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IMPEDANCE BRIDGE METHOD FOR LABORATORY MEASUREMENT OF RESISTIVITY AND DIELECTRIC CONSTANT OF EARTH MATERIALS: 100 Hz-100 MHz

By

R. C. Bigelow and W. R. Eberle

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IMPEDANCE BRIDGE METHOD FOR LABORATORY MEASUREMENT OF RESISTIVITY AND DIELECTRIC CONSTANT OF EARTH MATERIALS: 100 Hz-100 MHz

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ABSTRACT

A system of two-terminal bridges is used to measure the resistivity and dielectric constant of an earth material at decade intervals of frequency from 100 Hz to 100 MHz. Measurements are made by means of two transformer-type bridges (Wayne Kerr B221 and B601) and a self-contained, modified, Schering bridge (Hewlett Packard 250B). The null detector for the Wayne Kerr bridges is a tunable indicating amplifier (Rhode and Schwarz UBM) whose output is observed as a Lissajous pattern on an X-Y oscilloscope (Tektronix RM503).

The sample is connected to the measurement system through a chemically reversible electrode which is backed by a platinized platinum electrode. Silver and silver chloride are precipitated in a disk of blotting paper and subsequently soaked in a sodium chloride solution to form a chemically reversible electrode.

Platinum or platinum-plated brass substrates are electrochemically platinized in chloroplatinic acid to form the metal electrode. Brass is chemically platinum-plated in weak chloroplatinic acid. The electrodes are mounted with the sample in a Lucite test cell. The impedance of the electrodes is found to be $\lesssim 3.8$ percent of the sample impedances.

For frequencies between 100 Hz and 100 MHz, the resistivities and dielectric constants of a sample of material are equivalent to those of the material in the field if the resistivity of the sample at 100 Hz is equal to the low frequency or d-c resistivity of the material measured in the field. Water can be added to samples to change their electrical properties by saturating competent samples under vacuum or by injecting water into unconsolidated samples. Samples can be desaturated by packing them in contact with dry blotting paper to remove a portion of the pore water and soluable ions.

Liquids of known dielectric constant are used as standards to calibrate the bridge system and to generate corrections for the fringing capacitances of the test cells. Measurements on noninductive resistors are used to determine the effects of resistive loading, stray capacitance, and lead inductance on capacitance measurements on the B601 bridge and, if necessary, on the B221 bridge. A computer program calculates the resistivity and dielectric constant of the sample at each decade of frequency from the measured data and from the corrections.

Keywords: electromagnetic pulses, impedance, dielectrics, detectors, substrates, frequency, earth materials

INTRODUCTION

The a-c electrical characteristics of an earth material can be described in terms of the material's resistivity, ρ, relative dielectric constant, κ, and relative magnetic permeability, κ_m. In general, both ρ and κ are functions of frequency and depend on the physical characteristics of an earth material, on the amount of water, and on the ion content of the water contained in the material. However, except for magnetic earth materials, κ_m is approximately unity and its effects on the a-c electrical properties of earth materials can be neglected. If desired, κ_m can be determined from measurements of magnetic susceptibility on a commercially available susceptibility bridge.

Personnel of the USGS (U.S. Geological Survey) have developed a laboratory method for experimentally determining the resistivities and dielectric constants of earth materials in the frequency range 100 Hz (hertz) to 100 MHz (megahertz). Parts of the laboratory method are described in earlier reports by Scott, Carroll, and Cunningham (1967), Judy (1967), Judy and Eberle (1969), Eberle (1970), Carroll, Eberle, Cunningham, and Jones (1970), and the companion article to this report, Bigelow and Eberle (1972). The object of this report is to create a single-source reference for the laboratory method including updated material from the previous reports and current laboratory techniques, recipes, and methods of data analysis that have not been reported previously.

In this chapter, earth materials are discussed in terms of the experimental problems they create in the measurement system. Then, three different methods of measuring earth-material electrical properties are reviewed to indicate the reasons for choosing one of them. In subsequent chapters, the methods of making electrodes, preparing samples and making the experimental measurements are described. Methods of calibrating and correcting the measured values are given and an analysis of errors is performed. Chemical recipes and some formulas are presented in an appendix for convenient reference.

Problems of measurement

The problems of measuring the electrical properties of earth materials are affected by the physical properties of the materials. Many nonmetallic earth materials are insulators when dry but electrically conductive when wet. Water in the pore spaces of the material provides conduction paths through the material for ions dissolved in the water. Thus, conduction through earth materials is electrolytic not electronic. If an electric field is applied through metallic electrodes to a sample of rock or soil, the ions in the pore water will migrate until they reach the electrodes. Unlike electrons, the ions cannot, in general, enter the metal; rather, they form a polarization layer on the electrode. The electrical potential across the polarization layer and the capacitance of the layer are generally unknown. Thus, it is necessary to either avoid including the effects of polarization layers in measurements of earth-material impedances or to design electrodes that do not form such layers.

The percentage of pore space filled by water and the ion concentration in the pore water strongly affect the resistivity and dielectric constant of an earth material. The presence of clay minerals in pore spaces can change the ion concentration in the pore water owing to the large cation exchange capacity of clay (Keller and Frischknecht, 1966). Therefore, the ion concentration in the pore water is not a generally known quantity.

The resistivities of earth materials can range from much less than 0.1 ohm-m (ohm-meter) to greater than 1 megaohm-m (megaohm-meter); dielectric constants can range from more than 10^6 at 100 Hz to less than 10 at megahertz frequencies. Therefore, the measurement system must accommodate materials having resistivities and dielectric constants within those ranges.

Comparison of measurement systems

Emerson (1969) reviews several methods of measuring the electrical properties of earth materials. Only three of the measurement systems can be used to measure both resistivity and dielectric constant in earth materials: the inductive, the four-terminal, and the two-terminal systems. The inductive system is limited to extremely low resistivity earth materials ($\lesssim$0.1 ohm-m) in the range of frequencies 100 Hz to 100 MHz and is, therefore, not considered usable for most materials. The four-terminal measurement system has been used by Madden and Marshall (1958), Keevil and Ward (1962), and Emerson (1969). The two-terminal system is the basis of the USGS laboratory method.

The four-terminal system is shown in figure 1. The two current electrodes are separated from the two potential electrodes; conduction between the current electrodes takes place through the sample and through the electrolyte in the cells at the ends of the sample. The

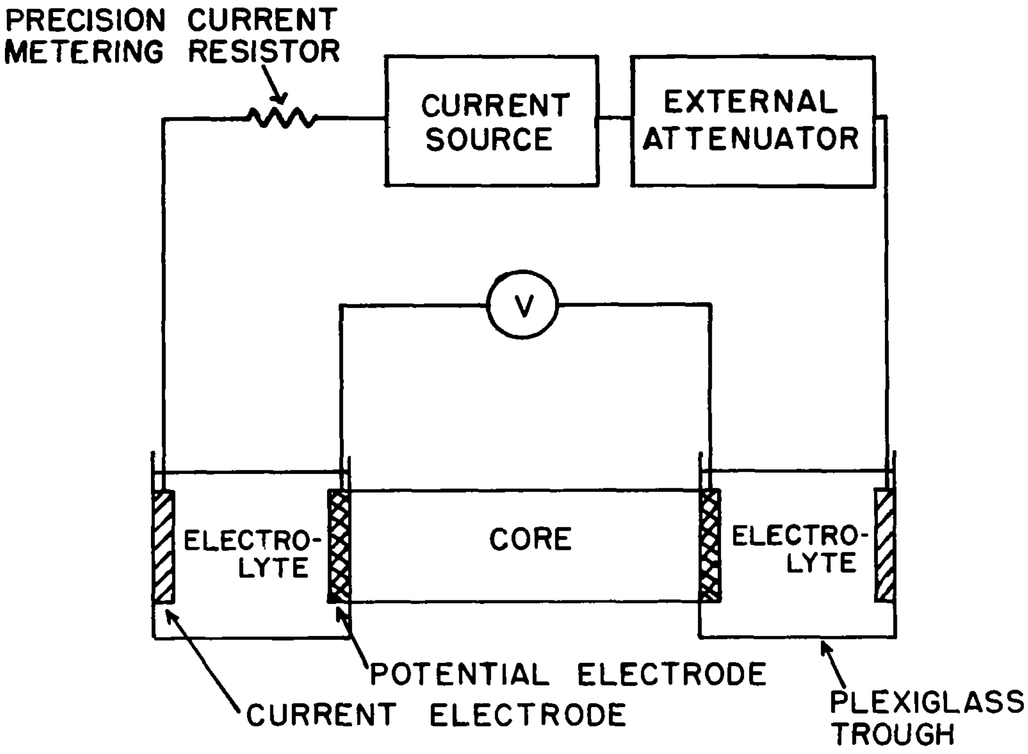


Figure 1.--Four-terminal measurement system. V is a voltmeter. (After Emerson, 1969.)

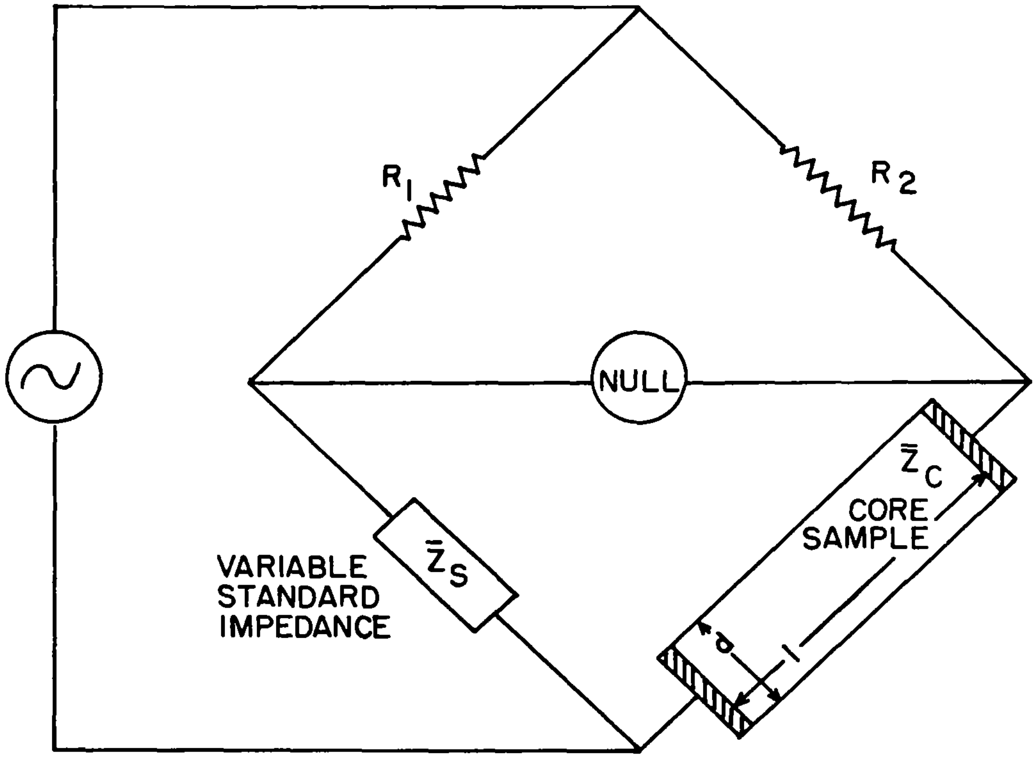
current, voltage, and phase between them are measured individually to determine the resistivity and dielectric constant of the sample.

The four-terminal system is designed to avoid the problem of polarization layers on the electrodes. Because current is continuous throughout the system, it is not affected by the potential drops caused by ionic layers on the current electrodes. The measured potential across the sample does not include the potential drops across the current electrodes. Thus, layers of ions on the current electrodes do not affect the measured resistivity of the sample. The high impedance of the voltmeter circuit insures that the current flow through the potential electrodes is small. Ions that accumulate on the potential electrodes as a result of current flow are chemically neutralized at the surfaces of the potential electrodes. (See Electrodes and test cell, p. 9, for a discussion of this point.)

The major advantage of the four-terminal system is that polarization layer effects are unambiguously avoided. Fuller and Ward (1969) have critiqued the system and noted several disadvantages: the earth material must be fully saturated with electrolyte; spurious coupling can occur between the current generator and the high impedance voltmeter; the circuit is sufficiently large that high-frequency measurements are difficult; and isolation transformers in the voltmeter circuit may cause high noise level and spurious phase shifts in the circuit.

The basic two-terminal system is shown in figure 2 (after Emerson, 1969). The bridge is null balanced when the voltage across the detector goes to zero. At null, the unknown impedance is read

Figure 2.--Two-terminal bridge system. (After Emerson, 1969.) R_1 and R_2 are fixed, standard resistances. At null: $\bar{Z}_c R_1 = \bar{Z}_s R_2$.



directly from the dials of the bridge and is only a function of the ratios of internal standard impedances.

The two-terminal system ideally suffers from none of the disadvantages associated with the four-terminal system; however, the impedance of the electrodes is included in the total measurement. As will be illustrated in the following chapter, the electrode impedance is minimized by using chemically reversible blotter electrodes backed by a platinized platinum electrode. As Fuller and Ward (1969) have pointed out, electrolyte in the blotters can diffuse into or out of the sample. With care, the diffusion can be limited so that incompletely saturated samples can be measured. Owing to the nature of the impedance bridge system, measurements can only be taken in the frequency domain and not the time domain. The method can be used from 100 Hz to 100 MHz with appropriate bridges, whereas the highest frequency at which the four-terminal system has been used is 1 MHz (Fuller and Ward, 1969). By comparison it is clear that the two-terminal system is more flexible and can be used at a wider range of frequencies than the four-terminal system, provided the electrode impedance on the former system is minimized.

ELECTRODES AND TEST CELL

In this chapter, the electrodes that are used in the two-terminal measurement system are described and the techniques for making them are given. Two types of electrodes are described: the chemically reversible blotter electrode and the platinized platinum electrode. The two types of electrodes are used in tandem to form a composite electrode; the assembly of the electrodes into a test cell with a prepared sample is illustrated in the Test cell section of this chapter (p. 18) and described in a following chapter, Procedures, p. 36.

The primary function of electrodes in the two-electrode-measurement system is to provide an interface between the earth material under measurement, in which the current is ionic, and the measurement system, in which the currents are electronic. Moreover, the electrodes must be nearly lossless and cause little or no phase shift between current and voltage as compared to the loss and phase shift caused by the earth material. The two conditions are met if the series resistance of the electrodes is much less than that of the earth material and if the series capacitance of the electrodes greatly exceeds that of the earth material.

