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NBS SPECIAL PUBLICATION 260-39

Standard Reference Materials:

THE EDDY CURRENT DECAY METHOD FOR RESISTIVITY CHARACTERIZATION OF HIGH PURITY METALS

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Standard Reference Materials:

The Eddy Current Decay Method For Resistivity Characterization Of High Purity Metals

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Special publication 260-39

U.S. DEPARTMENT OF COMMERCE, Peter G. Peterson, *Secretary*
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Issued May 1972

Library of Congress Catalog Card Number: 72-600100

National Bureau of Standards Special Publication 260-39
Nat. Bur. Stand. (U.S.), Spec. Publ. 260-39, 53 pages (May 1972)
CODEN: XNBSAV

Issued May 1972

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
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The Eddy Current Decay Method for Resistivity Characterization of High Purity Metals*

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Characterization of high purity metals by resistivity measurements at low temperatures is discussed. In particular, the eddy current decay method of resistivity measurement is described in detail. The advantages and limitations are presented along with the theoretical basis of the method. Detailed instructions are given for constructing and operating the apparatus.

Key Words: Apparatus; characterization; eddy current decay; electrical resistivity; high purity metals; homogeneity; low temperature.

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*This work was carried out at the National Bureau of Standards, Boulder, Colorado, under the sponsorship of the National Bureau of Standards, Office of Standard Reference Materials (NBS-OSRM), Washington, D. C.

1. Introduction

The chemical and physical purity of metals can be characterized by low temperature resistivity. As the temperature of a metal specimen is lowered, generally, the resistivity of the specimen decreases. At a sufficiently low temperature the resistivity becomes essentially independent of temperature. This value of resistivity, termed residual resistivity, is characteristic of the type and concentration of chemical impurities and physical imperfections in the specimen. Of course, only those impurities and imperfections that act as electron scatterers are important to resistivity. Resistivity characterization, perhaps, finds its greatest usefulness in detecting variations in purity among specimens of relatively homogeneous purity. These points will be discussed in more detail later.

Electrical resistivities are frequently measured using 4-terminal-potentiometric AC or DC methods. These methods all involve the connection of two current leads and two potential leads to the specimen. From the measurement of current through and voltage across the specimen one computes the resistance of the specimen; and the resistivity is then determined from the resistance and the geometrical form factor of the specimen. Often, the ratio of the resistivities at two temperatures is desired instead of the resistivity at one temperature. In this case, the form factor can be eliminated from the computation; which also means that the specimen does not need to be fabricated into some common uniform shape, such as a cylindrical rod. This is a distinct advantage for specimens that are either difficult to machine or measure. The potentiometric methods are generally very useful for specimens of reasonably high resistance. However, for very pure, large diameter and, thus, low resistance specimens it is frequently very difficult, if not impossible, to obtain an accurate measure of the potential across the specimen. Potentials in the nanovolt range are not uncommon. For example, the potential drop along a 3 cm long-1 cm^2 copper specimen with a residual resistivity ratio, $\rho(273\ K)/\rho(4\ K)$, of 15,000 is about 1 nanovolt for a current of 1 amp.

A relatively new method, the eddy current decay method, of measuring electrical resistivity and resistivity ratios has the advantage of being most accurate in this range where the potentiometric methods are least accurate. The eddy current decay method also has the added advantage that no electrical connections to the specimen are needed. This is especially important for pure specimens, to minimize the effects of chemical diffusion of impurities into the specimen and to minimize the effects of physical damage from mechanical strain. The measurement of metals such as mercury, potassium, sodium, and gallium is facilitated by the elimination of lead attachment. In many cases, the specimen can be left in the container in which it was prepared. The eddy current decay method is least accurate for the higher resistance specimens. Thus, the potentiometric method and the eddy current decay method of measuring resistivity are complementary methods for the measurement of a wider range of resistivities than either can accomplish separately.

This paper describes the theoretical basis of the eddy current technique and gives detailed instructions for constructing and operating an apparatus capable of monitoring eddy current decay over a wide range of decay rates at cryogenic temperatures. Also included is a discussion of the theoretical basis for purity characterization of metals by electrical resistivity at low temperatures.

2. General Description and Application

Briefly, the eddy current technique involves surrounding the specimen with two concentric coils. A current is established in the outer, primary, coil, and is allowed to come to a steady value. The primary current is turned off and the collapsing field induces eddy currents in the metal. These decaying eddy currents establish a decaying magnetic field that induces an emf in the inner, secondary, coil. It can be shown that the rate of decay of these eddy currents is a function of the specimen geometry, its magnetic permeability, and most importantly, its resistivity.[1][1]

The rate of eddy current decay is inversely proportional to the resistivity and directly proportional to the specimen's cross sectional area. Thus, as a specimen's resistivity increases or its dimensions decrease, the time constant of the decay becomes shorter. At sufficiently short times the transient response of the measuring apparatus will distort the eddy current signal. The response time of the system is determined primarily by the characteristic decay of the primary and secondary coils surrounding the specimen. These coils, when critically damped, typically have time constants from 50 microseconds for the smaller coils to several milliseconds for the larger coils. In practice, this limitation frequently prevents one from determining specimen time constants at temperatures much above that of liquid nitrogen or for specimen diameters less than a few mm. Of course, a certain latitude is possible by increasing the specimen size as the resistivity increases. Even room temperature resistivities are measurable if the specimen is large enough.

