Electrochemical double-layer capacitance of metals, including some precious metals: preliminary results

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Abstract: Spectral-induced polarization characteristics of four types of metals, including three precious metals, platinum, gold, and silver, and also stainless steel have been measured. The purpose was to determine their electrochemical double-layer capacitance (C_E) characteristics, because their effect requires elimination when using these metals as electrodes in a two-electrode rock- or soil-sample measuring system. Whereas four-electrode systems automatically eliminate such effects, complications develop when varied frequencies or pressures are used, and when rock or soil textural elements require examination.

Results indicate that the C_E and its frequency dependence coefficient (α_E) values for these metals are in the ranges of 3.09×10^{-5} F/cm^2 to 6.42×10^{-5} F/cm^2 and 0.185 to 0.350, respectively. These values are somewhat smaller than those of the graphite electrodes, which are generally in the ranges of 1.06×10^{-4} F/cm^2 to 4.07×10^{-4} F/cm^2 and 0.181 to 0.360, respectively.

Résumé : On a mesuré par polarisation provoquée spectrale les caractéristiques de quatre emétaux, soit trois métaux précieux (platine, or et argent) et l'acier inoxydable. L'objectif était de déterminer les caractéristiques de la capacité électrique de la double couche électrochimique (C_E), car il faut éliminer ces effets lorsque ces métaux sont utilisés comme électrodes dans un système de mesure à deux électrodes pour échantillons de sol ou de roche. Alors que les systèmes à quatre électrodes éliminent automatiquement de tels effets, des complications apparaissent lorsque des fréquences ou des pressions variées sont utilisées et lorsqu'il faut examiner des éléments texturaux du sol ou de la roche.

Les résultats obtenus indiquent que la C_E et son coefficient de dépendance en fréquence (α_E) pour ces métaux s'échelonnent respectivement de 3,09 x 10^{-5} F/cm² à 6,42 x 10^{-5} F/cm² et de 0,185 à 0,350. Ces valeurs sont quelque peu inférieures à celles des électrodes de graphite, qui en général s'échelonnent respectivement de 1,06 x 10^{-4} F/cm² à 4,07 x 10^{-4} F/cm² et de 0,181 à 0,360.

INTRODUCTION

The spectral-induced polarization characteristics of four types of metals, including three types of precious metals, platinum, gold, and silver, and also stainless steel, have been measured in order to determine the capacitance characteristics of their electrochemical double layers. A four-electrode system is often used for laboratory electrical measurements of rock or soil samples; however, this electrode arrangement causes complications for measurements at varied frequencies or confining pressures (Katsube and Scromeda-Perez, 2003) and, in addition, makes it difficult to study the effect of different rock-forming or soil-texture-forming components. For such reasons, a two-electrode sample-holder system is favoured; however under certain conditions such as for samples with low resistivities (Katsube and Scromeda-Perez, 2003), the two-electrode system introduces unwanted electrode effects, which are automatically eliminated in a four-electrode system. Usually, a measurement at certain single frequencies can be chosen to avoid the electrode effects, but only if the frequency characteristics of the sample are known can the results be accurate. In principle, for a two-electrode sample-holder system to cover a wide frequency, confining pressure, and sample resistivity ranges, it is necessary to subtract the electrode capacitance effect from the measurements (e.g. Katsube and Scromeda-Perez, 2003).

The purpose of this study is to determine the electrochemical double-layer capacitance values of a few different types of metals in order to know the electrode capacitance effects that have to be eliminated when using these types of electrodes in a two-electrode system. This paper follows the electrical theory and method of investigation described in a previous publication (Katsube and Scromeda-Perez, 2003), and presents the experimental results of these four metal electrodes.