If an earth material is placed between metal electrodes across which a d-c voltage is applied, ions move through the earth material under the influence of the applied potential, accumulate at the interface between the electrode and the earth material, and form a polarization layer. The ion layer and electrode surface become, in effect, two plates of an electrolytic capacitor. In time, current ceases to flow and all the applied voltage appears across the polarization layer. If an a-c voltage is applied, the buildup of the polarization layer depends on the period of the applied voltage; the longer the period, the greater the accumulation of ions at the interface during each half cycle before the voltage reverses. If the period is very short compared to the characteristic time of formation for the polarization layer, the layer and the potential drop across it are negligible. The study by Scott, Carroll, and Cunningham (1967) indicates that plain metal electrodes cause appreciable errors in the measurements of capacitances at frequencies as large as 1 MHz. Thus, to make accurate measurements in the range from 100 Hz to 100 MHz, the polarization layers must be minimized.

Silver-silver chloride blotter electrodes

One method of eliminating the polarization layer is to use chemically reversible reactions that convert the ionic current to electronic current. The silver-silver chloride electrode developed by Scott, Carroll, and Cunningham (1967) uses the principle of reversible electrochemical reactions.

If an earth material that contains an aqueous solution of sodium chloride in its pores is placed between two silver-silver chloride electrodes and a voltage is applied across the electrodes, chemical reactions take place between chloride ions and silver and between sodium ions and silver chloride.

The reaction between a chloride ion and silver is

$$Cl^{-}+Ag=AgCl+e^{-} \quad (1)$$

when e^{-} is an electron that is collected by the external circuitry. When a sodium ion leaves the earth material and encounters a silver chloride molecule, the reaction is

$$e^{-}+Na^{+}+AgCl=Ag+NaCl \quad (2)$$

where the electron is supplied by the external circuitry. The sodium chloride molecule dissociates into Na^{+} and Cl^{-} unless the electrolyte in the electrode is saturated with respect to sodium chloride; however, overall electrical neutrality is preserved after the reaction indicated in (1) takes place.

Two chemically reversible electrodes in an electrolyte form an electrochemical storage cell, for example, the cells of a lead-acid battery. When a storage cell is subjected to an a-c current, it charges during one half-cycle and discharges during the other half-cycle. Aside from heat generated in the cell, the net energy put into the cell during one full cycle approaches zero. Similarly, reversible electrodes exhibit low losses when subjected to a-c currents. Thus, the electrodes fulfill the primary criteria for electrodes: they neutralize the polarization layers by chemical reaction and exhibit low losses.

Instructions for making blotter electrodes

The silver-silver chloride electrodes developed by the USGS for the two-terminal-measurement system are disks of blotting paper in which silver and silver chloride are precipitated. The grains of silver and silver chloride are almost completely insoluble in water and tend not to migrate out of the blotters.

The disks are cut from clean white blotting paper to a diameter of 2 1/8 inches; they are chemically prepared in the following manner:

a) Three separate 0.1 normal working solutions of silver nitrate ($AgNO_3$), hydroxylamine-hydrochloride ($NH_2OH \cdot HCl$) and sodium chloride ($NaCl$) are prepared according to directions given in the appendix.

b) A disk of blotting paper is dipped in the $AgNO_3$ and then blotted between paper towels or dry blotting paper so that the disk is moderately damp but not saturated with solution.

c) The disk is dipped in $NH_2OH \cdot HCl$ and blotted again with clean towels or blotting paper as in step b. Hydroxylamine hydrochloride is a mild reducing agent that causes some of the silver ions in the blotter to precipitate as grains of silver.

d) The disk is dipped into the sodium chloride solution and blotted as in step b. The silver nitrate remaining in the blotter is converted to silver chloride precipitate.

e) The blotter electrode is rinsed in distilled water to remove any remaining sodium chloride and silver nitrate and is blotted nearly dry. The disk is then soaked in a sodium chloride solution whose resistivity approximates that of the solution in the pores of the earth material to be measured. The disk is again blotted damp dry.

f) The blotter electrodes should be used immediately if possible. If not, they should be stored in the dark to prevent photoreduction of the silver chloride.

Several points concerning the preparation and use of the blotters should be noted. First, the solutions are never mixed together. Second, electrodes that are used together should be prepared at the same time. Third, if blotting is insufficient, the hydroxylamine hydrochloride and sodium chloride solutions will quickly become contaminated; some contamination is normal and the solutions can be filtered to remove it. Fourth, if the resistivity of the saturant in the earth material to be measured is not known, step e can be omitted leaving the blotter saturated with approximately 0.1 NaCl; however, the earth material will usually absorb salt from the electrodes. (See comments under <u>Saturation and reconstitution techniques</u>, p. 23.)

Platinized platinum electrodes

The nonpolarizing character of the composite electrode system is enhanced if the contact between the blotter and the measurement circuit is made through a platinized platinum electrode. Platinization is a process of electrochemically depositing a coating of fine-grained platinum particles on a metal substrate. The coating is sufficiently fine grained and porous that it tends to trap and absorb light impinging on it; hence, another name for the coating produced by platinization is "platinum black."

Because platinum black is an uncompressed mass of particles on the surface of the substrate most of the surface area of the grains of platinum is exposed. Thus, the total effective area of a platinized surface is much larger than is the area of the same surface unplatinized.

If some of the ions that enter the blotter electrode from the earth material are not neutralized by the chemical reactions described previously, the ionic charge in the blotter will be unbalanced. The unbalanced charge accumulates forming a polarization layer on the surface of the metal electrode that is in contact with the blotter electrode. However, the greater area of a platinized surface as compared to the area of a plain metal electrode reduces the charge per unit area of the polarization layer. By Gauss' law, as the surface charge density on the electrode decreases, so does the potential between the charge layer and the electrode. Thus, platinized surfaces minimize the potential drops across polarization layers.

Platinization instructions

Metal electrodes are platinized by electrodeposition. A working solution of chloroplatinic acid is made up according to the instructions in the Appendix (p. 76) and 500 ml of working solution are placed in a 600-ml Pyrex beaker. A piece of platinum foil is immersed in the solution to serve as an anode and is connected to the positive terminal of a current-limited d-c power supply. The power supply is adjusted to deliver 40-50 ma (milliamperes). The anode need not be thick as it is not dissolved in the platinizing process. The electrode to be platinized is a 2 3/8-inch-diameter disk of metal approximately 5 mils thick. The metal may be either platinum or brass that is platinum plated by a method to be described subsequently (p. 17). The metal disk is covered on one side with masking tape or with rubber cement to prevent platinization on that side. The uncovered side of the disk is cleaned with trichloroethylene to remove dirt and grease, especially fingerprints. After cleaning, the disk is handled only by the edges to prevent recontamination of the surface.

The disk is connected to the negative terminal and the anode to the positive terminal of the power supply. Both disk and anode are immersed in the solution and a current of 40-50 ma is applied. The time required to deposit a coating of platinum black depends on the strength of the chloroplatinic acid solution, which varies because the platinum in the coating is supplied by the solution, not by the anode. The time required for a coating is from 15 to 40 minutes. The disk can be suspended in the solution by means of an alligator clip that is clipped to the edge of the disk. The alligator clip also serves as an electrical contact to the disk. When the coating begins to form, fine streams of bubbles rise from the surface of the disk. Large bubbles can be removed by lightly tapping the disk with a glass rod. Large patches of bubbles consistently appearing at one place on the surface indicate the presence of dirt or grease that must be removed by rewiping the surface with trichloroethylene. After the first coating has been applied, the disk is removed from the platinizing bath, rinsed off with distilled water and examined for imperfections. If the first coat appears uniform, a second coating is applied. The disk should be rotated about 90° to change the point of contact with the alligator clip. After at least two, but no more than four, coatings the electrode is thoroughly dried and examined for imperfections. The coating should be sooty black with few, if any, pinholes. If the coating is gray, it may be too thin or the chloroplatinic acid solution may be exhausted.

When a satisfactory coating is obtained, the masking tape is peeled off or the rubber cement is rubbed off the back of the metal electrode. The final traces of adhesive from the tape or rubber cement are removed from the back of the metal electrode with trichloroethylene. The platinum black coating is easily abraded and should not be touched. Therefore, the electrode is handled by its edges only. Finally, the completed electrodes are rinsed in distilled water to remove traces of chloroplatinic acid and are permitted to dry in air.

The chloroplatinic acid solution becomes exhausted in the process of platinizing and must be renewed occasionally. The strength of the solution is gaged by its color and by the amount of time it takes to deposit a layer of platinum black. The solution is a strong yellow orange when fresh but turns to a pale yellow when exhausted. The time required to deposit one coating ranges from 15 minutes for a fresh solution to about 40 minutes for a nearly exhausted solution. When the deposition time increases to beyond 40 minutes, the solution should be discarded.

More consistent coatings are obtained if the platinizing solution is filtered occasionally to remove tiny particles of platinum that become suspended in the solution. If allowed to accumulate, the particles of platinum will cause the solution to take on a greenish-yellow hue and may spoil the platinizing.

Platinum plating brass substrates

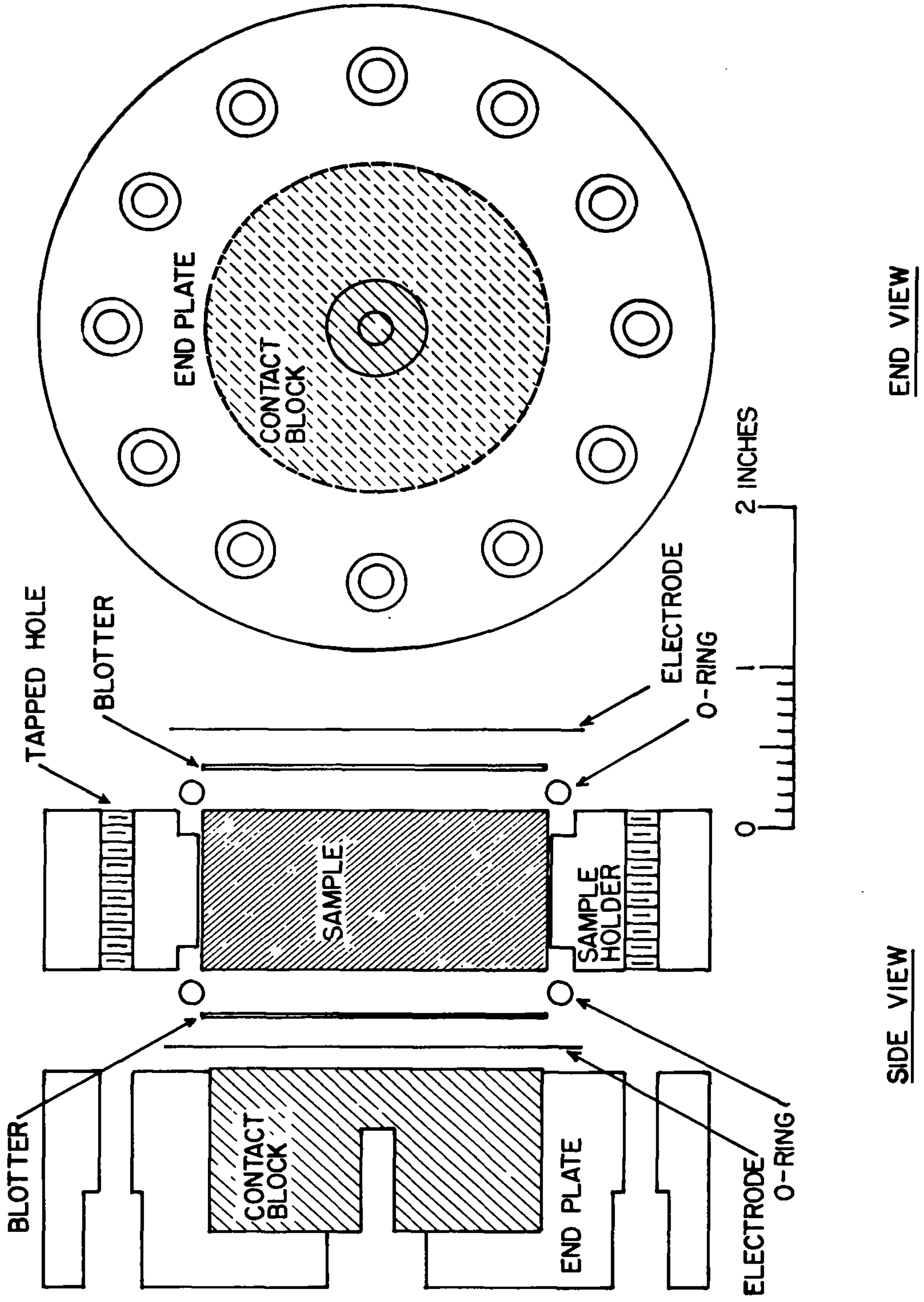
As previously stated, either platinum or platinum-plated brass can be used as the disk substrate. Platinum sheet is definitely easiest to use provided it is hardened anode-grade platinum which contains about 5 percent other elements closely related to platinum, such as palladium and iridium flowers. Platinum is quite expensive, and base metals, for instance brass, can be used in place of pure platinum provided that they are first plated with platinum. Brass is platinum plated by chemical deposition. Both sides of a brass disk are buffed on a wire wheel to brighten the surfaces. Then the brass disk is placed in a weak chloroplatinic acid solution such as exhausted platinizing solution (see Appendix, p. 76). The buffed brass disk is cleaned with trichloroethylene, placed in a 300 ml beaker, and covered with about 3-4 cm of weak chloroplatinic acid solution. After approximately 30 minutes, the brass is removed from the solution, lightly buffed, cleaned with trichloroethylene, and returned to the solution. After three or four platings, the surface should have an adequate coating of platinum; however, the process is not perfect and does leave pinholes. When brass substrate is platinized and is used in combination with the blotter electrodes, copper ions begin to migrate into the blotters. The copper contamination is not serious for periods of from several hours to one day; however, for longer periods of time the problem becomes serious. Green or blue discolorations in the blotter electrodes are evidence of contamination. Pale-violet coloration in used blotter electrodes is caused by photoreduced silver and is normal.

Test cell

The diagram (fig. 3) and much of the information given in this section first appeared in Judy and Eberle (1969); no major modifications of the test cells have been made since that report was issued. The test cell is designed to contain the earth material being measured in order to insure good electrical contact between the electrodes and the earth material and to prevent the evaporation of moisture from either the sample or the blotter electrodes.