In addition to the problem of measuring very short time constants, it is also difficult to measure very long time constants. With long time constants the time rate of change of the magnetic field is small,

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[1] Figures in brackets indicate the literature references on page 36.

resulting in a very small induced voltage. At sufficiently small voltages, the signal-to-noise ratio is too small to allow an accurate measurement. Bean et al.[1] suggest moving the specimen in and out of the coil of a flux-meter at regular intervals to measure the magnetic field decay rate of the specimen under these circumstances. Also flux gate meters or superconducting quantum interference devices[2] may provide attractive alternatives to coil type pickups for low level signals. We have had good success in using a low temperature Hall effect probe to measure the decaying magnetic field near the specimen. An advantage of the Hall probe is that it directly measures the magnetic field rather than the rate of change of the field. This eliminates the initial voltage spike caused by the rapid initial decay of the field within the secondary coil. Even with coil type sensors, one can improve the signal by using low pass filters and signal averagers to eliminate most of the noise.

In the following sections we will consider the basic equation governing the form of the eddy current decay and its characteristic decay time. The relation between this decay time and resistivity will be presented. This section is concluded with a discussion of some useful applications of resistivity characterization measurements. One such application is described by Kasen.[3]

2.1 Eddy Current Decay Time

In 1959, Bean et al.[1] described the eddy current decay technique for measuring the electrical resistivity of metals. The method involves setting up eddy currents in the metal, and then observing their decay. The equation describing the decay of a magnetic field in a metal is

$$\frac{\partial \vec{B}}{\partial t} = \frac{\rho}{\mu} \nabla^2 \vec{B} \qquad (1)$$

which relates the decay of the magnetic flux density, B, to the resistivity, ρ, and magnetic permeability, μ. Generally eq. (1) is applied only if the metal is non-magnetic, so that $\mu = \mu_o$. However, Bean postulates that the technique will work even with magnetic materials, provided the magnetic field is allowed to fall only to a value for which the metal is still saturated. A further assumption in eq. (1) is that the resistivity is isotropic, but J. E. Neighbor[4] has discussed a modification of the technique whereby the complete resistivity tensor can be determined from eddy current data. If the specimen is polycrystalline, one can still use eq. (1) by assuming an averaged resistivity.

For specimens of uniform cross-section and uniform isotropic resistivity, the decay of an axial B field is given by $B = C(e^{-t/\tau_1} + e^{-t/\tau_2} + e^{-t/\tau_3} + \ldots)$. Because $\tau_1 > \tau_2 > \tau_3 \ldots$, this becomes a simple exponential after a sufficiently long delay.*[1] Thus,

$$B \cong Ce^{-t/\tau} \qquad (2)$$

where C is a constant determined by the specimen's geometry, the initial field, and other properties, and τ is a constant proportional to ρ^{-1}. The constant of proportionality is dependent on the size and shape of the specimen as discussed in the next section. Most published solutions to eq. (1) assume an infinite length for the specimen. If the ratio

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* Arp et al.[5] have computed the error as a function of delay time due to neglect of the higher order terms. Some experimental results have been obtained that are in conflict with these calculations; however, it is presently not known whether these instances represent shortcomings in the theory or experimental procedure. Inadequacies in experimental procedure that may cause such behavior are discussed in a later section. The authors feel that for most specimens a delay of three time constants is sufficient to reduce the higher order terms so they can be neglected.

of length to diameter falls below about 8, then the measured time constant of the decay will be measurably smaller than the calculated value. Moulder et al.[6] performed a series of measurements at this lab on a cylindrical copper rod that was successively reduced in length. The secondary or pickup coil remained centered on the same material throughout the experiment. The results of this experiment are given in figure 1 as a correction factor for measured time constants when the L/D ratio is small. LePage et al.[7] have proposed a functional fit of this data, together with data of their own. Their expression takes the form

$$\frac{\tau_{\text{actual}}}{\tau_{\text{measured}}} = \frac{1}{1 - \exp[-1.2(L/D)^{0.68}]} \quad . \qquad (3)$$

2.2 Resistivity—Decay Time Relations

The next step is to find the relationship between τ, ρ, and the geometry of the specimen. Bean et al.[1] and Weinstein[8] have derived equations relating the eddy current relaxation time to the bulk resistivity for solid and hollow rods and rectangular parallelepipeds. These equations are given in Appendix A. As an example, the equation for rod-shaped specimens is $\tau = 2.17 \times 10^{-9} \mu r^2/\rho$. Using these equations one can compute the resistivity from the measured time constant and the specimen dimensions. Appendix B contains some values of τ for typical values of ρ and r for an aluminum specimen at various temperatures.