METHOD OF INVESTIGATION

Preparation for test

The four types of thin metal plates were cut into square sections, the dimensions of which are listed in Table 1. Sheets of filter paper cut to the same dimensions as the metal plates were soaked in separate beakers with a 0.01 N NaCl solution (resistivity, 7.71 Ω•m) prior to the measurements. For the silver and platinum plates, the packages prepared for measurement consisted of a sheet of filter paper placed on each side of a single metal plate. For the gold and stainless steel plates, the packages prepared for measurement consisted of two sheets of filter paper placed in between two metal plates of gold or stainless steel.

Sample holder and measuring system

The sample holder and electrical measuring system used in this study have been frequently described elsewhere (e.g. Katsube, 1975; Gauvreau and Katsube, 1975; Katsube and Walsh, 1987; Katsube and Salisbury, 1991; Katsube and Scromeda-Perez, 2003). The sample holder is a two-electrode system with stainless steel electrodes, as shown in Figure 1a. Its equivalent circuit is shown in Figure 1b (Katsube and Scromeda-Perez, 2003). The packages of filter paper and metal plates were placed between these two stainless steel electrodes, with graphite plates separating the electrodes from these packages for measurement.

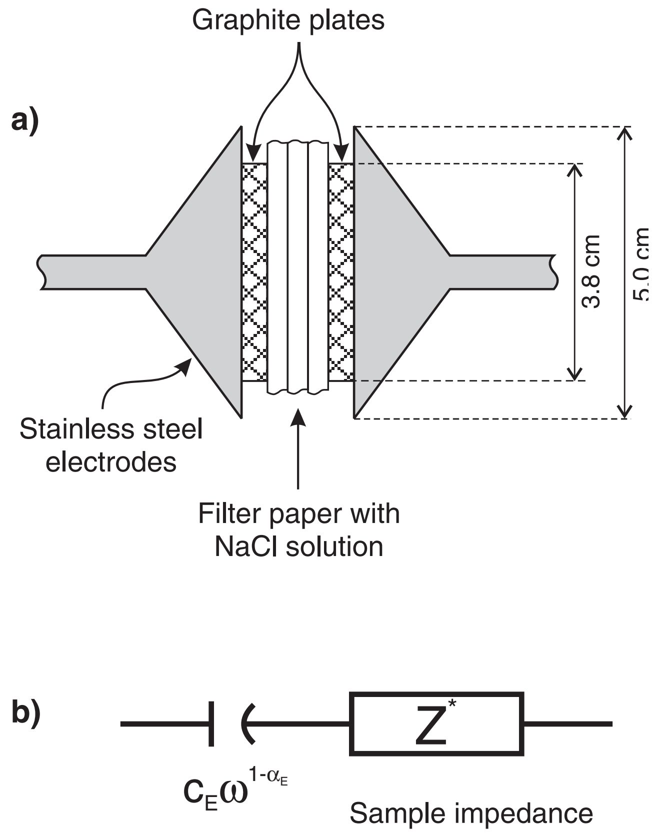

Figure 1. The **a)** two-electrode sample-holder system used in this study and **b)** equivalent circuit of this system (Katsube, 2001). The C_E is the electrochemical double-layer capacitance of the graphite electrodes.

Table 1. Dimensions of metal plates used in the electrochemical double-layer capacitance (C_E) measurements.

Sample	a_1 (cm)	a_2 (cm)	ℓ (cm)
Silver	3.250	3.310	0.026
Platinum	2.640	3.290	0.010
Gold	1.912	2.100	0.026
Stainless steel	2.630	2.646	0.102

a_1, a_2 : Length of the two sides of the metal plate.
ℓ : Thickness of metal plate.

In the case of the package prepared for the gold and stainless steel plates (consisting of two sheets of filter paper placed in between two metal plates), the graphite plates are in direct contact with metal plates on either side of the filter paper. Therefore, the measured results represent those of the electrochemical double-layer capacitance (C_E) of the metal plates in direct contact with the filter paper. In the case of the package prepared for the silver and platinum plates (with filter paper placed on either side of a single metal plate specimens), however, the graphite plates are in direct contact with the filter paper. Therefore, the measured results represent those of the C_E of the graphite electrodes in a series position as compared to the C_E of the metal plates. This implies that while the measured results for the cases of the gold and stainless steel plates represent the results of these metal plates, the measured results for the cases of the silver and platinum plates represent results from which the C_E of the graphite plates have to be eliminated to know the true C_E values of that of the metal plates.