A complete test cell consists of a sample holder and two end plates made of Lucite G and two copper contact blocks that are gold plated to prevent corrosion. The entire assembly in figure 3 is held together with as many as twelve 10-32X1-inch nylon screws. The

Figure 3.--End view and cross sectional view of an assembled test cell showing the relative positions of the metal electrodes, blotter electrodes, O-rings, and the sample. Holes around the periphery of the test cell are for 10-32X1-inch nylon screws.



central portion of the cell is 4 inches in diameter and 1 inch long. The center hole, in which the sample fits, is 2 1/8 inches in diameter. L-shaped grooves are cut around the edge of the inner hole to accomodate 1/16-inch-diameter teflon O-rings. When the cell is assembled, the O-rings press against the metal electrode and the sample to provide a moisture seal. Twelve equally spaced holes are drilled around a 3 1/8-inch-diameter circle and are tapped to receive the 10-32X1-inch nylon screws.

The end plates are 4 inches in diameter, 1 3/8 inches thick, and are milled out to accept the contact blocks that are 2 inches in diameter and 1 inch thick. The 5/32-inch-diameter hole in the contact block serves as a receptacle for a banana plug. Twelve clearance holes for the nylon 10-32X1-inch screws are drilled on a 3 1/8-inch-diameter circle and countersunk as shown in figure 3. The end plate is also clearance drilled in the center for the banana plug. The contact block should project a few thousandths of an inch beyond the surface of the end plate to insure good electrical contact between the block and the unplatinized surface of the metal electrode. When the test cell is assembled, the platinized surface of the metal electrode presses against the blotter and the blotter presses against the sample. While as many as twelve screws can be used on each end to hold the sample cell together, three or four on each end are usually sufficient to provide proper electrical contact and moisture sealing if the sample is not left in the test cell for more than a few hours.

SAMPLE PREPARATION

Methods of handling, cutting, and packing earth-material samples are described in this chapter as are techniques for controlling and measuring the moisture content of the samples. The methods and techniques used in preparing samples of competent rock are different from those used in preparing samples of unconsolidated materials; therefore, the preparation of each of the two types of earth material is discussed separately.

Preparation of competent samples

For the purpose of preparing samples, a rock material can be considered competent if unbroken, crack-free samples can be cut from it. Bulk rock material is drilled with an AMX coring drill bit to obtain cylindrical segments of rock about 2 1/8 inches in diameter and at least 4 inches long. If the core drilling is done in the field, the cores should be wiped free of drilling mud to minimize invasion of the core by moisture from the mud. Then the core is wrapped in aluminum foil and the foil-wrapped core is covered with beeswax to prevent evaporation of the core's pore water while the core is being shipped to the laboratory. If bulk material is supplied to the laboratory it should be wrapped similarly to prevent moisture loss during shipment. Bulk material should not be less than 6 inches on a side; smaller pieces of material are difficult to hold while coring or cutting and tend to break up.

After the core is obtained, 1-inch-long right-circular cylindrical samples are cut from it using a diamond-bladed rock saw or glass saw.

Saw marks can be removed by surface grinding hard materials such as granite; however, friable materials, such as some sandstones, can be handlapped on sand paper or grit paper. Surface parallelism should be held to within 1 mm.

Water is used as a lubricant in the cutting and coring processes and tends to invade a sample. Changes in the water content of a sample can be minimized if the surface water on a sample is wiped off immediately after cutting or coring. Evaporation of water from the interior of the sample can be minimized by tightly wrapping the samples in plastic sheeting or by placing it in a small plastic bag closed with twist-ties.

Samples may be marked for identification on their curved surfaces provided totally waterproof ink is used. The ink from so-called "waterproof" marking pens should be carefully tested for permanency before it is used. India ink and the ink from Sanford's Marker deluxe #1000 seem to be stable under water.

Preparation of unconsolidated earth materials

Extreme care should be used in gathering and transporting unconsolidated materials, such as sand, gravel, or soil, to avoid changing the density and moisture content of the material. A piece of pipe can be used to gather some materials. The pipe should be made of a noncorroding material such as polyvinylchloride. It should be at least 6 inches long, have at least a 2 1/8-inch inside diameter, and be of known weight. The pipe is driven into an earth material and withdrawn with a sample of the material in it. The ends of the pipe are plugged to prevent the material from moving and then sealed against leakage of sample moisture. The pipe is shipped to the laboratory where the sample and pipe are weighed, the end plugs are removed and weighed, and the average length of the material in the pipe is determined. With these measurements, the volume and density of the material in the pipe can be found. Material is then pressed out of the pipe directly into the sample holder of a test cell until the holder is filled. The test cell is assembled with electrodes and the sample is electrically measured as described in the next chapter.

Saturation and reconstitution techniques

Occasionally, it is desirable to deliberately change the water content or density of a sample in order to change the electrical properties of the sample. The techniques described in this section allow the water content or density of a sample to be changed in a known way. These techniques also can be used to help eliminate some of the uncertainty introduced by the sample preparation.

Both the amount and salinity of the water that saturates a sample must be measured. Weighing techniques, described in a following chapter, p. 43 , permit determination of the amounts of water in a sample. The salinity is measured indirectly. The conductivity of a saline solution is an almost linear function of its salinity for a given salt; thus, when the conductivity, or its inverse water resistivity, of the solution is known, its salinity is determined. Water resistivity is measured with a dip cell (see section on <u>water-resistivity measurements</u>, p. 27) connected to an audiofrequency impedance bridge.

Full and partial saturation techniques

The water content of a sample can be changed by adding either distilled or ion-containing water to the sample by vacuum saturation. To saturate a competent sample under vacuum, it is placed in a beaker and covered with fluid. The beaker is placed in a vacuum system which is then evacuated by a rotary mechanical pump. As the pressure over the water in the beaker is reduced, air begins to bubble out of the water and out of the sample. After the initial bubbling of air from both the sample and the water has ceased, a valve between the vacuum pump and the vacuum chamber is closed. The sample and water then remain under vacuum overnight. After 18-24 hours, the pump is restarted and the valve is opened. If air bubbles out of the sample when the pressure is lowered, the valve is shut off and the sample again remains under vacuum overnight. The process may be repeated as often as necessary; however, as long as the sample remains in the saturating fluid, diffusion of salts will take place from the sample to the solution or vice versa. The amount of time needed to saturate a sample varies with the permeability of the sample. If desired, the rate of saturation can be determined by weighing the sample after each evacuation to determine the amount of fluid taken up.

Native salts can be deliberately removed from a sample by diffusion into distilled water. A sample is covered with fresh distilled water every day and air is removed from the water by the vacuum saturation technique. As the salts in the sample diffuse into the distilled water, the resistivity of the pore water decreases. The resistivity of the water in which the sample has stood overnight and the sample's resistivity at 1 kHz should both be measured daily before the sample is covered with fresh distilled water. The sample resistivity will usually rise and approach an asymptotic value in several days or a week. If, however, an appreciable fraction of the sample material is soluble material, it may not be possible to remove all the native salt without altering or destroying the sample.

The foregoing technique is also applied in order to saturate a sample with salt solutions of known resistivity. Instead of fresh distilled water, the sample is covered each day with a fresh saline solution of known resistivity and then placed under vacuum.

After the sample has reached equilibrium, it adsorbs no further amounts of salt from the saline solution and the resistivity of the solution around the sample does not increase overnight. The resistivity of a saline solution may decrease about 3 percent after exposure to vacuum overnight because water evaporates from the solution.

Unconsolidated samples are usually saturated in their sample holders to avoid disturbing the sample. Vacuum saturation is not needed unless the particles in the unconsolidated sample are large enough to possess a pore structure that can trap air. A hypodermic needle inserted into the loose material is a convenient method of introducing fluids into an unconsolidated sample.

Samples can be partially saturated either by adding water to the dry sample or by removing water (desaturating) from a fully saturated sample. If distilled water is used for the partial saturation, the best method is to add the water to the dry sample. Dry competent samples can be allowed to stand in a beaker containing a known amount of water until the water is adsorbed. If a saline solution is added to a dry sample material, the resulting electrical characteristics of the material will depend on the clay in the material. Clays may adsorb positive ions from the incoming fluid if the clay is in an exchangeable state (Keller and Frischknecht, 1966). The clay adsorbs positive ions until it is saturated; thus, a generally unknown fraction of the ions supplied by the saline solution will be bound to the clay material.

A method of avoiding the ambiguities caused by the clays is to first saturate and then desaturate the sample. When the sample is saturated, the clays also saturate with positive ions. As the material is desaturated, the ions that are bound to the clay remain in the sample while the free ions migrate out of the sample in proportion to the water removed. To desaturate a saturated material, dry disks of clean blotting paper (not blotter electrodes) are pressed against the ends of the sample overnight or longer. The time must be sufficiently long that the free ions and the water come to equilibrium between the blotters and the sample. A disk of blotting paper 2 1/8 inches in diameter will adsorb approximately 1-2 g (grams) of water from a fully saturated sample. Before it is used for desaturation, the blotting paper should be tested for soluble ions by soaking a known amount of paper in a known amount of distilled water. If the conductivity of the water indicates soluble ions, the disks of blotting paper should be washed in distilled water and then dried before being used for desaturation.

Water-resistivity measurements

A conductivity cell is used to measure the conductivity or resistivity of the solutions with which earth materials are saturated. The cell consists of a pair of platinized platinum electrodes mounted in a glass tube. The cell is immersed in a fluid and the resistivity or conductivity of the fluid is read on a bridge, usually at 1 kHz.

The calibration of the cell is influenced by the spacing and area of the electrodes and by their proximity to the walls of the glass tubes. Thus small changes in the cell geometry make recalibration necessary. The cell is calibrated by immersing it in standard solutions of known conductivity. Potassium chloride solutions are usually preferred by chemists while sodium chloride solutions are more useful to geologists. The resistivities as functions of temperature for standard concentrations of both chlorides are given in the Handbook of Chemistry and Physics (Hodgeman and others, 1963, p. 2691).

A constant of proportionality is computed by finding the average ratio of ρ_w/R_{cell} where ρ_w is the resistivity of the standard solution and R_{cell} is the measured resistance of the fluid in the cell. Accuracies of calibration to within 1 percent or less are possible for measurements ranging over 3 decades of concentration.

ELECTRICAL MEASUREMENTS SYSTEM

As indicated in the Introduction, a system of impedance bridges is used to determine the resistivities and dielectric constants of earth-material samples. The measurements are made at decade intervals in the range from 100 Hz to 100 MHz on three bridges: the Wayne Kerr B221 and B601 and the Hewlett Packard 250B.

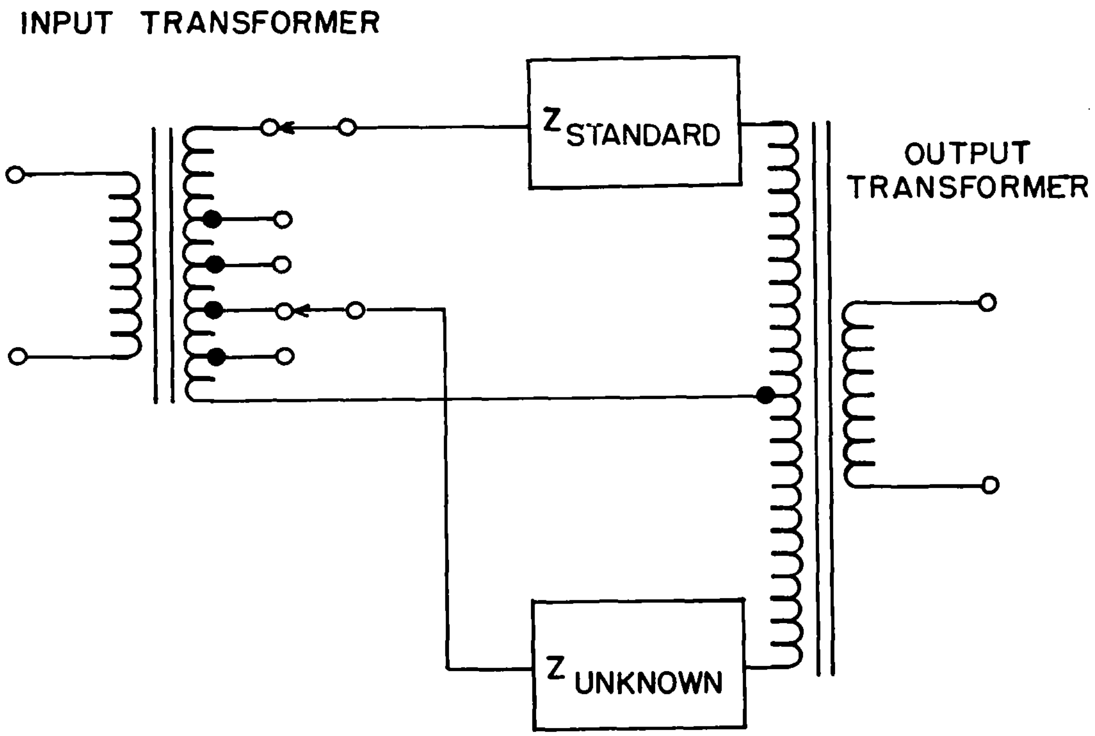
Audiofrequency and radiofrequency bridges

The Wayne Kerr B221 is a transformer-coupled audiofrequency bridge which indicates the parallel equivalent conductance and capacitance of an unknown impedance at its terminals. By use of external generators and detectors, the B221 can be used for measurements in the audiofrequency range 20 Hz to 20 kHz. The B221 is used to make measurements on earth materials at 100 Hz, 1 kHz and 10 kHz.

A basic schematic diagram of a transformer bridge is shown on figure 4. When the currents through the known and unknown impedances are equal, the net current through the primary winding of the output transformer is zero, the voltage across the secondary winding of the transformer is zero, and the bridge is said to be null balanced. Because little or no net current flows in the primary of the output transformer, the transformer does not saturate.

The secondary of the input transformer is tapped to allow several different voltages to be connected to the standard and unknown impedances. Changing the tap connections changes the ratio of known to unknown impedance for which the net current in the primary of the output is zero. By changing tap connections, seven decades of conductance and capacitance values can be measured on the bridge with four-figure accuracy. The tap system scales the total impedance of the unknown impedance to the total known standard impedance. Thus,

Figure 4.--Transformer bridge circuit. The ratio of unknown impedance to standard impedance for which the bridge balances is determined by the settings of the switches that connect the impedances to the secondary winding of the input transformer. (After Wayne Kerr, undated, a.)



the resistive and reactive components of the unknown impedance should be within an order of magnitude of each other to obtain the greatest accuracy of measurement for each component. On the B221 there is an additional circuit not shown on figure 4 that increases the sensitivity of the capacitance range by a factor of 10. The factor of 10 is important because the capacitance impedance of an earth material is usually much higher than the shunting resistive impedance of the material. Thus, the sensitivity of an audiobridge must be greater for capacitance than for resistance measurements.