Characterization of overall purity of metals also can be accomplished from the ratio of high temperature to low temperature resistivity. The high temperature resistivity is characteristic of the base metal while the low temperature resistivity is characteristic of the purity of the particular specimen. By measuring only the ratio of

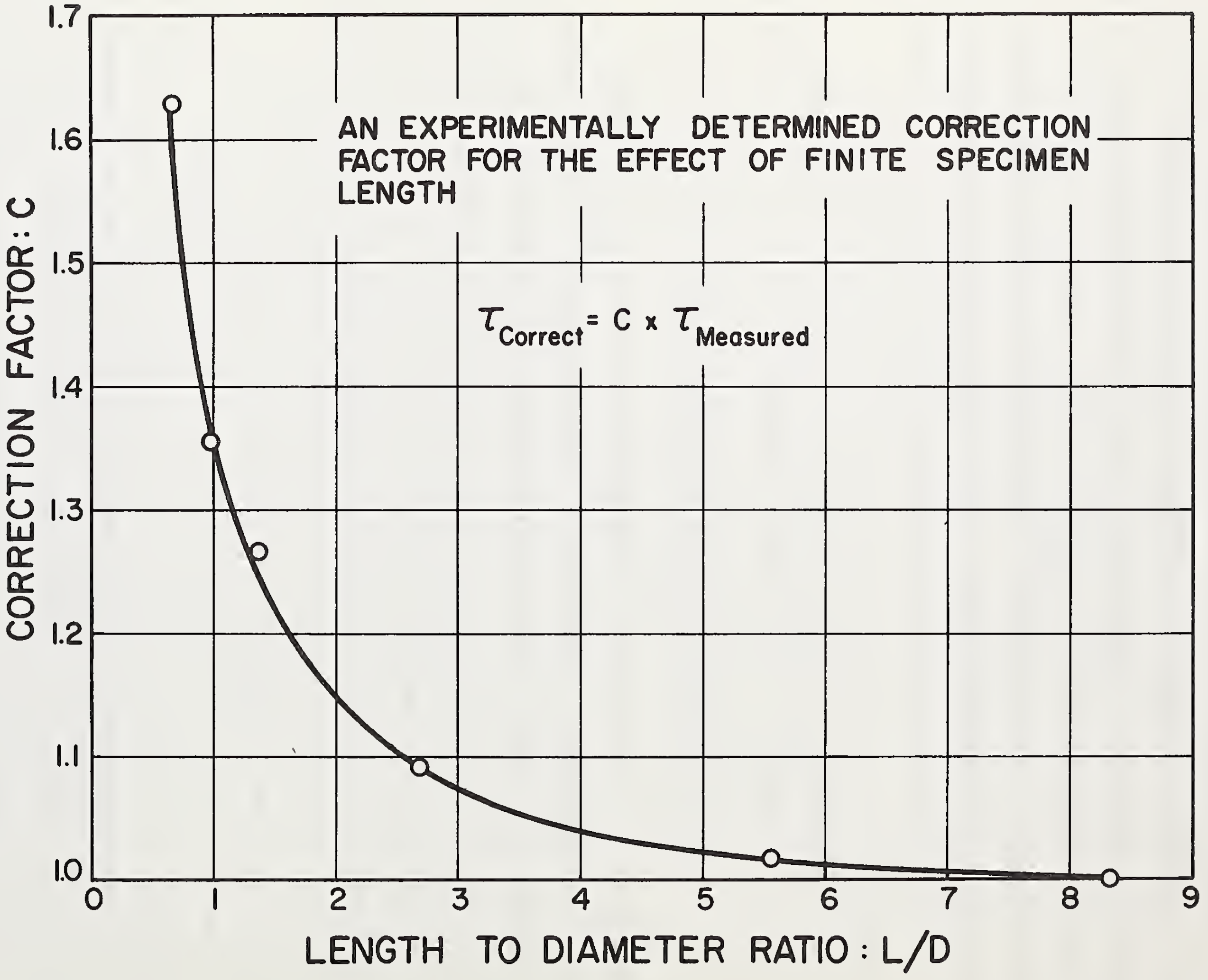


Figure 1. Correction Factor for Length to Diameter Ratio.

resistivities it is possible to eliminate most of the geometrical dependence. With the four-terminal potentiometric methods one usually uses the ice point (273 K) for a high temperature point and the helium point (4 K) for a low temperature point. The eddy current decay apparatus is, however, not well suited for measurement of any metal at the ice point because of the high resistivity at this temperature. The resistivity of many metals is, however, still mainly characteristic of the base metal as low as liquid nitrogen temperatures (76 K). The resistivity is significantly lower at 76 K than at 273 K and, therefore, the eddy current decay method is more applicable at this lower temperature. Thus, one can measure $\tau(4\ \mathrm{K})/\tau(76\ \mathrm{K})$ and from this obtain $\rho(76\ \mathrm{K})/\rho(4\ \mathrm{K})$ since $\rho \propto \tau^{-1}$. It is to be noted that the geometrical factor does not totally cancel due to the effect of thermal expansion. For most metals the dimensional change amounts to less than 1/2% between room temperature and absolute zero. Any crystallographic phase change in the material may cause more pronounced effects.