Graphite plates are often used as electrodes because their C_E values are usually considerably larger and their impedance considerably smaller compared to those of the samples being measured (Katsube, 2001; Katsube and Scromeda-Perez, 2003), therefore allowing their effect on the measurements to be ignored. In this case, however, it appears that it is necessary to eliminate their effect to increase the measured accuracy for the silver and platinum plates. The C_E in Figure 1b, which normally represents the capacitance of the electrode electrochemical double layers, in this study, can also be that of the surfaces of the metal plate specimens since they are in direct contact with the filter paper, such as the case of the package prepared for the silver and platinum plates.

The electronic measuring system used in this study, the Solartron SI-1260 Impedance/Gain-Phase Analyzer, is displayed in Figure 2. The constant current source (0.1 mA) of

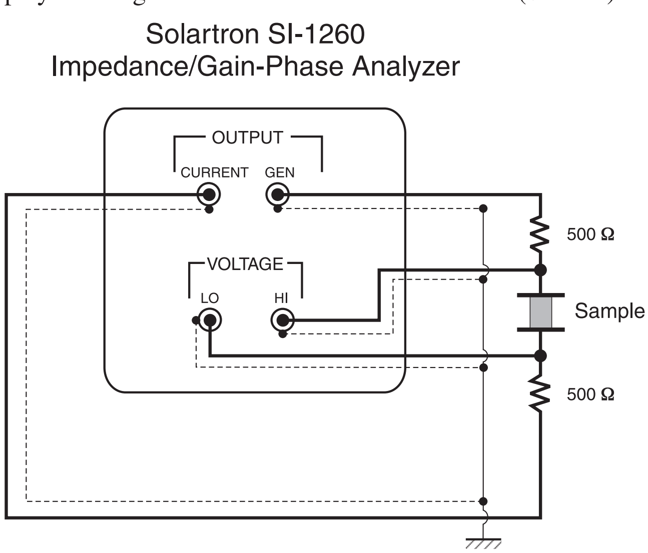

Figure 2. The electronic measuring system (Solartron SI-1260 Impedance/Gain-Phase Analyzer) and sample measuring circuit used in this study.

the generator is connected to the electrode-specimen through 500 Ω resistors on either side of the sample holder. Although this system has the capability for making measurements in a four-electrode mode, it has been used as a two-electrode system in this case.

ANALYTICAL PROCEDURE

The complex impedance (Z*) which is used to determine the spectral-induced polarization characteristics is expressed by (Katsube and Scromeda-Perez, 2003),

$$Z^* = Z' - jZ'' \qquad (1)$$

where Z′ and Z″ are the real and imaginary impedances, respectively, and j is $\sqrt{(-1)}$.

The imaginary impedance can be expressed by (Katsube and Scromeda-Perez, 2003),

$$Z'' = 1/(C_E \omega^a), \qquad (2)$$

$$\omega = 2\pi f, \qquad (3)$$

$$a = 1 - \alpha_E \qquad (4)$$

where C_E and α_E are the metal specimen electrochemical double-layer capacitance and its frequency coefficient, respectively. The ω is the angular frequency, a is a coefficient, and f is the frequency. Examples of the Z″-f relationship for the four metals are displayed in Figure 3. The C_E and α_E values of the metals are determined by matching a linear logarithmic curve (equation 2) to the Z″-f curve at the lower frequency end, as shown in those figures. The theory and this procedure used for determining C_E and α_E from the Z″-f curve are described in detail elsewhere (Katsube, 2001; Katsube and Scromeda-Perez, 2003).