The measurements at 100 kHz are made on a Wayne Kerr B601 R-F bridge that operates on principles similar to those of the B221. However, owing to the higher frequencies at which it is designed to operate, 15 kHz-5 MHz, the internal circuitry of the bridge is somewhat different from that of the B221.

Resistance and capacitance are read to approximately three-place accuracy on the dials of the B601. However, the resistance-measuring potentiometer, used in the B601 circuitry, exhibits stray capacitance from its wiper to ground and causes errors in the capacitance measurements made on the B601. The stray capacitance varies with the position of the wiper arm; thus, the capacitance error varies with the readings on the resistance dials. A method for eliminating stray capacitance effects is outlined in the chapter on <u>Corrections and calculations</u> (p. 45).

Connection of an unknown to the B601 bridge is by means of one of three sets of terminals; the connection used depends on the magnitude of the unknown impedance. There are also two switches by which the readings on the resistance and capacitance dials can be independently multiplied or divided by factors of 10. The B601 is more flexible in its application than the B221 but less easily used. Like the B221, the B601 R-F bridge can measure unknown capacitances in the presence of low resistance shunts because of its transformer-coupled design. In the present system, the B601 is used for measurements at 100 kHz only.

Both the audio and R-F bridges require an external oscillator and detector system. The oscillator is a Hewlett Packard (HP) 200 CDR sine wave oscillator adjusted for a 3 volt RMS (root-mean-square) output. The oscillator frequency is monitored with an HP5243L counter. The detector system is a Rhode & Schwarz UBM tunable indicating amplifier and a Tektronix RM513 oscilloscope. A tuned amplifier is used to obtain the greatest possible sensitivity and selectivity for null balancing the bridges at a single frequency. The major factors limiting the accuracy of an a-c bridge are usually the sensitivity of the null detecting devices and the presence of harmonics in the oscillator wave form. Harmonics are of concern because the impedances at which bridges null balance are different for different frequencies. Thus, when the bridge is nulled at the fundamental frequency of a complex wave form, a nonzero signal caused by the harmonics appears at the input to the null detector and masks the null. The UBM tunable amplifier provides 80 db (decibels) or more voltage amplification at the frequency to which it is tuned but little or no gain at the harmonics; the minimum detectable signal is 10 μv (microvolts) or less. Another tunable amplifier that can be used is in the General Radio 1232A, which is battery operated and less susceptible to 60

Hz interference than the Rhode & Schwarz unit.

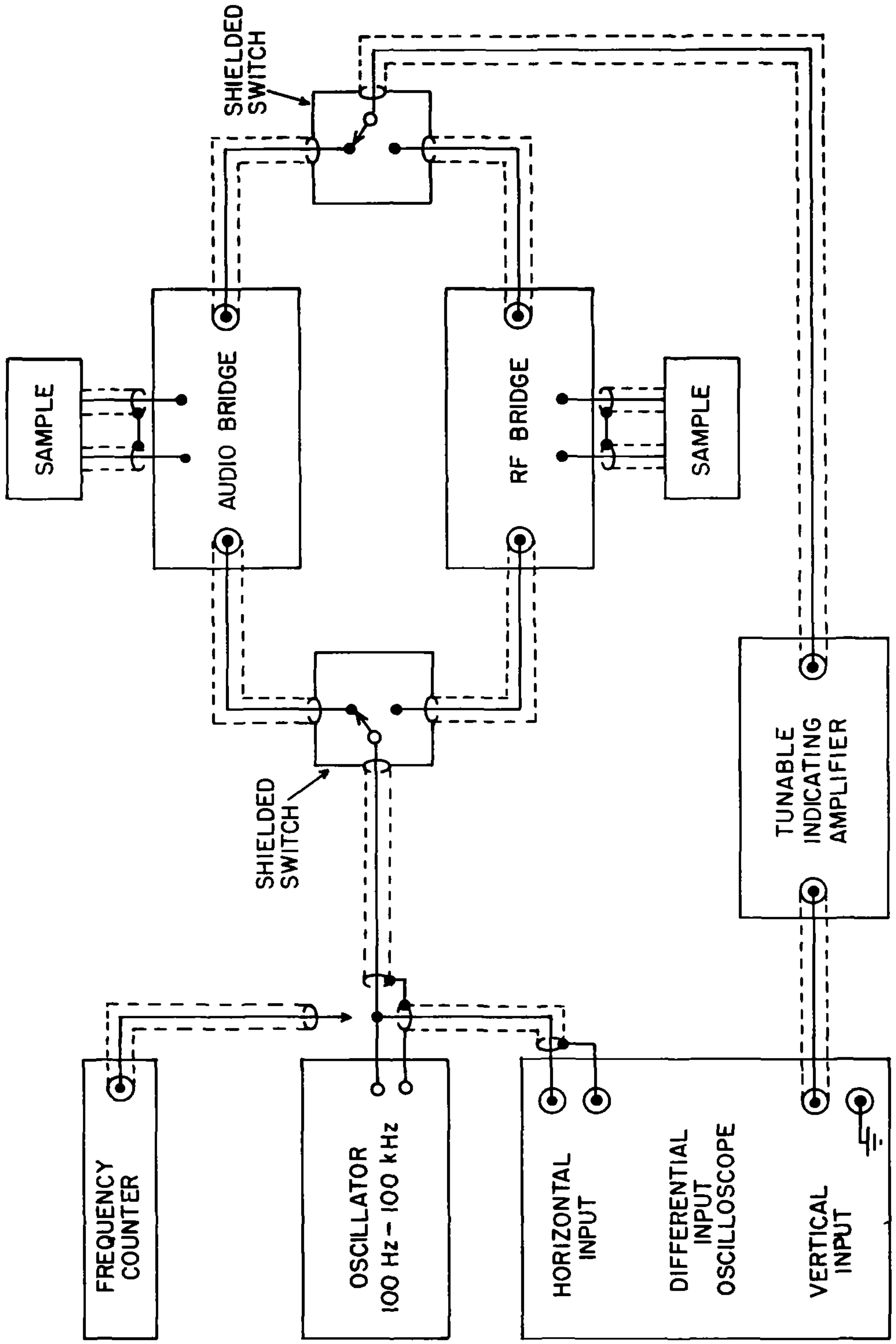
The two bridges, the oscillator, and the oscilloscope are interconnected as shown in figure 5. All interconnections between instruments are by shielded coaxial cable; the switches are shielded and are also connected by means of coaxial cables. To prevent 60 Hz pickup, it is necessary to avoid ground loops completely. A single-point ground is established at one of the terminals of the HP 200 CDR oscillator and all other shields are left floating where possible.

The chassis of the bridges and the casings on the switches must be electrically isolated from each other except for the connections by shielded cable. Because the inputs to the horizontal and vertical amplifiers on the oscilloscope are both connected to the measuring system, one amplifier must operate in differential mode to avoid having two grounds at the oscilloscope. The oscilloscope should not be grounded to earth by a third wire; rather, the oscillator should be grounded by a third wire ground.

The frequency counter can be temporarily connected to the oscillator output to determine the frequency, and then disconnected. The ground loop temporarily imposed by the connection of the counter to the oscillator does not disturb the frequency measurement but, unless disconnected, will introduce 60 Hz noise while the bridge system is being null balanced. The frequency of the oscillator should be checked each time it is changed, or once every half hour if a long series of measurements are being made at one frequency.

The test leads that are used to connect the test cell to a bridge are made from two pieces of coaxial cable. The outer con-

Figure 5.--Interconnection diagram for the impedance measuring equipment at audio and RF frequencies. Shielded leads should be connected as shown. The frequency counter is connected to the oscillator only when needed.



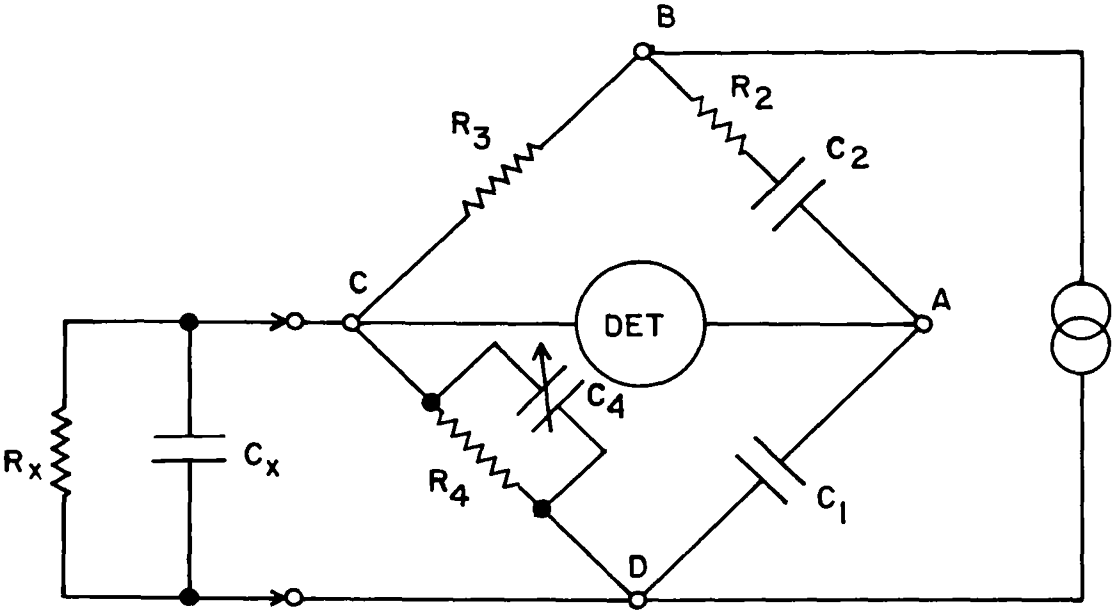
ductors of the cable are connected together at the bridge ground point while the inner conductors of the cables are connected to the terminal posts of the bridge. The inner conductors at the free ends of the test leads are soldered to banana plugs that plug into the contact blocks of the test cell. The designs of the transformer bridges cancel the effects of stray capacitance to ground, however, test lead inductance is not canceled. Thus, when the test leads are connected to the test cell, they should be arranged to minimize their inductance by minimizing the distance between the coaxial cables over most of their length.

VHF bridge

In the present systems, measurements at 1, 10, and 100 MHz are made on a self-contained bridge system, the HP 250B R-X impedance bridge. The bridge measures resistance and capacitance over the range 500 kHz to 250 MHz. The 250B consists of an internal oscillator, a Schering impedance bridge and a super-hetrodyne detection system in one chassis. An earlier model of the bridge, the 250A, was manufactured by Boonton Corp. and is almost identical to the HP 250B.

The basic Schering bridge circuit is shown in figure 6. The advantage of the bridge over bridges of other design is that the only calibrated moving parts are air-gap capacitors; thus, mechanical wear is almost eliminated from the standards. The 250B measures resistances between 15 ohms and infinity in parallel with capacitances from +20 pf (picofarads) to -100 pf. A negative capacitance reading implies that the reactance of the measured unknown is an inductance

Figure 6.--Schering bridge circuit. R_x and C_x represent unknowns. (After Hewlett Packard, 1967.) The circle marked DET represents the detector circuit. R_2, R_3, and R_4 are standard resistors. C_1 is a fixed capacitor. C_2 and C_4 are variable, air-dielectric capacitors. R_x and C_x are the unknown resistance and capacitance, respectively.



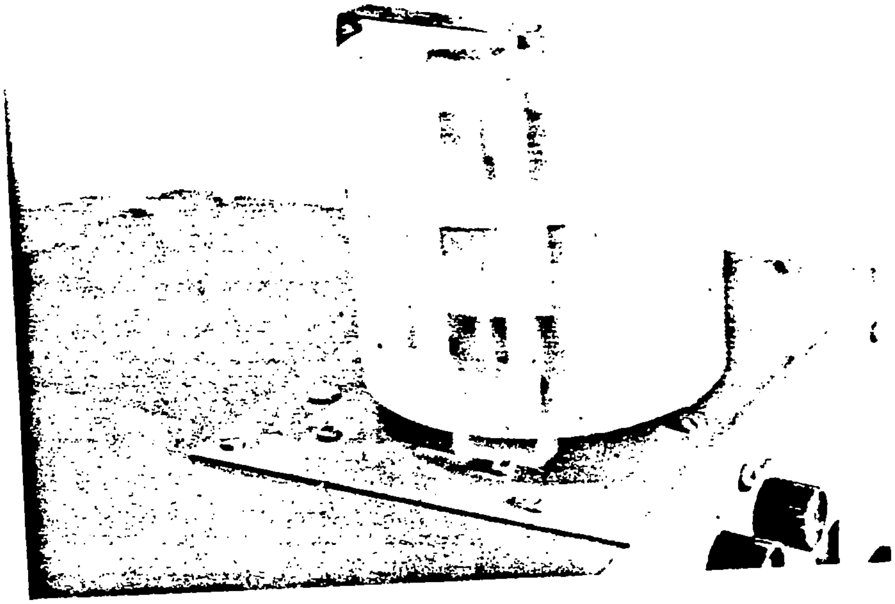
that is resonated by a capacitor of the indicated number of picofarads at the frequency of measurement. The negative capacitance concept is also used as a measure of inductive reactance on the Wayne Kerr bridges.

The HP 250B bridge measures impedances at its terminals, which are only three-quarters of an inch apart; thus, an adapter is needed to connect the test cell to the terminals.

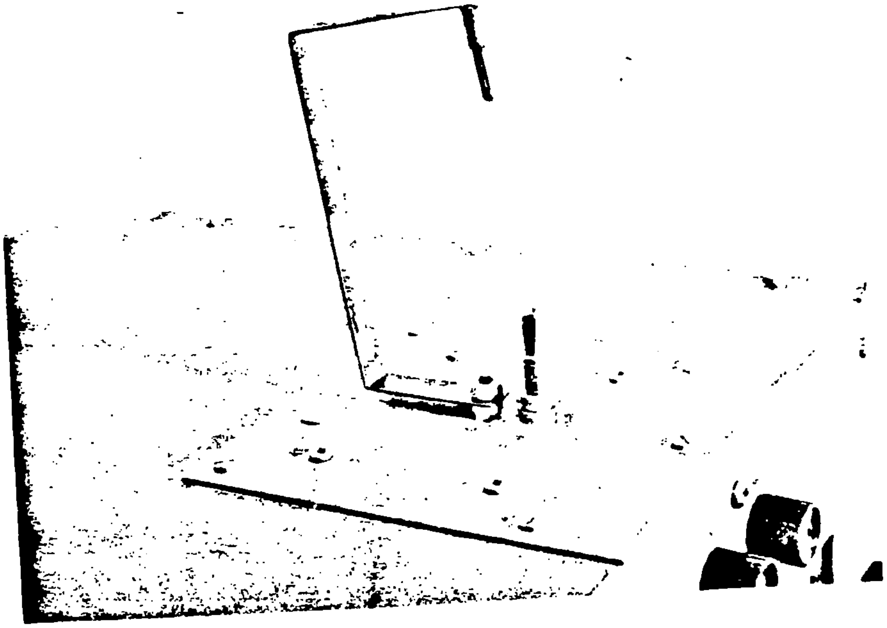
As shown in figure 7 a banana plug is threaded onto the ungrounded terminal of the bridge and the test cell is mounted coaxially over the terminal so that the banana plug may be inserted into one of the contact blocks. Lucite blocks are used to hold the cell at the correct height. A phosphor bronze band is bolted onto the ground terminal. A banana plug, which is soldered to the phosphor bronze band, is inserted into the uppermost contact block of the mounted test cell to provide a ground return. The band is made of phosphor bronze so that repeated bending caused by inserting and removing its banana plug in the contact block will not exceed the elastic limits for the material. The band exhibits inductance when it is connected to the test cell, and the inductance depends on the geometry of the band. The band inductance must be measured to correct for its effects on the values of capacitance and resistance measured on the bridge. The technique of measuring the inductance is given in the section on *Hewlett Packard 250B bridge corrections*, p. 53.

