \ll \overline{\varepsilon} \), as pertains close to permittivity-match in the matching method. In (1) \( \varepsilon(r) \) describes the spatial fluctuation of the permittivity via vector \( r \), and the volume average of \( \varepsilon(r) \) is
where $(\epsilon(r) - \overline{\epsilon})^2$ is the volume-average square deviation of $\epsilon(r)$ from $\overline{\epsilon}$. For an homogeneous dielectric of permittivity $\epsilon$ then $(\epsilon(r) - \overline{\epsilon})^2 = 0$ and (1) gives the expected result $\epsilon = \overline{\epsilon}$. For an heterogeneous dielectric $(\epsilon(r) - \overline{\epsilon})^2 > 0$ regardless of the permittivity spatial distribution and (1) shows that $\epsilon < \overline{\epsilon}$. If a composite dielectric has components #1 and #2 of volume fractions $q_1$ and $q_2$, and permittivities $\epsilon_1$ and $\epsilon_2$, then $\overline{\epsilon} = q_1\epsilon_1 + q_2\epsilon_2$. As $(\epsilon(r) - \overline{\epsilon})^2 = \epsilon(r)^2 + \overline{\epsilon}^2 - 2\epsilon(r)\overline{\epsilon}$, $\epsilon(r) = \overline{\epsilon}$, and $\overline{\epsilon(r)}^2 = q_1\epsilon_1^2 + q_2\epsilon_2^2$ then (1) gives

$$\epsilon = \overline{\epsilon} - q_1q_2(\epsilon_1 - \epsilon_2)^2/(3\overline{\epsilon}) \, ,$$

which shows that $\epsilon \leq \overline{\epsilon}$ if $\epsilon_1 \neq \epsilon_2$. Note that this result (equation 2.11 of [6]) was obtained without appeal to any dielectric or electrodynamic model. We use it later to compare various mixture rules.

We consider the use of a liquid of known permittivity $\epsilon_1$ which may be varied, e.g. by varying the composition of two miscible liquids. This liquid may suspend a powder of grains of permittivity $\epsilon_2$. If the permittivity of the suspension is denoted by $\epsilon$, then in the case of a perfect match between the liquid and the powder permittivity we have

$$\epsilon = \epsilon_1 = \epsilon_2 \, .$$

In the case of imperfect match, $\epsilon_1 \neq \epsilon_2$, and a Taylor expansion of $\epsilon$ around $\epsilon_2$ gives

$$\epsilon = \epsilon_2 + \sum_{n=1}^{\infty} c_m (\epsilon_1 - \epsilon_2)^n \, ,$$

in which $c_1 = 1$, and the other coefficients are given by

$$c_m = \frac{(-1)^{m+1}}{m!} \left( \frac{d^n \epsilon}{d\epsilon_1^n} \right)_{\epsilon = \epsilon_2} \, .$$

Equation (5) reiterates that $\epsilon = \epsilon_2$ for $\epsilon_1 = \epsilon_2$. In practice it is necessary that the coefficients $c_m$ must differ significantly from zero in order that sufficient permittivity mismatch occurs (i.e. $\epsilon_2 > \epsilon_1$ or $\epsilon_2 < \epsilon_1$) to identify the experimental permittivity match.

### 2.2. Existing dielectric mixture rules

To describe the mixture permittivity $\epsilon(\epsilon_1, \epsilon_2, q_1, q_2)$ in terms of the component permittivities $\epsilon_1$, $\epsilon_2$, and volume fractions $q_1$ and $q_2$, a large number of mixture rules exist [7]. The various approaches are effective medium approximations in which the heterogeneous length-scale is much smaller than the wavelength of the applied electric field. These rules give approximate $c_m$ to validate the experimental permittivity mismatch measurement method.

Some rules may be written [8]

$$q_2 = \frac{(\epsilon - \epsilon_1)(\epsilon_2 + 2\epsilon_1 + v(\epsilon - \epsilon_1))}{(\epsilon_2 - \epsilon_1)(\epsilon_2 + 2\epsilon_1 + v(\epsilon - \epsilon_1))} \, ,$$

in which $v = 0, 1, 2,$ or $3$ according to the internal electric field assumed in their formulation. For $v = 0$ the Maxwell Garnett rule is obtained. Suffix #1 refers to an external component, while #2 refers to the included component. Other relations have been proposed [7] such as

$$q_2 = (\epsilon^n - \epsilon_2^n)/(\epsilon_2^n - \epsilon_1^n) \, ,$$

and the Lichtenecker rule

$$q_2 = \log(\epsilon/\epsilon_1)/\log(\epsilon_2/\epsilon_1) \, .$$

Equation (8) if $n = 1/2$ becomes the complex refractive index rule used in electromagnetic logging formation-evaluation [9,10] and if $n = 1/3$ it becomes the Looyenga rule [11] which has a theoretical basis [12]. These and similar rules have been summarized [7]. Equations (8) and (9) are symmetric in
the disposition of the components #1 and #2, i.e. the value of \( \varepsilon \) remains the same if the suffixes are exchanged, e.g. from 1 to 2 or vice versa. We note that the relation of (7) is generally non-symmetric, as expected from a rule that distinguishes between the internal and the external components. The exception is for \( \nu = 2 \), when the symmetric Polder-van Santen or symmetric Bruggeman rule is

\[
q_1 \left( \varepsilon_1 - \varepsilon \right) + q_2 \left( \varepsilon_2 - \varepsilon \right) = 0.
\]