EXPERIMENTAL RESULTS

Results of the spectral-induced polarization measurements, represented in terms of complex impedance amplitude (Z^+), real impedance (Z′), and imaginary impedance (Z″) for the four metal plates are listed in Tables 2a and 2b for the frequency range of $1–10^6$ Hz. The Z^+ is expressed by the following equation (Katsube and Scromeda-Perez, 2003)

$$Z^+ = \sqrt{(Z'^2 + Z''^2)}. \qquad (5)$$

Measurements were made 24 h after NaCl solution saturation of the filter paper, to ensure that they represent impedance values that are stable with time (Katsube and Salisbury, 1991). Under this condition, it is expected that the NaCl solution would have chemically equilibrated with the filter paper. Results for the electrochemical double-layer capacitance (C_E), in terms of farads per square centimetre, and frequency-coefficient (α_E) values determined for the four metal plate are listed in upper sections of Tables 2a and 2b.

The C_E values in Table 2b for the gold and stainless steel plates are correct, because the two plates for each specimen are acting like two electrodes facing each other separated by filtered paper; however, the single platinum and silver plates have the graphite plate electrodes on both sides separated by the filtered paper layers. That situation causes the electrochemical double-layer impedance of the graphite electrode surfaces to be in series with those of the metal plates. This causes an error in the measured C_E values listed in Table 2a for these two metals. That is, equation 2 becomes

$$Z'' = 1/(C_{EM}\omega^{aM}) = 1/(C_{GE}\omega^{aGE}) + 1/(C_E\omega^{a}) \qquad (6)$$

for the case that the two graphite electrodes are in series with the metal plate. The C_{GE} and C_{EM} are the electrochemical double-layer capacitances of the graphite electrodes and that of the combined effect of the graphite electrodes and metal plates. The a_{GE} and a_M are the coefficients for the graphite electrodes and the combined effect of the graphite electrodes and metal plate, which are

$$a_{GE} = 1 - \alpha_{GE} \qquad (7)$$

$$a_M = 1 - \alpha_M, \qquad (8)$$

where α_{GE} and α_M are the corresponding frequency coefficients. The C_{GE} values of the graphite electrodes used in this study for the platinum and silver metal packages are 1.72×10^{-4} F/cm^2 and 1.06×10^{-4} F/cm^2, respectively (Scromeda and Katsube, 2006), and the corresponding two α_{GE} values for the same electrodes are 0.235 and 0.230, respectively.