PROCEDURES

A very basic procedure is outlined in this chapter but many variations to suit individual needs are possible. The procedure is



(a)



(b)

Figure 7.--Hewlett Packard 250B R-X meter and connections to the test cell. Photograph (a) shows the test cell in place, and (b) shows the test cell removed.

designed to obtain the following information: the measured resistance and capacitance of a sample at each decade of frequency from 100 Hz to 100 MHz inclusive; the wet, dry, and saturated weights of the sample; and the length and diameter of the sample. By means of formulas given in the following chapter (Corrections and calculations, p. 45), the resistivity and dielectric constant of the sample at each frequency are computed. Formulas for computing the dry bulk density, porosity, fractional water content, and percentage water by volume of the sample are given in the Appendix.

Worksheet

It is convenient to arrange the measured data on a worksheet such as the one shown in figure 8 that is used by the USGS. The measured conductances, resistances, and capacitances of the samples are recorded under G_I, R_I, and C_I, respectively. The R_o and C_o columns are used to record those quantities measured on the Hewlett Packard 250B bridge (p. 43). The subscript, I, implies that the test cell containing the sample is connected or "in" the measurement circuit; the subscript, o, implies that the test cell is disconnected or "out" of the circuit.

The C_o column is also used to record corrections for lead length or resistive loading when needed for the B221 and B601 bridges; the corrections are discussed in the next chapter (p. 45). The corrections are almost always needed for capacitances that are read on the B601 but only rarely for those read on the B221. The information marked "for 10^5 readings" refers to the input connections

Sample designation________________ Run by________________

Date________________

Sample or water temp.________________ °F °C

Length________________cm

Diameter________________cm Water conductivity________________

Frequency (Hz)	G_I (mhos)	R_I (ohms)	C_I (farads)	R_o (ohms)	C_o (farads)
100				---	
1,000				---	
10,000				---	
100,000			pf	∞	pf
for 10^5 readings	connection:	0.1 R, 10 C 1.0 R, 1.0 C 10 R, 0.1 C	ranges:	0.1 R 1.0 R 10 R	0.1 C or 10 L 1.0 C or 1.0 L 10 C or 0.1 L
1 M			pf	KΩ	pf
10 M			pf	KΩ	pf
100 M			pf	KΩ	pf
Check 1,000					

Wt for 100% saturation________________gm 1 Saturation________________%

Wet wt________________gm 2 H_2O by wt________________%

Dry wt________________gm 3 H_2O by vol________________%

1 - 3________________gm

2 - 3________________gm

Figure 8.--U.S. Geological Survey laboratory worksheet.

and settings of range switches on the B601. The appropriate information is circled at the time of measurement. The length and diameter of the sample are entered at the top of the form, as are the temperature and the conductivity of the saturating water, if known. The weight of the sample fully saturated, the wet weight at the time of measurement, and the dry weight of the sample are entered at the bottom of the form.

Measurement procedure

A sample must be gathered, prepared, and, if necessary, reconstituted by methods previously described (p. 21-26). Also, a set of two metal and two blotter electrodes must be prepared before the measurements can be made. The metal electrodes can be prepared at any time and stored until they are needed. The blotter electrodes, however, should be made up immediately before they are to be used to minimize the amount of photoreduction of silver chloride to silver.

After the sample and the electrodes are prepared, they are packaged into a test cell as shown in figure 3. The sample is placed inside the sample holder between two blotter electrodes. The platinized surfaces of the metal electrodes are pressed against the blotter electrodes by the end plates of the test cell. A teflon or viton O-ring, placed in the groove at each end of the sample holder, forms a moisture-proof seal against the metal electrode when the screws that hold the end plates to the sample holder are tightened. At least three screws are used to hold each end plate to the sample holder, although as many as 12 screws may be used to obtain a good moisture seal between the metal electrode and the O-ring.

The cell is allowed to stand for 15-30 minutes to permit the blotters and sample to come to equilibrium. The oscillator is warmed up and adjusted to a frequency of 100 Hz as measured on a frequency counter. The audiofrequency impedance bridge is connected into the measurement circuit by means of the shielded switches.

With the Wayne Kerr B221 bridge slightly unbalanced, the amplifier is tuned to the signal frequency and adjusted for the greatest amplification that is possible without causing the amplifier to oscillate. The display on the oscilloscope should be an oval or a flattened oval similar to a Lissajous pattern. The bridge dials are set to zero then the zero adjustment controls are tuned until the meter on the tunable amplifier reads zero and the display on the oscilloscope is a horizontal straight line.

The test cell is now connected to the circuit by the test leads from the bridge and conductivity and capacitance of the sample in the test cell are measured by nulling the bridge. Null is indicated by a zero amplifier reading and a horizontal straight line on the oscilloscope. The null at 100 Hz is observed for a few minutes. If the measured conductance changes or drifts by more than a few tenths of a percent the sample is too unstable to continue the measurements. The measured conductance of a sample changes because of moisture diffusion between the blotters and the sample or because the blotters are insufficiently pressed against the sample. The former condition may be alleviated by waiting for the diffusion to slow down or by repacking the sample in the test cell, the latter by tightening the nylon screws or by repacking the sample. The drift should be less than 5 percent over the time required, usually about 30 minutes, for a full set of measurements.

If the drifts in the measured quantities are acceptably low, the measured conductance is recorded as G_I and the capacitance is recorded as C_I on the worksheet. The cell is disconnected and the measurement procedure is repeated (except for observing the drift) at 1 and 10 kHz. The same measurement procedure is used at 100 kHz with the B601 bridge switched into the measurement circuit. The data are recorded as R_I and C_I on the worksheet. The connection and range settings on the bridge must be noted on the worksheet because the corrections to the capacitance readings on the B601 are different for each combination of connection and range setting.

The measurements at 1, 10, and 100 MHz are made on the self-contained Hewlett Packard 250B bridge. The bridge is tuned to 1 MHz then the frequency is measured by temporarily connecting a coaxial cable from the terminal of the bridge to the frequency counter. The cable is removed and the bridge is zero balanced. The banana plug is threaded onto the ungrounded terminal at the bridge. The test cell is mounted on the banana plug and the phosphor bronze band is plugged into the top of the cell. A trial balance is made to determine whether the bridge can be balanced without using a shunting inductance across the terminals. If the capacitance can be read on the scale, an inductance is not needed. If the capacitance of the test sample is greater than 20 picofarads, placing a fixed inductance across the bridge terminals shifts the total reactance of the inductance and capacitance into the range of the instrument. The instructions for selecting the proper range-shifting inductance are found in the Hewlett Packard instruction manual for the 250B bridge. Once the measured resistance and capacitance are measured and recorded, as R_I and C_I, respectively, the banana plug on the phosphor bronze band is unplugged from the test cell, as shown in figure 7. The test cell is not removed at this time nor are the phosphor bronze band or any fixed inductors removed from the terminals of the bridge. The bridge is again nulled and the apparent resistance, R_O, and capacitance, C_O, are recorded. R_O and C_O are corrections to the measured values R_I and C_I; they include the effect of a range-shifting inductance, if used. The four readings are used in a computer program, described subsequently, which calculates the resistivity and dielectric constant of the test sample. Once R_O and C_O are found, the test cell is removed and the procedure is repeated at 10 and 100 MHz. If a range-shifting inductance is used, it must be changed each time the frequency of measurement is changed.

When all the electrical quantities have been measured, the conductance and capacitance of the test sample are remeasured at 100 Hz to determine whether the drift in the sample conductance is less than 5 percent. If not, corrective action (see p. 41-42) is taken and the sample is remeasured at each frequency.

Weighing and drying procedures

After the electrical measurements are made, samples are weighed to determine their own weight and that of the water in them. Because a sample that is exposed to air can lose or gain milligrams of water by evaporation or adsorption in a few minutes, samples are always weighed in closed plastic bags. The bags and the twist-ties that are used to close them are weighed before they are used. Weighings should be made to within 1 milligram on a balance that has at least 160 g capacity. A Mettler H6 balance is adequate but is somewhat less convenient than other balances. The sample is removed from the plastic bag and is saturated with distilled water; then it is reweighed to determine the saturated weight of the sample.

Samples are ovendried at 90°C to drive off chemically unattached water. Drying times vary for samples of different materials but most samples will dry in less than two days. Dried samples can be stored in sealed containers over fresh desiccant.while they cool. Cannister-type coffee cans with plastic lids are useful as sealed containers.

If preferred, an unconsolidated sample can be weighed in the sample holder provided thin sheets of plastic are used to cover the ends of the holder to retain the sample and its moisture. The sample is saturated in the holder by adding distilled water and is then reweighed. The sample is then removed from the holder, dried at 90°C, and weighed again to determine its dry weight and the amount of water it has lost. The volume of an unconsolidated sample is assumed to be that of the open space in the sample holder. The wet, saturated, and dry weights are used in the formulas given in the Appendix to determine the physical properties of the sample material.

CORRECTIONS AND CALCULATIONS

The measured values of resistance and capacitance are affected by the impedance of the electrodes, the presence of the test cell around the samples, and a number of effects associated with the impedance bridge system. In this chapter, the methods of determining the effects of electrodes, test cell, and impedance bridges on the measurements are described and correction formulas are derived where needed. The probable or estimated errors of measurement associated with the effects are discussed in a subsequent chapter (p. 62).

Electrode effects and separation of impedances

The separation-of-impedances technique was first described by Scott, Carroll, and Cunningham (1967) and then developed by Judy (1967) and Judy and Eberle (1969) to determine the effects of the composite electrode system on the measurement of sample impedances in the two-terminal bridge system. The development given below is taken primarily from the latter paper.

The impedance of a sample is proportional to its length; however, the impedance of a pair of electrodes is independent of sample length. Thus, if different length samples of a material are measured electrically, the impedance of electrodes should be separable from that of the samples.

The equivalent circuit for a sample is shown in figure 9. The equivalent circuit for the sample is a resistance, R, in parallel with a capacitance, C, where both R and C are functions of the

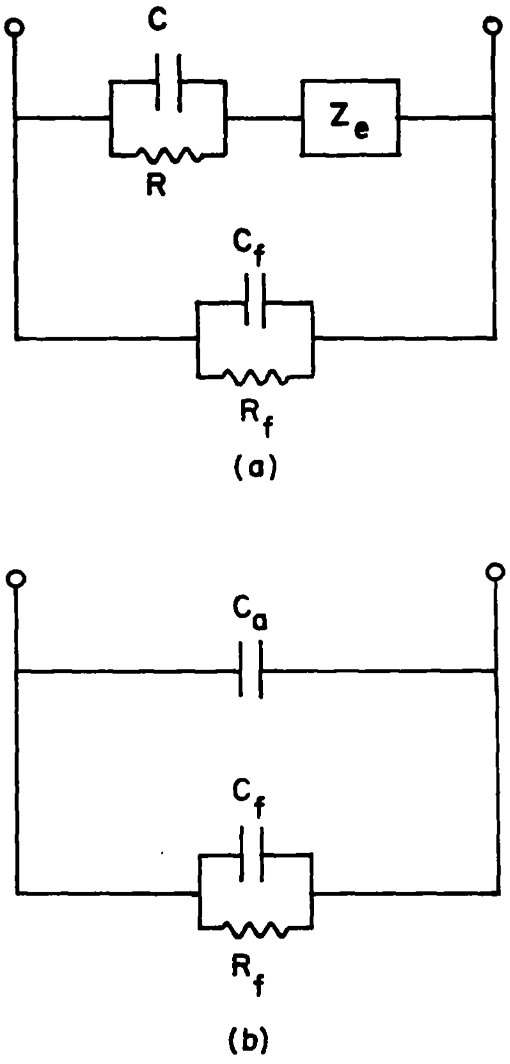


Figure 9.--Electrical equivalent circuits of the test cell; (a) containing the sample, (b) containing air. C_a is the capacitance of the cell when filled with air; see p. 45-49 for meanings of other variables. (After Judy and Eberle, 1969.)

frequency of measurement.

The electrode impedance, Z_e, is in series with the impedance, Z, of the sample resistance and capacitance. The sample impedance is proportional to the length, ℓ, of the sample but the electrode impedance, which is localized at the sample-electrode interfaces, is independent of sample length. When different length samples of the same earth material are measured, the dependence of the total electrode-plus-sample impedance, Z_t, is

$$Z_t=Z_e+Z(\ell) \tag{3}$$

The electrode impedance is found by letting ℓ go to zero.

The sample impedance is found by transforming the parallel combination of R and C into their series equivalents.

$$Z=\frac{R}{1+\omega^2R^2C^2}-j\omega\frac{R^2C}{1+\omega^2R^2C^2} \tag{4}$$

where ω equals the radian frequency (multiplied by 2π). The total impedance, Z_t, is

$$Z_t=\left[R_e+\frac{R}{1+\omega^2R^2C^2}\right]-j\omega\left[I_e+\frac{R^2C}{1+\omega^2R^2C}\right] \tag{5}$$

where Re and ωI_e are the real and imaginary parts of the electrode impedance, respectively. The resistivity and dielectric constant of a right-circular cylinder of material are given by:

$$\rho=R\frac{A}{\ell};\ K=C\frac{\ell}{\epsilon_0 A} \tag{6}$$

where A is the area of the end surfaces of the cylinder and ϵ_0 is the permittivity of free space, $\epsilon_0=8.854\text{X}10^{-12}$ f/m (farad per meter). Substitution from (6) into (5) gives

$$Z_t = \left[R_e + \left(\frac{\rho/A}{1+\omega^2\rho^2K^2\varepsilon_o^2} \right) \ell \right] - j\omega \left[I_e + \left(\frac{\rho^2 K\varepsilon_o/A}{1+\omega^2\rho^2K^2\varepsilon_o^2} \right) \ell \right] \qquad (7)$$

As ℓ goes to zero, Z_t approaches $R_e - j\omega I_e$, the complex electrode impedance. To determine the electrode impedance, the real and imaginary parts of Z_t are measured for several lengths of an earth material. Then the real and imaginary parts of Z_t are separately plotted against the sample lengths. The best straight lines are found by the least-squares method for the two plots; the intercepts of the lines at the $\ell=0$ axis give the real and imaginary parts of the electrode impedance. The coefficients that multiply ℓ in equation 7 are found from the slopes of the plots. The two resulting equations have two unknowns, ρ and K, for which they can be solved to find the true values of ρ and K.