The various dielectric functions \( \delta(\varepsilon_1, \varepsilon_2, q) \) possess upper and lower bounds. Statistical continuum theory [5, 6] shows the bounding functions depend on the volume fractions of the components, and on various correlation functions that describe the geometrical disposition or structure of the dielectric’s components. If there is no correlation function information and the only relevant parameters are the volume fractions, then the closest possible bounds for a two-component medium are those of Hashin and Shtrikman [5,6]. If \( \varepsilon_2 > \varepsilon_1 \), we have the lower (LHS) and upper (UHS) bound H-S mixture rules

\[
q_2 = \frac{3(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_2 - \varepsilon_1)(2\varepsilon_2 + \varepsilon_1)},
\]

\[
q_1 = \frac{3(\varepsilon_1 - \varepsilon)}{(\varepsilon_2 - \varepsilon_1)(2\varepsilon_1 + \varepsilon_2)},
\]

respectively, and vice-versa for \( \varepsilon_2 < \varepsilon_1 \). Equation (11) corresponds to the Maxwell Garnett (MAG) rule from (7) with \( \nu = 0 \) where #1 denotes the external component, while (12) also corresponds to (7) with \( \nu = 0 \) but where #2 denotes the external component. All the rules above have the same term \( c_1 \) given by (6) as

\[
c_1 = q_1.
\]

From (6) the dielectric permittivity \( \varepsilon \) sufficiently close (\( \varepsilon_1 \approx \varepsilon_2 \)) to the match condition \( \varepsilon_1 = \varepsilon_2 \) is

\[
\varepsilon = \varepsilon_2 + q_1(\varepsilon_1 - \varepsilon_2) = q_1\varepsilon_1 + q_2\varepsilon_2 = \varepsilon^*.
\]

hence regaining the leading term of (3). However, the various rules give different relations for the terms \( c_2, c_3 \), and for higher-order terms. Table 1 shows that \( c_2 \) obtained from the statistical relation (3) agrees with \( c_2 \) from the relations of (11), (12) and with the Looyenga rule with \( n = \frac{1}{4} \).

| Mixture rule equation | \( c_2 \) | \( c_3 \) |
|-----------------------|----------|----------|
| 3                     | \( -q_1 q_z / (3\varepsilon) \) | undefined |
| 8 \( (n = \frac{1}{2}) \) | \( -q_1 q_z / (4\varepsilon) \) | \( -q_1 q_z / (8\varepsilon^2) \) |
| 8 \( (n = \frac{1}{2}) \) | \( -q_1 q_z / (3\varepsilon) \) | \( -q_1 q_z (9 + q_z) / (54\varepsilon^2) \) |
| 9                     | \( -q_1 q_z / (2\varepsilon) \) | \( -q_1^3 / (6\varepsilon^2) \) |
| 11                    | \( -q_1 q_z / (3\varepsilon) \) | \( -q_1 q_z (2 + q_z) / (9\varepsilon^2) \) |
| 12                    | \( -q_1 q_z / (3\varepsilon) \) | \( +q_1 q_z^2 / (9\varepsilon^2) \) |

3. Permittivity-matching measurements

Electroporation cells (Sigma Aldrich) were used to hold about 3 ml of suspension sample. The impedance was measured of about 0.4 ml of sample between two parallel aluminium electrodes 2 mm apart in the cell, connected to the component fixture 1J1011 of a Wayne Kerr 6500B impedance analyser. Permittivity measurements were made in the frequency range 1 kHz to 50 MHz. Mixtures of various concentrations of n-decane and butan-1-ol were used to obtain a liquid permittivity range of 2–16. The permittivities of the liquids (\( \varepsilon_{\text{liq}} \)) and the mineral suspensions (\( \varepsilon_{\text{sus}} \)) showed negligible frequency dependences above 10 kHz and data were averaged over 0.1–10 MHz.