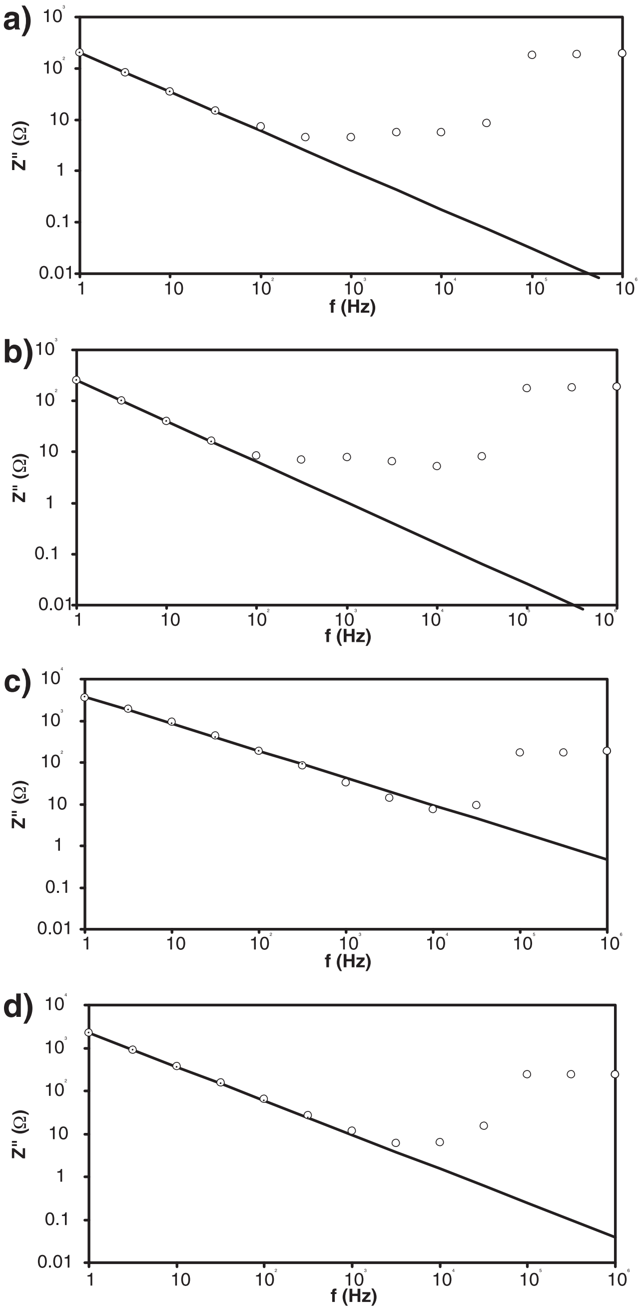

Figure 3. Examples of Z_E-f curves expressed by equation 2 using the derived values of α_E and C_E for: **a)** platinum where $C_E = 4.76 \times 10^{-5}$ F/cm^2 and $\alpha_E = 0.237$, **b)** silver where $C_E = 3.54 \times 10^{-5}$ F/cm^2 and $\alpha_E = 0.202$, **c)** gold where $C_E = 3.09 \times 10^{-5}$ F/cm^2 and $\alpha_E = 0.350$, and **d)** stainless steel where $C_E = 3.98 \times 10^{-5}$ F/cm^2 and $\alpha_E = 0.207$. Minor adjustments were made to these derived values in order to make a visual best fit with the linear section of the Z″-f curve.

Table 2a. Results of Z^+, Z', and Z'' over a frequency range of 1–10^6 Hz for platinum and silver plates, measured with one sheet of filter paper saturated in 0.01 N NaCl on each side of metal plate.

Frequency (Hz)	Platinum $C_E = 4.756 \times 10^{-5}$ F/cm^2, $\alpha_E = 0.237$, A = 5.00 cm^2			Silver $C_E = 3.538 \times 10^{-5}$ F/cm^2, $\alpha_E = 0.202$, A = 9 cm^2		
	Z^+ (Ω)	Z' (Ω)	Z'' (Ω)	Z^+ (Ω)	Z' (Ω)	Z'' (Ω)
1	221.00	95.60	200.00	273.00	103.00	252.00
3	97.60	52.00	82.60	116.00	56.40	102.00
10	48.00	33.40	34.50	55.40	38.30	40.10
30	29.40	25.40	14.90	35.20	31.10	16.50
10^2	22.70	21.50	7.19	28.80	27.60	8.42
3×10^2	19.60	19.10	4.57	25.20	24.20	7.06
10^3	17.40	16.80	4.56	20.30	18.70	7.75
3×10^3	14.20	13.00	5.60	14.30	12.70	6.55
10^4	10.80	9.17	5.72	10.90	9.58	5.18
3×10^4	11.30	7.35	8.61	11.80	8.49	8.15
10^5	190.00	66.90	178.00	189.00	64.90	178.00
3×10^5	199.00	74.90	184.00	197.00	72.60	183.00
10^6	211.00	87.20	192.00	209.00	84.70	191.00

Z^+ = Complex impedance amplitude.
Z' = Real impedance.
Z'' = Imaginary impedance.
C_E = Electrochemical double-layer capacitance of metal plates.
F = Farads.
α_E = Frequency coefficient.
A = Area of filter paper.