From $\rho(76\ \mathrm{K})/\rho(4\ \mathrm{K})$ and tabulated values of the intrinsic resistivities, $\rho_i(273\ \mathrm{K})$ and $\rho_i(76\ \mathrm{K})$,[9] one can compute $\rho(273\ \mathrm{K})/\rho(4\ \mathrm{K})$, which is the value normally used for material characterization. This computation is done by assuming Matthiessen's rule, which is written as

$$\rho(T) = \rho_i(T) + \rho(4\ \mathrm{K}) \ . \qquad (4)$$

We then write

$$\frac{\rho(76\ \mathrm{K})}{\rho(4\ \mathrm{K})} = \frac{\tau(4\ \mathrm{K})}{\tau(76\ \mathrm{K})} = \frac{\rho_i(76\ \mathrm{K})}{\rho(4\ \mathrm{K})} + 1$$

and

$$\rho(4\ \mathrm{K}) = \rho_i(76\ \mathrm{K})/[\tau(4\ \mathrm{K})/\tau(76\ \mathrm{K}) - 1] \ .$$

Thus

$$\mathrm{RRR} = \frac{\rho(273\ \mathrm{K})}{\rho(4\ \mathrm{K})} = \frac{\rho_i(273\ \mathrm{K})[\tau(4\ \mathrm{K})/\tau(76\ \mathrm{K})-1]}{\rho_i(76\ \mathrm{K})} + 1 \qquad (5)$$

It should be noted that changing the lower temperature, generally, is not critical since ρ is independent of T at sufficiently low temperature.

For metals of reasonable purity, $\rho(273\ \mathrm{K})$ is dominated by thermal, phonon, scattering and is essentially independent of purity.[9] Thus, by using the ratio of eq. (5), one not only eliminates the geometric factor, but also refers the ratio to $\rho(273\ \mathrm{K})$, which is essentially constant for these reasonably pure metals. For example, since the non-thermal contribution to $\rho(273\ \mathrm{K})$ is $\rho(4\ \mathrm{K}) = (\rho(273\ \mathrm{K}))(\mathrm{RRR})^{-1}$, the variation in $\rho(273\ \mathrm{K})$ for specimens of a metal having RRR > 1000 will be ≤ 0.1%.

Thus, the RRR for well annealed samples is a direct measure of the resistivity contributed by impurities as long as one can ignore both magnetoresistive and size effect contributions. Copper of ordinary electrolytic purity has a RRR of about 100. Measurements on copper and aluminum having RRR in excess of 35,000 have been made in this laboratory. In the following two sections we discuss characterization by resistivity measurement.

2.3 Residual Resistivity as a Measure of Purity

For metals having a single major impurity, it is usually possible to use the RRR to estimate the impurity concentration level in atomic percent. Even if the metal contains multiple impurities, one can sometimes make a more detailed analysis of the impurity concentration levels. If the metal is sufficiently pure and the various impurities do not interact, one can assume that the total impurity contribution to the resistivity is the sum of the contributions of the individual impurities. Thus, for a set of n impurities one can write

$$\rho\text{total} = \rho_1 + \rho_2 + \_\_\_ + \rho n \qquad (6)$$

where ρ_i is the contribution of the i^{th} impurity to the total resistivity. The resistivity contributions per unit impurity concentration of various impurities in given metals, called specific resistivities, are usually written as

$$R_i = \rho_i / C_i \qquad (7)$$

in units of μΩ cm/atomic percent. C_i is the impurity concentration in atomic percent. Then we have

$$\rho_i = R_i C_i \qquad (8)$$

and

$$\rho\text{total} = \sum_{i=1}^{n} R_i C_i \qquad (9)$$

Even if the effect of a given impurity is unknown, one can often estimate its effect from the known effect of another impurity by considerations of relative valence, atomic volume, electronic configuration, crystal structure, etc.[9]

As mentioned earlier, residual electrical resistivity arises from the presence of electron scattering centers. Certain impurities such as the transition elements are strong scatterers, and hence contribute strongly to resistivity. Some impurities, such as silicon, are often present as oxides or other compounds that scatter electrons to a much lesser extent. If the impurities segregate to localized sinks such as grain boundaries, then the effect on resistivity is reduced as compared to distributions of impurities in solid solution.

It should be clear, that there are many problems and uncertainties in applying residual resistivity data to the determination of concentrations of specific impurities. Unless a great deal is known about the history and composition of a given sample, little can be ascertained, other than an estimate of overall purity. However, if the impurity concentrations in a specimen are well known, or if a RRR representative of the bulk material is available, then the eddy current technique offers a very convenient method for tracing the effects of various treatments on the physical perfection of the crystals or on the segregation of impurities at specific sites.