Test cell calibration and correction for fringing

The effects of the test cell on the measured impedance of the sample are compensated for by a set of corrections derived below. The development presented here is substantially the same as the one previously given by Judy and Eberle (1969).

The schematic diagram, figure 9, exhibits the electrical equivalent circuits for a test cell containing a sample and for a test cell containing air. The impedance Z_e can be disregarded (see Error analysis, p.62) compared to C and R, thus the total capacitance, C_{tc}, of the test cell and sample is

$$C_{tc} = C + C_f \tag{8}$$

where C_f is the fringing capacitance caused by the test cell and the total parallel resistance, R_{tc}, is

$$\frac{1}{R_{tc}} = \frac{1}{R} + \frac{1}{R_f} \tag{9}$$

where R_f is the fringing resistance. The dielectric constant and resistivity of the sample material can be substituted into equations (8) and (9) from equation (6)

$$C_{tc} = K\epsilon_o\frac{A}{\ell} + C_f \tag{10}$$

$$\frac{1}{R_{tc}} = \frac{1}{\rho}\frac{A}{\ell} + \frac{1}{R_f} \tag{11}$$

The test cell is also measured without a sample in it. The resistance R' and capacitance C' of an air-filled test cell are

$$C' = \epsilon_o\frac{A}{\ell} + C_f \tag{12}$$

$$R' = R_f \tag{13}$$

By substitution, the equations for resistivity and apparent dielectric constant of the sample are found in terms of the measured quantities R_{tc}, C_{tc}, R', and C'.

$$K_a = \frac{\ell}{A\epsilon_o}(C_{tc}-C') + 1 \tag{14}$$

$$\rho = \frac{A}{\ell}\left(\frac{1}{R_{tc}} - \frac{1}{R'}\right) \tag{15}$$

In practice, R_f and C_f are not constant. The fringing field depends on the resistivity and dielectric constants of the sample material and the test cell. R_f makes only a small contribution to equation (11) because the resistivity of Lucite (of which the test cell is constructed) is extremely high and variations in R_f may be disregarded. The dielectric constant of Lucite, however, is not negligible nor is the fringing capacitance in the test cell; therefore, a calibration procedure is carried out to account for the effects of fringing capacitance.

Several organic liquids that have known dielectric constants (table 1) are used to calibrate the cell. The liquids listed have little or no solvent effect on the test cell.

The test cell is first measured empty to find R' and C' at each frequency, then R_{tc} and C_{tc} are determined for each of the liquids in the test cells. Apparent values of dielectric constant, κ_a, are computed from equation (14) and are related to the true values of dielectric constant, κ_T, for each liquid by means of the equation

$$\kappa_T = m\kappa_a + b \qquad (16)$$

At each frequency, coefficients m and b are determined from the calibration data by the method of least squares. When m and b are known at each frequency, equation (16) is used to correct computed dielectric constants of earth material for the fringing capacitance of the test cell.

Wayne Kerr bridge corrections

The capacitance that is indicated on the Wayne Kerr bridges B601 and B221 during the measurement of a sample may depend on the indicated resistance of the sample if the sample resistance is quite low. The dependence of indicated capacitance on indicated

Table 1.--Calibration standards for resistivity and dielectric constant.

[After Judy and Eberle, 1969.]

Material	Temperature (°C)	Frequency (hertz)	ρ (ohm-meters)	κ
Water[1]	25	10^{5}	5.75×10^{3}	78.2
		10^{6}	5.75×10^{3}	78.2
		10^{7}	5.00×10^{3}	78.2
		10^{8}	4.61×10^{2}	78
Methanol[1]	25	10^{6}	2.90×10^{3}	31
		10^{7}	2.23×10^{3}	31.0
		10^{8}	1.54×10^{2}	31.0
1-Propanol[1]	25	10^{6}	4.97×10^{4}	20.1
		10^{7}	5.26×10^{3}	20.1
		10^{8}	4.76×10^{1}	19.0
1-Butanol[1]	25	10^{4}	8.61×10^{4}	17.4
		10^{5}	1.03×10^{5}	17.4
		10^{6}	1.09×10^{6}	17.4
		10^{7}	4.30×10^{3}	17.4
		10^{8}	4.50×10^{1}	14.8
2-Methyl-1-Propanol[2]	30	3.16×10^{7}	5.69×10^{2}	17
		9.74×10^{7}	4.64×10^{1}	16.5
		1.65×10^{8}	1.96×10^{1}	13.6
1-Heptanol[2]	25	1.00×10^{7}	--------	11.7
		1.26×10^{7}	1.52×10^{3}	11.6
		9.59×10^{7}	3.86×10^{1}	7.86
		1.30×10^{8}	3.29×10^{1}	7.05
Benzene[2]	25	0	--------	2.28
		9.00×10^{9}	--------	2.28

[1] Von Hippel (1954).

[2] Buckley and Maryott (1958).

resistance has three known causes: first, the output transformers of the bridges are excessively loaded and become nonlinear when the sample resistance is very low; second, the inductance of the connecting leads between the bridge and the test cell acts in series with the sample and is measured together with the sample. The mathematics that show the effects of a series inductance between a bridge and a sample impedance are developed in the following section (p. 53); and third, on the B601 only, the resistance measurement potentiometer has stray capacitance to ground that varies with the setting of the potentiometer.

The compensation of the bridges for the foregoing effects is done with a set of noninductive resistors. One-percent-precision deposited film resistors, such as Daleohm type DCM or IRC type MFC, have extremely low inductances; thus, when they are measured on the bridges, any indicated capacitance can be considered an error capacitance.

A test cell is modified so that the resistors can be measured with the cell in place. A hole is drilled into the copper contact block through the curved side of each test cell end plate. The block is tapped so that the shank of a binding post can be threaded into it. The end plates are mounted on the sample holder so that the binding posts are parallel. The test resistors are fastened between the binding posts.

To eliminate the air capacitance of the cell from the calibration measurements, the bridge is zero balanced, and the modified test cell is connected to the test leads. At least 10 resistances per decade of resistance should be measured for each capacitance correction curve; the standard values of resistance used in electronics form a well-spaced sequence.

An individual calibration must be made for each combination of input connection and range switch settings on the B601; however, the corrections for measurements made with the high-resistance input connection may be negligibly small. Corrections to the readings on the B221 are usually negligible except on ranges 6 or 7 when the measurement frequency is 10 kHz; such corrections are generated with the noninductive resistors in the same manner as with the B601.

The indicated capacitances are plotted against the resistance or conductance dial readings on log-log graph paper. The algebraic sign of the correction should be made clear to avoid confusion when the graphs are used. In the present system the correction for a given measurement is determined from the graphs and entered on the work sheet as C_o after the electrical measurements are made.

The measured resistance of a sample is only slightly dependent on the capacitance being measured and no correction to measured resistance for capacitor settings appears to be necessary.

Hewlett Packard 250B bridge corrections

The Hewlett Packard (HP) 250B R-X bridge measures the parallel equivalent resistance R_p and capacitance C_p of passive devices at its terminals. When a test cell is measured on the 250B, a phosphor bronze band connects the grounded terminal on the bridge to one side of the test cell. An equivalent circuit for the sample in the test cell is shown in figure 10. The band is represented as a resistance R_L in series with an inductor, L, and the sample is represented by a resistance R in parallel with a capacitance C. When the test cell is mounted on the ungrounded bridge terminal and the phosphor bronze band is unplugged from the test cell, R_o and C_o are the measured stray resistance and capacitance to ground.

Expressions for R and C are derived in terms of R_I, C_I, R_o, C_o, and L by a sequence of transformations that are illustrated in figure 10.

The sequence begins by expressing R and the magnitude of the impedance, $(j\omega c)^{-1}$, in terms of the series equivalent impedance elements R_s and X_s where the subscript, s, implies a series quantity.

$$R=R_s\left(1+\frac{{X_s}^2}{{R_s}^2}\right) \tag{17}$$

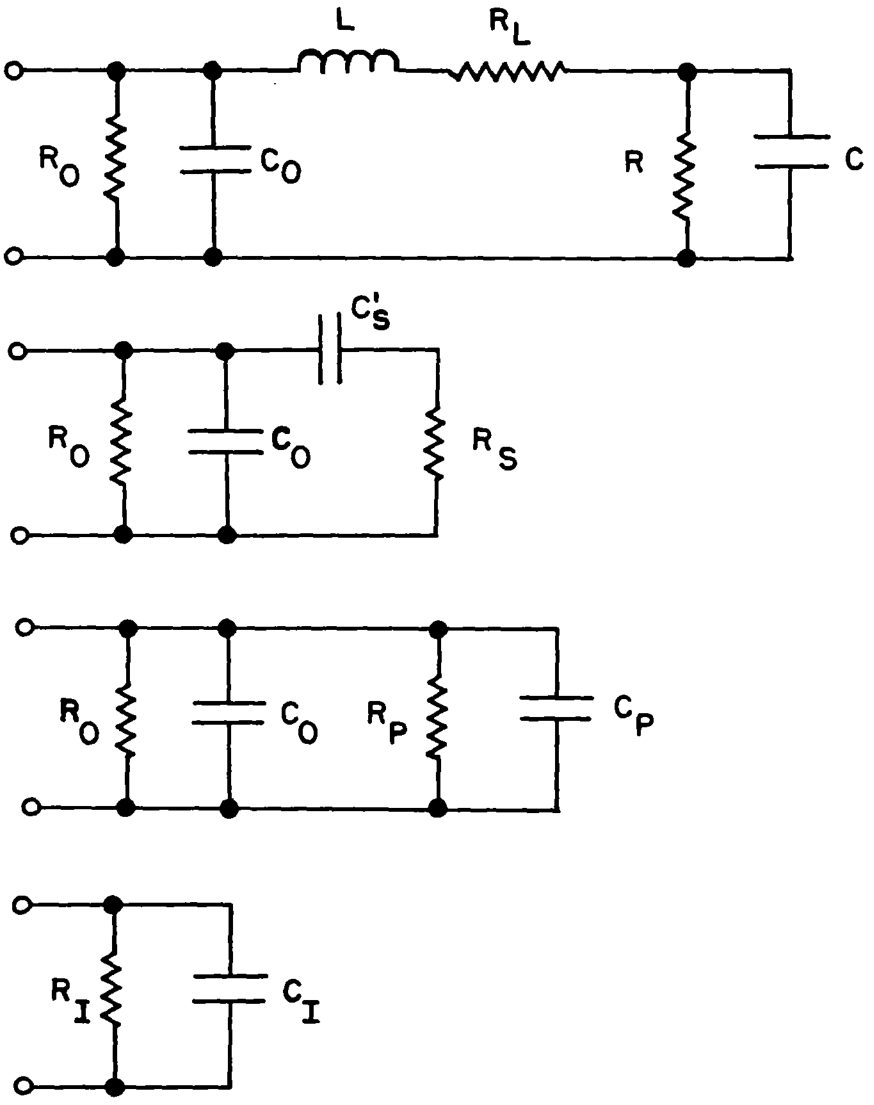
$$X=X_s\left(1+\frac{{R_s}^2}{{X_s}^2}\right) \tag{18}$$

The total series reactive impedance of the inductive band and the sample in the test cell is

$$X'_s=X_s+\omega L_s \tag{19}$$

Because R_L is of the order of milliohms, it can be disregarded and R_s is approximately the total series resistance of the sample and the inductive band to ground. It is convenient to define R_p and X_p as the parallel equivalent impedance components of the inductive band and test cell.

Figure 10.--Successive impedance transformations of the resistance, R, and capacitance, C, of the test cell, the inductance, L, and resistance, R_L, of the phosphor bronze band. See p. 54-56 for definitions of other resistances, capacitances, and inductances.



$$R_s = R_p\left(\frac{X_p^{\ 2}}{X_p^{\ 2}+R_p^{\ 2}}\right) \tag{20}$$

$$X'_s = X_p\left(\frac{R_p^{\ 2}}{X_p^{\ 2}+R_p^{\ 2}}\right) \tag{21}$$

The quantity $\frac{-1}{\omega C_p}$ is equal to X_p. By successive substitution of the last three equations into the first two:

$$R = R_p+\omega^2 L_s^{\ 2}\left(\frac{1}{R_p}+R_p\omega^2 C_p^{\ 2}\right)+2\omega L_s R_p C_p \tag{22}$$

$$C = \frac{C_p(1+\omega^2 C_p L_s) + \frac{L_s}{(R_p)^2}}{(1+\omega^2 C_p L_s)^2+\frac{\omega^2 L_s^{\ 2}}{(R_p)^2}} \tag{23}$$

R_p and C_p are the net equivalent resistance and capacitance of the sample and inductor in series. They are also the quantities that would be measured on the 250B bridge if R_o and C_o were not present. Thus, R_p and C_p are the net measured parallel resistance and capacitance of the system.

The quantities actually measured are R_I, C_I, R_o, and C_o, where R_I and C_I are measured with the inductive band plugged into the test cell and R_o and C_o are measured with the band unplugged. R_p in parallel with R_o is R_I

$$(R_I)^{-1} = (R_p)^{-1}+(R_o)^{-1} \tag{24}$$

and C_I is C_p in parallel with C_o

$$C_I = C_p+C_o \tag{25}$$

Equations (22) and (23) can be rewritten as

$$R = \frac{R_I R_o}{R_o - R_I} + \omega^2 L_s{}^2 \left[\frac{1}{R_I} - \frac{1}{R_o} + \omega^2 (C_I - C_o)^2 \frac{R_I R_o}{R_o - R_I} \right]$$

$$+ Z\omega^2 L_s (C_I - C_o) \left(\frac{R_I R_o}{R_o - R_I} \right) \tag{26}$$

$$C = \frac{(C_I - C_o)[1 + \omega^2 L_s (C_I - C_o)] + L_s \left(\frac{1}{R_I} - \frac{1}{R_o} \right)^2}{[1 + \omega^2 L_s (C_I - C_o)]^2 + \omega^2 L_s{}^2 \left(\frac{1}{R_I} - \frac{1}{R_o} \right)^2} \tag{27}$$

Equations (26) and (27) are quite cumbersome to use unless they are programmed into a computer. A flow chart for calculating R and C from the equations is included in the next section (p. 59). No corrections for the presence of the test cell around the sample are included in the foregoing equations; the test cell correction techniques developed by Judy and Eberle (1969) and outlined earlier in this chapter are used to compensate for the effects of the test cell.