Table 2b. Results of Z^+, Z', and Z'' over a frequency range of 1–10^6 Hz for gold and stainless steel plates, measured with two sheets of filter paper saturated in 0.01 N NaCl in between the two metal plates.

Frequency (Hz)	Gold $C_E = 3.09 \times 10^{-4}$ F/cm^2 $\alpha_E = 0.350$ A = 3.06 cm^2			Stainless steel $C_E = 3.98 \times 10^{-4}$ F/cm^2 $\alpha_E = 0.207$ A = 23.8 cm^2		
	Z^+ (Ω)	Z' (Ω)	Z'' (Ω)	Z^+ (Ω)	Z' (Ω)	Z'' (Ω)
1	4653.00	2980.00	3570.00	2390.00	728.00	2270.00
1.6	3530.00	2140.00	2810.00	1650.00	521.00	1560.00
2.5	2660.00	1520.00	2180.00	1140.00	377.00	1080.00
4.0	1980.00	1080.00	1660.00	798.00	274.00	750.00
6.3	1460.00	766.00	1250.00	560.00	201.00	523.00
10	1080.00	547.00	927.00	395.00	147.00	366.00
16	787.00	395.00	681.00	279.00	108.00	257.00
25	576.00	290.00	497.00	198.00	79.80	181.00
40	421.00	217.00	361.00	141.00	59.40	128.00
63	309.00	166.00	260.00	101.00	44.70	90.10
10^2	227.00	130.00	186.00	72.20	34.20	63.60
1.6×10^2	169.00	105.00	133.00	52.20	26.70	44.90
2.5×10^2	129.00	88.00	98.80	38.30	21.40	31.70
4.0×10^2	101.00	76.50	65.80	28.60	17.70	22.40
6.3×10^2	82.70	68.40	46.40	22.00	15.10	16.00
10^3	70.90	62.90	32.60	17.50	13.20	11.50
1.6×10^3	63.50	59.20	23.00	14.60	11.90	8.49
2.5×10^3	58.90	56.70	16.30	12.80	11.00	6.58
4.0×10^3	56.20	55.00	11.80	11.70	10.30	5.58
6.3×10^3	54.60	53.90	8.91	11.30	9.89	5.44
10^4	53.60	53.10	7.42	11.40	9.58	6.25
1.6×10^4	53.10	52.60	7.15	12.50	9.32	8.26
2.5×10^4	52.80	52.20	8.14	15.00	9.05	11.90
4.0×10^4	53.00	51.90	10.70	20.10	8.62	18.10
6.3×10^4	53.80	51.50	15.50	29.20	7.63	28.10
10^5	168.00	10.70	168.00	295.00	170.00	241.00
1.6×10^5	169.00	11.20	168.00	295.00	171.00	240.00
2.5×10^5	171.00	13.10	170.00	298.00	175.00	241.00
4.0×10^5	172.00	14.70	171.00	299.00	178.00	241.00
6.3×10^5	176.00	18.90	175.00	306.00	186.00	242.00
10^5	191.00	32.70	188.00	323.00	210.00	245.00

Z^+ = Complex impedance amplitude.
Z' = Real impedance.
Z'' = Imaginary impedance.
C_E = Electrochemical double-layer capacitance of metal plates.
F = Farads.
α_E = Frequency coefficient.
A = Area of filter paper.

Table 3. Results of C_E and α_E values for the four metal plates determined from the measured results in Tables 2a and 2b.

Metal plates	C_E (F/cm^2 x 10^{-5})	α_E
Platinum	6.42	0.231
Silver	5.28	0.185
Gold	3.09	0.350
Stainless steel	3.98	0.207

C_E = Electrochemical double-layer capacitance of metal plates.
F = Farads.
α_E = Frequency coefficient.