2.4 Residual Resistivity as a Measure of Homogeneity

One application for which the eddy current method seems especially well suited is the comparison among specimens of relatively homogeneous purity. For example, one could prepare a sufficient number of identical specimens from the bulk material to get an adequate sampling of local variations. Then, a random subset of these specimens could be carefully analyzed to obtain a quantitative measure of the average concentrations of the various impurities. If one then compared the RRR of each specimen with the average RRR of the analyzed subset, quantitative variations in purity could be traced throughout the bulk material. Note that it is necessary to assume that the relative proportions of the various impurities remain unchanged if one wishes to directly correlate variations in RRR with variations in the concentration of a specific impurity. Similarly, if the most likely contaminants are known, along with their specific resistivity and the RRR of the specimen, then these data can be used as an independent check on the impurity concentrations determined by other methods of analysis. In general, purity predicted from RRR will tend to be somewhat higher than the real value, since some impurities may not act as electron scatterers. Thus, it is usually only possible to set limits of purity by this method.

Bean et al.[1] comment that the pickup coil should be sensitive mainly to the material it encloses, and that one can therefore look for variations in resistivity or purity along a continuous rod or bar of metal. However, LePage et al.[7] state that their experiments with joined rods of dissimilar metals show that the sensitivity to a step change in resistivity is very poor. The L/D correction discussed previously shows that some rather long range dependencies exist and may explain this poor sensitivity.

3. Specimen Preparation

Specimen preparation for RRR measurements is relatively simple. Specimens of virtually any size or shape may be used. However, to insure straightforward data analysis, the specimen should have uniform cross-section and a length to diameter ratio of at least eight. The former requirement insures an unambiguous solution to eq. (1), although Bean describes a technique for interpreting data from irregular samples. This technique, however, requires that $\tau(76\ \mathrm{K})$ is measurable. The restriction on the L/D ratio is simply due to the fact that most of the available solutions to eq. (1) assume specimens of infinite length. If $\tau(76\ \mathrm{K})$ is measurable, the limitations on L/D disappear, as eq. (5) then can be used to eliminate the geometrical factors. A further restriction concerns the minimum thickness of a given specimen. If the specimen becomes so thin that the electronic mean-free-path is comparable to the minimum specimen dimension, surface scattering of electrons may become a significant contributor to the resistivity. Unless this contribution can be calculated, thin specimens should be avoided. This problem usually does not occur except with very high purity metals and specimens of quite small diameter. For example, a 4 mm diameter aluminum specimen with a measured RRR of 16,000 requires a size effect correction factor of about 10 percent.

If a specimen is to be representative of the bulk material, it is essential that the surface of the specimen be free of contamination. This is because of the r^2 (r = radius) dependence of the time constant, which tends to give extra weight to the surface material. Thus, it is wise to heavily etch each specimen to remove any surface contamination. This should be done after the specimen is shaped, but before it is annealed. Various chemical and electrolytic etching procedures can be found in the Metals Handbook[10] or in Teggart.[11] The etch should leave the surface smooth and unpitted, preferably polished. If eddy current analysis is to be used to estimate chemical impurity, it is necessary to anneal the specimen to remove strains and dislocations; resistivity determinations done on unannealed metals will usually contain appreciable contributions due to lattice defects. Annealing procedures can be found in the various metallurgical handbooks. It is better to anneal in a vacuum to avoid possible effects due to the atmospheric gasses. The cooling to room temperature at the end of the anneal should be done very slowly; rapid cooling may introduce lattice defects. The specimen is now ready for testing.

4. Experimental Apparatus

A schematic diagram of the eddy current decay apparatus is shown in figure 2. The basic electronic equipment required consists of a current supply, amplifier, and an appropriate recording device. The mechanical equipment necessary is a specimen holder probe and a container for the cryogenic fluid. It was indicated in an earlier section of this paper that problems may be encountered when measuring either very short time constants (approximately less than 1 ms) or very long time constants (approximately greater than 1 minute). The problem associated with observation of short time constants is distortion of the