The matching method was used to study number of nominally pure minerals of grain sizes 1 - 10 \( \mu \text{m} \), the mineral permittivity being denoted by \( \varepsilon_{\text{min}} (= \varepsilon_0) \). For example, figure 1 (solid line) for SiO\(_2\) is a
plot of $\varepsilon_{\text{sus}} - \varepsilon_{\text{liq}}$ versus $\varepsilon_{\text{liq}}$. The line shows a linear fit to data giving $\varepsilon_{\text{min}} = 4.44$ when $\varepsilon_{\text{sus}} - \varepsilon_{\text{liq}} = 0$. This compares closely with $\varepsilon_{\text{min}} = 4.47$, being the mean of $\varepsilon_{11} = \varepsilon_{22} = 4.41$ and $\varepsilon_{33} = 4.60$ for this anisotropic mineral [13]. Similarly good agreement was found between the matching method results and literature data for CaCO$_3$, Al$_2$O$_3$, and ZrO$_2$.

Permittivity-matching measurements were made on mixtures of minerals to simulate real rocks which usually comprise a range of different mineral grains. Figure 1 (broken line) is a plot of experimental results for $\varepsilon_{\text{sus}} - \varepsilon_{\text{liq}}$ versus $\varepsilon_{\text{liq}}$ for a mineral mixture comprising 25.2% v/v CaCO$_3$ + 74.8% v/v Al$_2$O$_3$. The line shows a linear fit to data giving $\varepsilon_{\text{min}} = 9.61$ when $\varepsilon_{\text{sus}} - \varepsilon_{\text{liq}} = 0$. Literature data [13] gives $\varepsilon_{\text{min}} = 8.58$ for CaCO$_3$ and $\varepsilon_{\text{min}} = 10.03$ for Al$_2$O$_3$, and shows that $\varepsilon_{\text{min}} = 9.61$ measured for this mineral mixture lies between $\varepsilon_{\text{min}}$ of the constituent minerals as expected. The measured $\varepsilon_{\text{min}}$ compares closely with $\varepsilon_{\text{min}} = 9.68$ calculated from (8) with $n = \frac{1}{2}$ using the above constituent minerals data. The permittivity for various mixtures of CaCO$_3$, Al$_2$O$_3$ and SiO$_2$ was also measured by the matching method. Figure 2 shows good agreement between measured data for the mixtures and the permittivity predicted by (8) with $n = \frac{1}{2}$, using the $\varepsilon_{\text{min}}$ data above for CaCO$_3$, Al$_2$O$_3$ and SiO$_2$.

The effect of imaginary permittivity on the method can be estimated from mixture rules generalized for a complex permittivity, and show that a loss tangent < 0.1 of either the mineral or the liquid gives < 0.5% error in the real permittivity measured by the matching method.

![Figure 1](image.png)

Figure 1. Plots of $\varepsilon_{\text{sus}} - \varepsilon_{\text{liq}}$ versus $\varepsilon_{\text{liq}}$ for SiO$_2$ powder (solid line) and for a powder mixture of 25.2% CaCO$_3$ + 74.8% Al$_2$O$_3$ (broken line).
Figure 2. Plot of data markers with error bars to compare measured with predicted data for permittivities of two-part powder mixtures. The trend line is of unit gradient.

4. Summary
A permittivity-matching method is described to obtain the permittivity \( \varepsilon_{\text{min}} \) of mineral particles. The method is independent of particle shape, size, and irregularity. It measures the permittivity \( \varepsilon_{\text{sus}} \) of suspensions of particles for suspending liquids of different permittivity \( \varepsilon_{\text{liq}} \) and determines when \( \varepsilon_{\text{liq}} = \varepsilon_{\text{sus}} = \varepsilon_{\text{min}} \). It is supported by dielectric statistical continuum theory and does not assume the validity of any particular dielectric model (or mixture rule). The method was investigated and validated for various mineral types and mixtures.

5. References
[1] Archie, G E 1942 Petroleum Transactions of AIME 146 54-62
[2] Hizem M, Budan H, Devillé B, Faivre O, Mossé L, Simon M 2008 SPE116130
[3] Böttcher C F J 1952 Theory of Electric Polarization (Amsterdam: Elsevier)
[4] Robinson D A, Friedman S P 2003 J Geophys Res 108(B2) 2076 doi:10.1029/2001JB000691
[5] Beran M J 1968 Statistical Continuum Theories (New York: Interscience)
[6] Batchelor G K 1974 Ann Rev Fluid Mech 6 227-255
[7] Jylhä L, Sihvola A 2007 J Phys D: Appl Phys 40 4966-4973
[8] Kärkkäinen K, Sihvola A, Nikoskinen K 2001 IEEE Trans Geosci Remote Sensing 39 1013-1018
[9] Birchak J R, Gardner C G, Hipp J E, Victor J M 1974 Proc IEEE 62 93-98
[10] Freedman R, Vogiatzis JP 1979 Geophys 44 969-986
[11] Looyenga H 1965 Physica 31 401-406
[12] Landau L D, Lifshitz E M 1960 Electrodynamics of Continuous Media (Oxford: Pergamon)
[13] Kaye G W C, Laby T H 1995 Tables of Physical and Chemical Constants (Teddington: NPL)