In order to eliminate the graphite electrode effect, equation 6 at two angular frequencies, ω_1 and ω_2, are used as follows:

$$1/(C_E\ \omega_1^{a}) = 1/(C_{EM}\omega_1^{aM}) - 1/(C_{GE}\ \omega_1^{aE}) \quad (9)$$

$$1/(C_E\ \omega_2^{a}) = 1/(C_{EM}\omega_2^{aM}) - 1/(C_{GE}\ \omega_2^{aE}) \quad (10)$$

The two frequencies chosen for this correction are 10 Hz and 100 Hz, or in terms of angular frequencies, they are 31.4 and 314. Details of this correcting procedure are discussed in a previous publication (Katsube and Scromeda-Perez, 2003). The result of using equations 9 and 10 to determine the correct C_E and α_E values for the platinum and silver metals are listed in Table 3. As a result, the C_E values for the four metals are in the ranges of 3.09×10^{-5} F/cm^2 to 6.42×10^{-5} F/cm^2. The α_E values for the same set of four metals are in the ranges of 0.185 to 0.350.

DISCUSSION AND CONCLUSIONS

The results for the electrochemical double-layer capacitance (C_E) and frequency coefficient (α_E) determinations indicate that their values (Table 3) are in the ranges of 3.09×10^{-5} F/cm^2 to 6.42×10^{-5} F/cm^2 and 0.185 to 0.350, respectively, for the four metal plates (Pt, Ag, Au, and stainless steel). These C_E and α_E values are somewhat smaller than those for the graphite electrodes, in general, which are 1.06×10^{-4} F/cm^2 to 4.07×10^{-4} F/cm^2 and 0.181 to 0.360, respectively (Scromeda and Katsube, 2006), and which are 1.06×10^{-4} F/cm^2 to 1.72×10^{-4} F/cm^2 and 0.230 to 0.235, respectively, specifically for the graphite electrodes used in this study.

The C_E values for the graphite electrodes used in this study were not large enough so that their effect on the measurements could be disregarded for the cases where the graphite electrodes were in a series relationship with the metal plates, such as those for the Pt and Ag plates in this study. Therefore the measured C_E and α_E values for the platinum and silver plates have been corrected by eliminating the graphite electrode effects.

The imaginary impedance versus frequency (Z''-f) curves in Figure 3 for the four metal plates indicate that the linear sections, at the lower frequency end of the curves, have a frequency range wide enough to determine the C_E and α_E values with good accuracy. This implies that the C_E and α_E values for the four metal plates can be considered to have good accuracy.

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REFERENCES

Gauvreau, C. and Katsube, T.J., 1975. Automation in electrical rock property measurements; *in* Report of Activities, Part A; Geological Survey of Canada, Paper 75–1A, p. 83–86.

Katsube, T.J., 1975. The electrical polarization mechanism model for moist rocks; *in* Report of Activities, Part C; Geological Survey of Canada, Paper 75–1C, p. 353–360.

Katsube, T.J., 2001. An analytical procedure for determining spectral induced polarization characteristics of anisotropic rocks, Yellowknife mining district, Northwest Territories; Geological Survey of Canada, Current Research 2001–E3, 29 p.

Katsube, T.J. and Salisbury, M., 1991. Petrophysical characteristics of surface core samples from the Sudbury structure, Ontario; *in* Current Research, Part E; Geological Survey of Canada, Paper 91–1E, p. 265–271.

Katsube, T.J. and Scromeda-Perez, N., 2003. A method to determine electrode polarization characteristics; Geological Survey of Canada, Current Research 2003–H2, 7 p.

Katsube, T.J. and Walsh, J.B., 1987. Effective aperture for fluid flow in microcracks; International Journal of Rock Mechanics and Mining Sciences and Geomechanics Abstracts, v. 24, no. 3, p. 175–183. doi:10.1016/0148-9062(87)90525-0

Scromeda, N. and Katsube, T.J., 2006. Electrochemical double layer capacitance of graphite electrodes: preliminary results; Geological Survey of Canada, Current Research 2006–H1, 7 p.

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