All the variables that are needed to compute R and C from equations (26) and (27) are measured with the sample in place on the HP 250B bridge except the inductance of the phosphor bronze band, which is found by a separate calibration measurement, outlined below.

A nonferrous solid metal rod five-eighths of an inch in diameter and 3 inches long is used as a "standard" inductor. In each end a 5/32-inch-diameter hole is drilled to a depth of five-eighths of an inch. The Hewlett Packard 250B bridge is tuned to a frequency of 10 MHz or more and is zero balanced with the phosphor bronze band mounted on the ground terminal.

One end of the metal rod is mounted onto a banana plug on the ungrounded terminal of the bridge and the phosphor bronze band is plugged into the other end of the rod. The "negative capacitance" of the band and rod is measured on the bridge. The inductive band is disconnected from the metal rod and the capacitance of the rod to ground is measured on the bridge. The inductance of the band and rod combination is calculated using the relationship:

$$L_T = \frac{1}{\omega^2 \Delta C} \tag{28}$$

where ΔC is found by adding the magnitude of the "negative capacitance" to the capacitance of the rod to ground. The self inductance of the rod is found from the formula (Smythe, 1961, p. 5-28)

$$L_R \approx 2\ell \left[\ln (2\ell/a) - 1 + \kappa_m/4\right] \times 10^{-7} \tag{29}$$

where L_R is the inductance of the rod in henrys, ℓ is the length of the bar in meters, and a is the radius of the rod in meters. κ_m is the relative magnetic permeability of the material of the rod and can be taken equal to unity. The inductance of the phosphor bronze band is found by subtracting L_R from L_T. In the USGS system, the inductance of the band was found to be 1.09×10^{-7} h (henry).

Two additional corrections must be made for measurements on the Hewlett Packard 250B bridge. If a measured value of capacitance at 100 MHz is large and negative it must be corrected by a factor of about -2 percent or less for a stray inductance within the bridge. A more important correction is for the terminal inductance, L_T, of the bridge at 100 MHz. The correction for terminal inductance is applied to R_I, C_I, R_o, and C_o before they are used in the foregoing equations:

$$R_t = R_a \left(1 - \frac{C_a}{K}\right)^{-1} \tag{30}$$

$$C_t = C_a(1 + \omega^2 L_T C_a)^{-1} \tag{31}$$

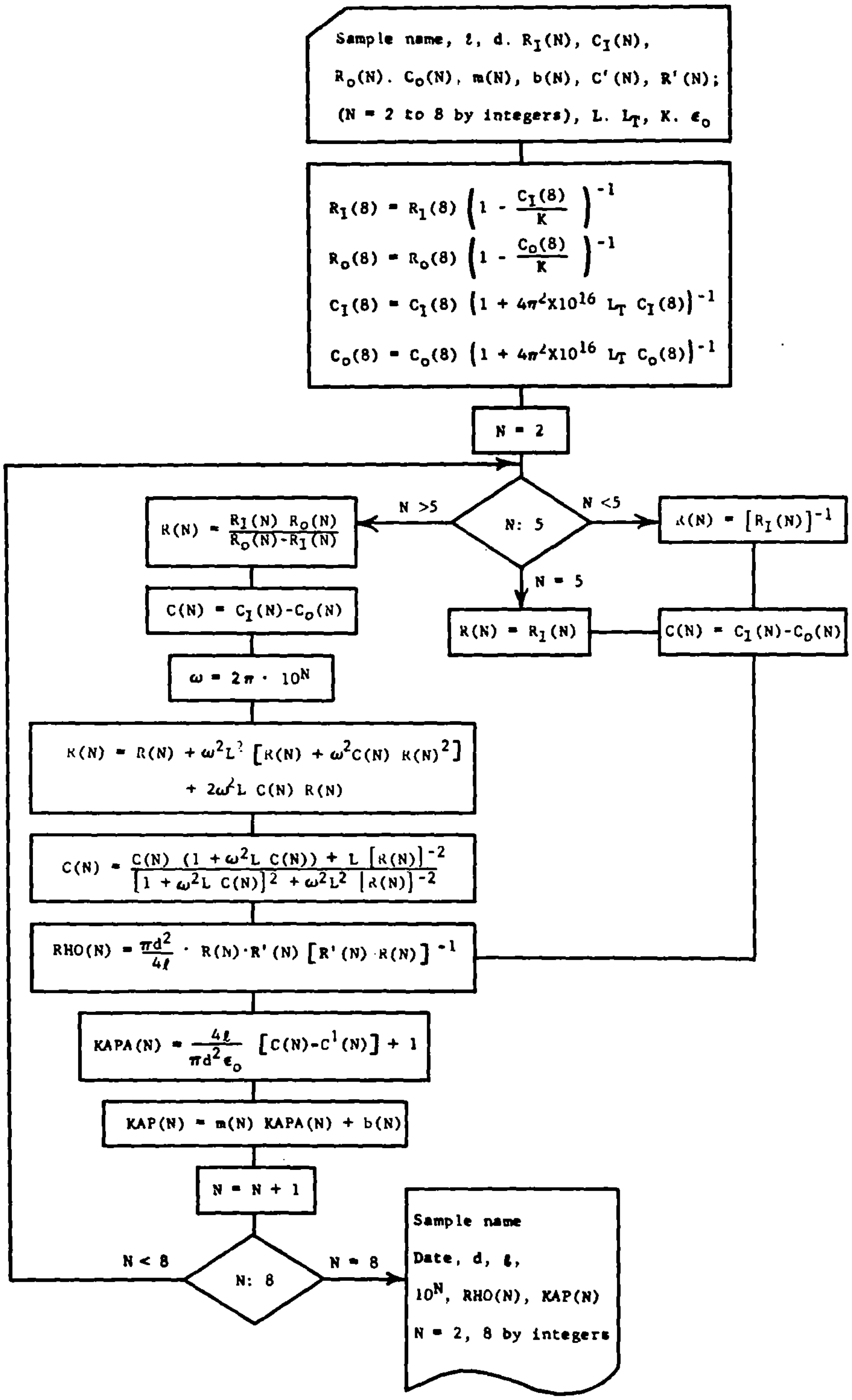
where the subscript, a, refers to an apparent value and the subscript, t, to a true or corrected value of the measured quantity. K is approximately equal to 4.2×10^{-10} at 100 MHz and L_T is approximately 3×10^{-9} h. The corrections are about 2 percent or less of the measured quantities unless C_a is much larger than 20 pf.

Sequence of corrections and flow chart

The corrections derived in this section are applied to the measured values of R_I, C_I, R_o, and C_o in a sequence that is given below. Corrections to the data that are not programmable into the computer are made first. These include the -2 percent correction to large negative values of measured capacitance at 100 MHz and the corrections for capacitance measurements on the Wayne Kerr bridges at 10 and 100 kHz, if any. The latter corrections can be entered on the worksheet as C_o values at 10 and 100 kHz. The order of the remaining calculations is indicated by the flow chart diagram (fig. 11).

The flow chart is based on the computer program used by USGS to convert the raw data from the worksheet (fig. 2) into resistivity and dielectric constant. The program used by USGS is written in machine language for a programmable desktop calculator (Wang 720B)

Figure 11.--Flow chart for programming the computations of resistivity and dielectric constant from measured data and instrument corrections. See p. 61 for definitions of the variables.



and is not directly usable in other machines. The flow chart, however, can be used as the basis of a program in FORTRAN, BASIC, or other programming language that is suited to the user's equipment.

The sequence of the flow chart begins with a data-loading step. The variables ℓ and d are the length and diameter of the sample, respectively, and N is an integer, $2 \leq N \leq 8$, that indicates the frequency of measurement through the relation $f=10^N$. The variables R_I, C_I, R_o, and C_o are entered from the worksheet. R_I and C_I are the measured quantities when the test cell is connected to one of the bridges ($2 \leq N \leq 8$). For N=2, 3, or 4, the measured conductance of the test cell, G_I, is entered from the worksheet in place of R_I. For $N<5$, R_o is not used and need not be entered. For N=3, 4, or 5, C_o is a correction factor as discussed above (p. 38-43). The measured R_o and C_o on the Hewlett Packard 250B (N=6, 7, or 8) are the quantities that are measured with the test cell connected to the ungrounded terminal of the bridge and the phosphor bronze band unplugged from the test cell. C', R', m, and b are corrections for the test cell and the calibration constants. The variable, L, is the inductance of the phosphor bronze band, L_T is the terminal inductance on the 250B bridge, K is the constant used to correct R_a to R_t (see previous section), and ϵ_o is the permittivity of free space.

The program begins execution by converting R_a to R_T and C_a to C_T at 100 MHz. The equations follow the computing convention that an equal (=) sign implies replacement of the quantity on the left with the results of the computation on the right-hand side of the equation. After new values of R_I, C_I, R_o, and C_o are computed at 100 MHz the program cycles seven times starting with N=2 (f=100 Hz) and ending with N=8 (f=100 MHz). If N=2, 3, or 4, the conductance entered under R_I is inverted to convert it to resistance in ohms; and C_o is subtracted from C_I. If N=5 the resistance, R_I, is retained as R and C_o is subtracted from C_I. If N>5, R is equivalent to R_p in equation (22) (p. 56) and C is equivalent to C_p in equation (23) (p. 56). The long equations for R and C are equivalent to equations (26) and (27) which eliminate the effects of the inductance, L. The corrections for test cell resistance and capacitance are incorporated in the equations for RHO and KAPA, the resistivity and apparent dielectric constant, respectively. The effect of the fringing capacitance is eliminated in the equation for KAP which is the "true" dielectric constant. After all seven cycles from N=2 to N=8 are completed, the information is printed out as shown in figure 11.

ERROR ANALYSIS

The major sources of error in the laboratory method fall into two categories: errors caused by unwanted changes in the water content or density of the sample and errors of measurement. The former are qualitatively discussed and the latter quantitatively discussed in this chapter. Much of the material presented here has appeared in previous reports by Scott, Carroll, and Cunningham (1967), Judy (1967), Judy and Eberle (1969), Carroll, Eberle, Cunningham, and Jones (1970), Eberle (1970), and in the companion report by the authors (Bigelow and Eberle, 1972).

Water content and water resistivity

The expected error in the resistivity and dielectric constant owing to uncertainties in the water content ($S_w\emptyset$) and resistivity ρ_w, of the water that invades an earth material can be estimated in the following way. The low-frequency ($\lesssim$100 Hz) resistivity of an earth material is given approximately by the formula

$$\rho=\rho_w(S_w\emptyset)^{-n} \qquad (32)$$

where n is a constant (Scott and others, 1967). The partial derivitives of ρ with respect to ρ_w and ($S_w\emptyset$) are indicative of the expected error.

$$\frac{\delta\rho}{\rho}=\sqrt{n^2\left(\frac{\delta(S_w\emptyset)}{S_w\emptyset}\right)^2+\left(\frac{\delta\rho_w}{\rho_w}\right)^2} \qquad (33)$$

Experience indicates that $\delta\rho_w/\rho_w$ can be held to 3 percent or less; the changes in water resistivity occur primarily as a function of temperature. The water content can be monitored by weighing; the uncertainty in the water content measurements can be held to a percent or less.

The value of n is often approximately 2; thus, the uncertainty in the low-frequency resistivity owing to measurement errors in water content and water resistivity is approximately 4 percent. While no similar equation to (32) exists for the dielectric constant of an earth material, the evidence in the companion report (Bigelow and Eberle, 1972) indicates that there is a one-to-one relationship between the resistivity and dielectric constant of an earth material at any frequency below 1 MHz. Thus, the uncertainty in dielectric constant owing to measurement error in ρ_w and ($S_w\emptyset$) is probably of the same order as that for $\delta\rho$.

For a given earth material, the relative dispersion of resistivity with frequency depends primarily on the low-frequency resistivity of the material according to experimental evidence presented in the companion report. Thus, when a sample is reconstituted to a field value of resistivity by changing the water content of the sample, the dispersion of resistivity with frequency is also reconstituted. The estimated accuracy of the reconstituted relative dispersion of resistivity is within 5 percent from 100 Hz to 10 MHz and within 10 percent at 100 MHz. The correlation between dielectric constant and resistivity frequencies below 1 MHz implies that dielectric constant is also reconstituted to within about 30 percent over the full frequency range (Bigelow and Eberle, 1972). At megahertz frequencies some variance may be observed because the dielectric constant depends on S_w and ϕ independently.

Reconstitution of resistivity by changing the density of an earth material has been qualitatively tested on soils and appears to restore the dispersions of resistivity and dielectric constant of the materials to nearly their original values (Carroll and others, 1972, in press).

Electrodes and test cell

Judy and Eberle (1969) estimate that the error incurred by neglecting electrode impedance in comparison with sample impedance is 3.8 percent, based on measurements in soils and alluvium. The estimate is confirmed by direct measurements of electrode resistance and capacitance.

The resistances of several electrodes that had been used for sample measurements were measured directly at 1 kHz. In no case were the observed resistances of the electrodes as great as 1 percent of the sample resistance. The series capacitance of the blotters was measured by filling a test cell with 32 blotters and applying a direct current of known amplitude. Because the blotters acted as a storage cell "battery" that was being charged by the current, the voltage across the terminals of the cell slowly increased. The relationship

$$I=C\frac{dV}{dt} \tag{34}$$

was applied to determine the effective capacitance of the "battery." C was found to be much greater than 6 f or 0.18 farads per blotter. The largest observed capacitance in earth material samples are of the order of microfarads. The error incurred by ignoring the larger capacitance in series with the smaller is approximately the ratio of the sample to the electrode capacitance. Thus, the error in capacitance should usually be less than 1 percent. The foregoing measurements are much less precise than the separation of impedances method; thus, the estimate of 3.8 percent error is probably valid.

If the resistance in parallel with the sample capacitance is very low, the error caused by electrode capacitance is increased as may be seen in equation (5) from the previous chapter. As either R or ω goes to zero, the series imaginary impedance of the sample becomes small with respect to the electrode impedance.