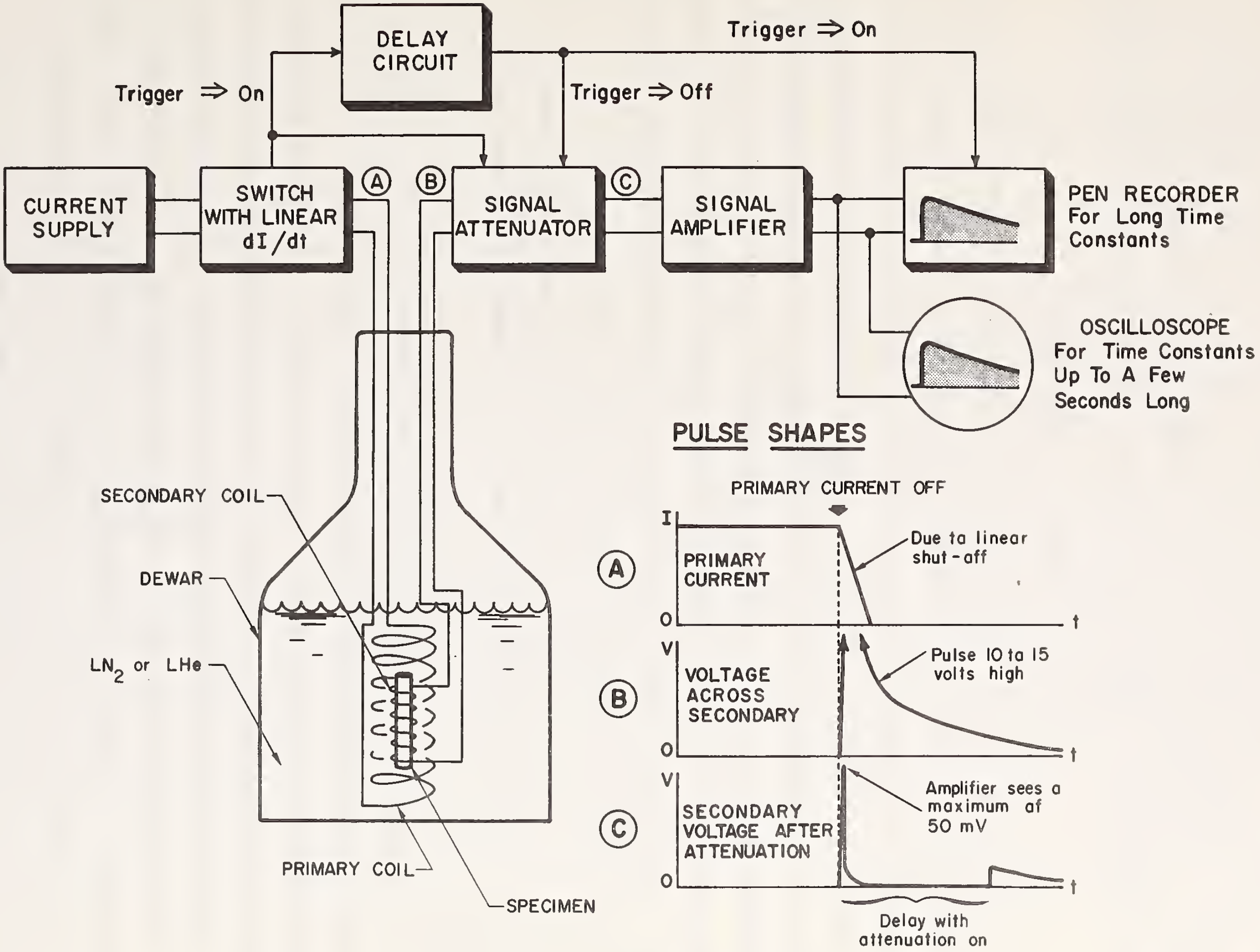


Figure 2. Experimental Schematic and Pulse Shapes.

eddy current decay signal by the transient response of the system. The additional electronics such as (a) linear current shut off, (b) delay circuit, and (c) signal attenuator shown in figure 2 result from the necessity to minimize the effect of this distortion. In the following section we discuss the basis for the design and selection of the electronic components. Later the specimen holders are described in detail.

4.1 Electronic Equipment

To satisfy the above mentioned requirements at both short and long time constants one must obtain a system which has a rapid, error free transient response with a minimum of long term baseline drift. The importance of this statement is best understood by considering the sequence of events beginning with current shut-off, progressing through the primary current decay, and ending with the eddy current decay. At the instant the current is shut-off a finite rate of decrease of the primary current commences. The rate of decrease is determined by the characteristics of the power supply and the coils. With the decrease of primary current the magnetic field within the primary coil also decreases. At the same time eddy currents are established within the specimen.

The secondary coil senses the field change caused by eddy current decay and that caused by the collapse of the magnetic field within the gap between the secondary coil and the specimen. The field decay within the gap generally is much more rapid than the eddy current decay and, thus, results in an initial voltage spike induced in the secondary coil. The magnitude and duration of this spike is determined by the characteristic decay time of the primary-secondary coil system. Thus, there is no advantage in a current shut-off more rapid than this decay time. This establishes the lower limit of time constants that can be measured. This depends on the size of the coil used and is as high as several milliseconds for our larger coils and as low as 10-50 microseconds for our smaller coils. The problem of switching off the current rapidly with a minimum of noise has been troublesome. Purely mechanical switches are too slow and erratic and even mercury wetted relays have sufficient contact bounce to give frequent difficulty. A fast, relatively noise free, solid state switch was designed at this laboratory to eliminate the problems encountered using mechanical switching.

At present, we use a high current (3 A) power supply, figure 3, for series III probes (these probes are described in a later section) and a low current (110 mA) power supply, figure 4, for the series I and II probes. The 110 mA power supply has a linear current shut-off feature in the current switch. This is done to control the magnitude of the initial voltage spike and to minimize ringing in the secondary coil. It is accomplished by using a field effect transistor in its constant current mode that is turned off with the voltage decay from an RC circuit. The adjustable rate of current decay together with an adjustable shunt resistance across the primary coil allows one to produce a noise-free, critically-damped decay of the current.

The linear current shut-off described in the previous section is incorporated primarily to minimize the magnitude of the initial voltage spike. However, this voltage spike is still significantly larger than the eddy current decay signal to be measured. The voltage spike is typically from 3 to 15 volts and the eddy current decay signal is often less than 50 μV. Any amplifier adjusted to respond to 50 μV is likely to be severely saturated by a signal of several volts. The effect of such saturation is likely to continue for appreciable time after the initial spike is gone, thus distorting the true eddy current signal. Even with an amplifier carefully selected for rapid recovery it would be prudent to attenuate the voltage spike to reduce saturation effects. The delay

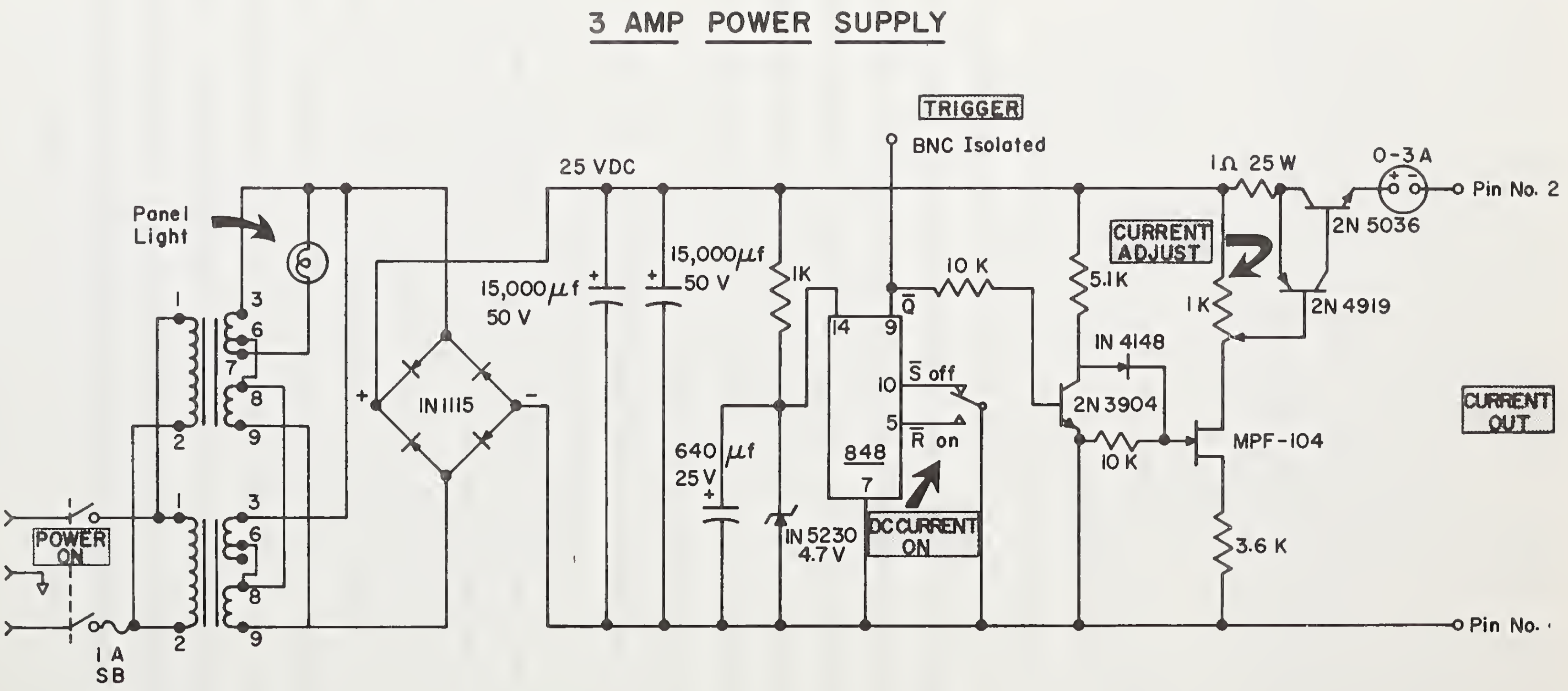


Figure 3. 3 A Power Supply Schematic.