The present experience indicates that the electrode impedance will be negligible compared to sample impedance if the parallel sample resistance is greater than about 30 ohms (or the resistivity is greater than about 3 ohm-m) and the frequency of measurement is greater than or equal to 100 Hz. There is also some indication (Scott and others, 1967; Eberle, 1970) that materials that contain 50 percent or more water may not be accurately measured at 100 Hz and 1 kHz.

The values for m that were found by least-squares fit to the test cell calibration data were close to unity for all frequencies (Judy and Eberle, 1969) and the maximum value of b was 2.36 pf (1.17 pf average absolute value). Hence, K_T and K_a are nearly equal and the corrections for fringing are small. The scatter of the points on the K_T versus K_a correction curves is a measure of the expected accuracy of the calibration. The average standard deviation of the plotted points from predicted values is 1.8 picofarads ranging from 1.4 to 2.1 picofarads. Thus, errors in the dielectric constant, K_T, arising from errors in the calibration of the test cell are negligible.

Conduction along the walls of the test cell is possible if they are wetted by saline solution. While there is no formal method of quantifying this source of error, qualitative testing of the cells does not indicate that such conduction is a problem if the cells are kept clean.

Temporal changes in sample properties

Errors are caused at all frequencies by changes within the sample during the time measurements are being made. Because of moisture evaporation from the test cell, exchange of moisture between the blotter electrodes and the sample, and insufficient pressure of the electrodes against the sample, the measured electrical properties of the sample can change with time. The best precaution is careful preparation of the sample; particular care should be paid to the thickness of the sample. If the sample is too thick, ordinary O-rings will not seal the cell although thicker ones may do so. A sample that is too thin makes poor contact with the electrodes. If necessary, as many as four blotter electrodes can be used, two on each end of the sample, to insure a solid contact between the electrodes and the sample.

Drift is measured by repeating the measurements at 100 Hz or 1 kHz after a complete set of measurements are made from 100 Hz to 100 MHz. Measurements of resistances usually drift more than measurements of capacitance at 100 Hz or 1 kHz: 3-4 percent versus 2-3 percent, respectively, in 30 minutes. The entire set of measurements should be retaken if the sample resistivity changes more than 5 percent in 30 minutes or in the time it takes to make a set of measurements.

Bridge measurement errors

The errors of measurement on the three bridges are listed in table 2. The tabulated data are adapted from the instruction manuals for the three bridges. The tabulated values refer to the measurement of either a pure resistive or reactive impedance element at the terminals of the bridges.

Table 2.--Accuracies of measurement for the B221, B601, and 250B bridges

[Accuracies are quoted for measurements of pure resistance or pure capacitance only. The listed accuracies for the 250B bridge are for measured capacitances of 100 pf (picofarads) or less and for measured resistances of 20 k (kiloohms) or less.]

Bridge	Frequency	Measurement accuracies			
		Resistance		Capacitance	
		percent	ohms	percent	pf
B221	10^2-10^4	±0.2	----	±0.25	----
B601	10^5	±1	----	±1	----
250B	10^6	±4	±0.2	±0.5	±0.15
250B	10^7	±4.5	±0.2	±0.55	±0.15
250B	10^8	±5.0	±0.2	±5.5	±0.15

The actual errors of measurement on the low-frequency bridge (Wayne-Kerr B221) are generally those stated in table 2 except for some capacitance measurements on the highest conductivity ranges (ranges 6 and 7) and some measurements at 10 kHz.

The accuracy of capacitance measurements on the B221 suffers at 10 kHz whenever the sample's conductance is much larger than its capacitive admittance. In extreme instances, only the least two of four significant figures register other than zero on the capacitance measurement dials. As table 2 indicates, the bridge is rated at 2.5 parts per thousand for a four-significant-digit measurement; readings that utilize only the two least-significant digits are between 10 and 100 times less accurate.

The accuracy of resistance measurements made at 100 kHz on the Wayne-Kerr B601 bridge is given in table 2. The capacitance readings must also be corrected for resistive loading, test lead inductance, and the stray capacitance of the resistance-measuring potentiometer by the use of correction curves as previously described (p. 51-53). The correction curves are estimated to be accurate to within 5 percent of the correction; the estimate is based on repeated measurements of similar noninductive resistors. The reactances of the noninductive resistors were measured on the Hewlett Packard 250B at 500 kHz, the lowest frequency at which the bridge operates, in order to estimate the effective capacitance of the resistors at 100 kHz. The capacitances of the noninductive resistors range from approximately 0 to 3 pf. Thus, the estimated error of the corrections is ±5 percent ±1.5 pf.

The major sources of measurement error on the Hewlett Packard 250B impedance bridge, given in table 2, are computed from formulas given in the operating manual (Hewlett Packard, 1967). Possible sources of error that have not been allowed for are radiation at 100 MHz and stray capacitances that are incompletely compensated for by the measurements. Radiation should be minimal because the cell is much smaller than one wave length at 100 MHz and below. The bridge must be carefully grounded to reduce stray capacitance changes; however, the movement of personnel or objects near the bridge is sufficient to cause some measurable capacitance changes at 100 MHz and should be avoided during the measurements.

Computational errors: 1-100 MHz

The estimated errors in the computed sample resistance and capacitance at 1, 10, and 100 MHz are not, in general, equal to the probable errors of measurement listed in table 2. In this section, formulas are derived to relate the estimated errors of computation to the tabulated errors of measurement.

The resistance, R, and capacitance, C, of a sample are related to the net measured resistance, R_p, and capacitance, C_p, by equations (22) and (23). The expected errors in R and C are found by taking their partial derivative, with respect to R_p and C_p, and identifying the infinitesimals of each variable with the expected error in that quantity.

$$\delta R\Big|_{C_p=\text{const}}=\delta R_p\left[(1+\omega^2 L_s C_p)^2-\frac{\omega^2 L_s{}^2}{R_p{}^2}\right] \qquad (35)$$

$$\delta C\Big|_{R_p = \text{const}} = \delta C_p \frac{\left[(1+\omega^2 L_s C_p)^2 - \dfrac{\omega^2 L_s^{\,2}}{R_p^{\,2}}\right]}{\left[(1+\omega^2 L_s C_p)^2 + \dfrac{\omega^2 L_s^{\,2}}{R_p^{\,2}}\right]^2} \tag{36}$$

$$\delta R\Big|_{R_p = \text{const}} = \delta C_p \; 2\omega^2 L_s R_p (\omega^2 L_s C_p + 1) \tag{37}$$

$$\delta C\Big|_{C_p = \text{const}} = \delta R_p \left[\frac{-2L_s}{R_p^{\,3}}\right] \frac{\left[(\omega^2 L_s C_p + 1) + \dfrac{\omega^2 L_s^{\,2}}{R_p^{\,2}}\right]}{\left[(1+\omega^2 L_s C_p)^2 + \dfrac{\omega^2 L_s^{\,2}}{R_p^{\,2}}\right]^2} \tag{38}$$

The total estimated errors in computed resistance and capacitance are:

$$\delta R = \sqrt{\left(\delta R\Big|_{C_p = \text{const}}\right)^2 + \left(\delta R\Big|_{R_p = \text{const}}\right)^2} \tag{39}$$

$$\delta C = \sqrt{\left(\delta C\Big|_{C_p = \text{const}}\right)^2 + \left(\delta R\Big|_{R_p = \text{const}}\right)^2} \tag{40}$$

The quantities R_p and C_p are related to the net measured quantities R_I, C_I, R_o, and C_o by similar relationships derived from equations (24) and (25) on p. 56.

$$\frac{\delta R_p}{R_p^{\,2}} = \sqrt{\frac{(\delta R_o)^2}{R_o^{\,4}} + \frac{(\delta R_I)^2}{R_I^{\,4}}} \tag{41}$$

$$\delta C_p = \sqrt{(\delta C_I)^2 + (\delta C_o)^2} \tag{42}$$

Because R_I, C_I, R_o, and C_o are quantities that are actually measured, their estimated errors can be computed from the information in table 2.

The dependence of δR on C_p and δC on R_p is caused by the inductance of the phosphor bronze band. As L_s goes to zero, equations (37) and (38) vanish and the multipliers of δR_p and δC_p in equations (35) and (36) approach unity. Typically, $\omega^2 L_s C_p$ and $\omega^2 L_s^2/R_p^2$ are both much less than 1, and L_s terms can be disregarded; however, for some combinations of C_p and R_p at 100 MHz neither condition holds and δC may become quite large.

Because C_p is the difference between two measured capacitances, it can be sufficiently large and negative that $(1+\omega^2 L_s C_p)^2$ approaches zero and equation (36) becomes:

$$\delta C\Big|_{R_p} = \text{const} \approx -\delta C_p \left(\frac{R_p^2}{\omega^2 L_s^2}\right) \qquad (43)$$

If R_p^2 is large compared to ωL_s^2 then δC is large compared to δC_p. The physical interpretation given to the vanishing of $(1+\omega^2 L_s C_p)^2$ is that the inductive band is series resonant with the capacitance of the sample. The condition is easily diagnosed at the time of measurement because C_I becomes large and negative and the Hewlett Packard 250B bridge will usually not balance.

If R_p^2 is much smaller than $\omega^2 L_s^2$, equation (38) becomes

$$\delta C\Big|_{C_p = \text{const}} \approx \delta R_p \left(\frac{-2}{R_p \omega^2 L_s}\right) \qquad (44)$$

In worst-case condition, the estimated error in equation (44) can be of the order of 10 pf. The error, δR, in equation (35) will also be large if the $(1-\omega^2 L_s C_p{}^2)^2$ term is negligible. In practice, low values of R_p are associated with samples having water resistivities of 0.3 ohm-m or less. Computed sample capacitances and dielectric constants tend to be high for such samples; instances may be found in the companion article (Bigelow and Eberle, 1972).

SUMMARY

The two-terminal impedance bridge system described in this report is used for frequency domain measurements of the resistivities and dielectric constants of nonmagnetic earth materials at decade intervals of frequency from 100 Hz to 100 MHz. The measured samples may be either competent or unconsolidated and may be either fully or partially saturated with water. Because the electrode system works by electrolytic conduction, the samples may not be totally dry.

If measurements of samples of a material in its natural state are desired, both the moisture content and the density of the material should be preserved during the preparation of the sample. However, if desired, the electrical properties of a sample can be deliberately changed by saturation or desaturation techniques. A sample whose electrical properties have changed from natural state because of changes in moisture content or density can have its native state electrical properties restored by adding or removing water until the resistivity of the sample matches the resistivity of the material in its natural state.

The measurement system includes two Wayne Kerr transformer-type bridges, the B221 for measurements of conductance and capacitance at 100 Hz and at 1 and 10 kHz, and the B601 for measurements at 100 kHz. The oscillator that drives the bridges is a Hewlett Packard

200 CDR and the null detector is a Rhode and Schwarz UBM tunable amplifier feeding a Tektronix 513 oscilloscope. Measurements at 1, 10, and 100 MHz are made on a Hewlett Packard 250B R-X meter which consists of an oscillator, Schering bridge, and null detector in a single package.

Contact from the measurement system to a sample is made through a pair of composite electrodes. Each composite electrode consists of a chemically reversible electrode backed by a platinized platinum electrode. A chemically reversible electrode is formed when silver and silver chloride are precipitated in a disk of blotting paper, which is then soaked in an aqueous solution of sodium chloride. The blotter electrode chemically converts the ion current to an electron current and prevents ion polarization layer buildup at the electrode-sample material interface. Platinized platinum electrodes have extremely large effective surface areas which reduce the electrical effects of polarization layers.

The separation-of-impedances technique has been used to show that impedances of composite electrodes are usually negligible compared to the impedances of samples.

Liquids of known dielectric constant are used to calibrate the measurement system and to eliminate the effects of fringing capacitance of test cells from measurements of earth material capacitances. Noninductive resistors are used to generate correction curves for the capacitance measurements on the Wayne Kerr B601 bridge and, where needed, on the B221. The graphical corrections compensate for lead inductance, resistive loading, and stray capacitance effects on the transformer bridges.

The inductance of the phosphor bronze band that connects one side of the test cell to the ground terminal of the Hewlett Packard 250B bridge acts in series with the paralleled resistance and capacitance of a sample in a test cell and affects the data measured on the bridge. A computer program corrects the measured values of resistance and capacitance for the effects of the band inductance and for the terminal inductance of the 250B bridge. The computer program then computes the resistivity and dielectric constant of a sample material of each frequency from the measured quantities after applying corrections to the data.

The major uncompensated sources of error in the laboratory method include: variations in the water content and density of the samples; uncertainties in the calibration of the B601 using the noninductive resistors; changes in the resistance and capacitance of the sample during the time of measurement; bridge errors; near-resonance conditions of the phosphor bronze band with the sample capacitance at 100 MHz; and resistive loading of the measurements at 100 MHz. The sources of error can be minimized by careful preparation of the samples, by keeping lead lengths short, and by lowering the inductance of the phosphor bronze band.

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APPENDIX

A stock solution for both platinum plating and for platinizing (depositing platinum black) can be made up by dissolving

4.6 g hexachloroplatinic hexahydrate crystals

($H_2PtCl_6 \cdot 6H_2O$)

and 0.25 g lead acetate ($Pb(C_2H_3O_2)_2$)

into 1 liter H_2O

(Chemicals are available from J. T. Baker Chemical Co., Phillipsburg, N.J.)

Working solutions are made up by diluting as follows:

Plating solution	Dilute stock solution 10:1
Platinizing solution	Dilute stock solution 1:1

Solutions for blotter electrodes:

16.9888 g $AgNO_3$ (silver nitrate) into 100 cc of H_2O

6.949 g $NH_2OH \cdot HCl$ (hydroxylamine hydrochloride) into 100 cc of H_2O

5.844 g NaCl (sodium chloride) into 100 cc H_2O

To make the three 0.1 normal working solutions, dilute each stock solution in the ratio of 1 part stock to 9 parts H_2O. The three solutions are <u>not</u> mixed together at any time.

Computations of physical properties

The dry bulk density of a right-circular cylinder of material of diameter d and thickness ℓ is given by

$$D_b=4W_d/(\pi d^2\ell)$$

where W_d is the weight of the material dry. The porosity of the same material is given by

$$\emptyset=4(W_s-W_d)/(\pi d^2\ell D_w)$$

where W_s is the weight of the material when saturated with water and D_w is the density of water, nominally 1.0 g/cc. The fractional water content of a partially saturated sample is given by

$$S_w=\frac{W_p-W_d}{W_s-W_d}$$

where W_p is the weight of the sample partially saturated with water. The water content of the material by volume, $S_w\emptyset$, is given by

$$S_w\emptyset=4(W_p-W_d)/(\pi d^2\ell D_w)$$

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