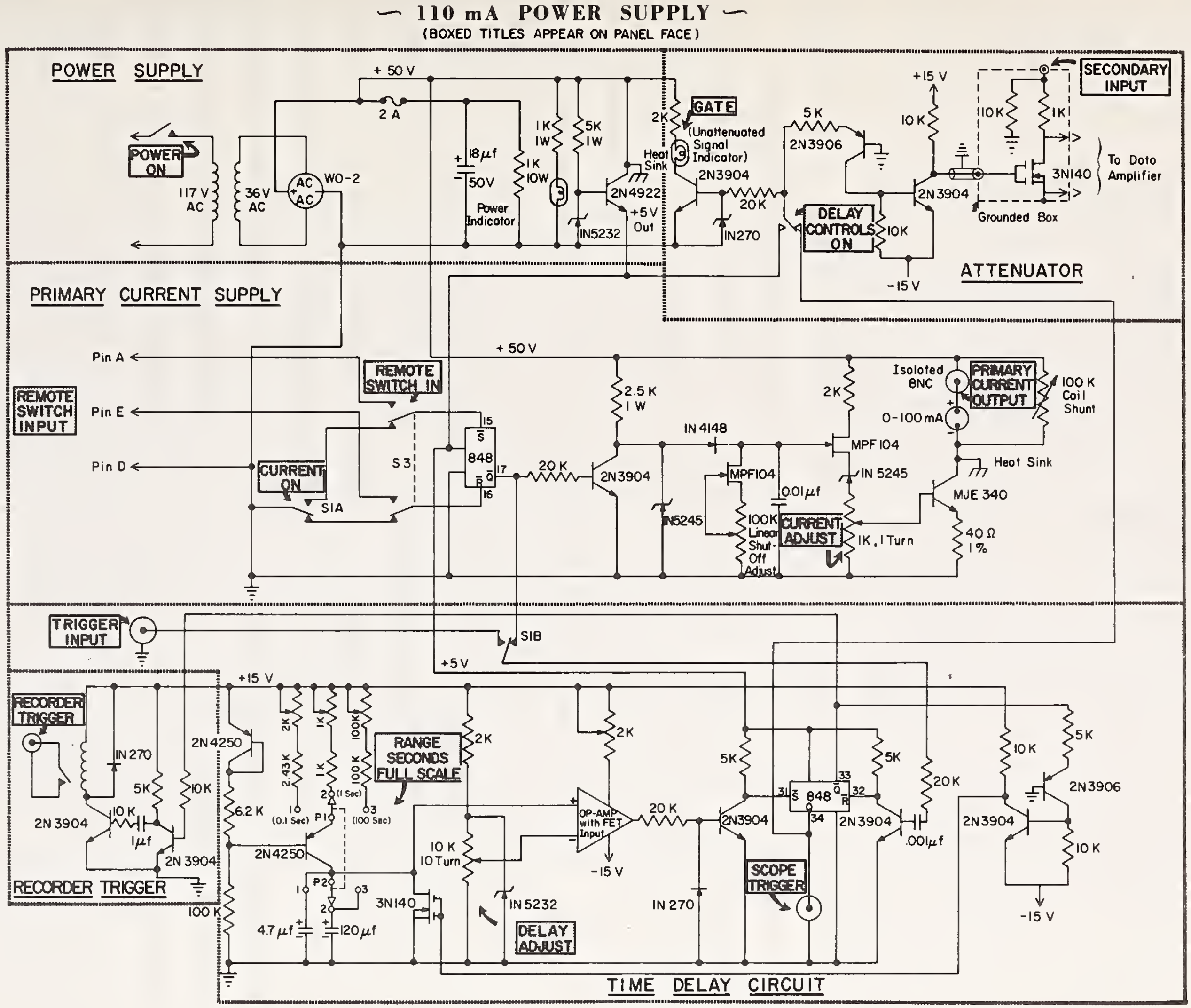


Figure 4. 110 mA Power Supply Schematic; Including Current Shut-Off, Time Delay, and Attenuator Circuits.

circuit and signal attenuator shown in figure 2 and 4 accomplish this attenuation. The delay circuit is designed to gate the signal attenuator for times varying from 0.3 ms to 100 s. This timing circuit also provides a trigger pulse to be used to start the sweep of the recording unit. The effect of this attenuation on the signal is shown in figure 2. The attenuator delay circuit is on the same chassis as the 110 mA current supply. The 3 A current supply is on a separate chassis, but provides a trigger pulse capable of activating either a scope or the attenuator-delay circuit in the 100 mA supply. The primary coil is connected to the appropriate current supply, but the secondary coil is always connected to the secondary input of the 110 mA supply in order to make use of the attenuator circuit. If the attenuator-delay circuit is not being used, one merely shuts off the delay circuit. One limitation of this delay circuit might be a serious defect in some applications. The minimum delay possible is about 0.3 ms. Most specimens at elevated temperatures or thin wires at any temperature might require shorter delays. One solution is to redesign the delay circuit, as the limitation is there, rather than in the attenuator. Another solution is to pass the unattenuated signal directly into the amplifier, and trigger a scope delay unit directly off of the initial spike. At these short specimen time constants, the signals due to the decay of the primary field and the decay of eddy currents in the specimen are of comparable magnitude. Thus, the attenuator is unnecessary for protection of the amplifier. There is the additional problem of distinguishing between the eddy current decay signal and the primary current decay signal. Stern et al.[12] have used bucking coils or adjustable RC circuits to cancel the signal due to the primary current.

For recording the signals, we use either a persistant display oscilloscope or a pen recorder with a time base. The pen recorder trace is initiated by an actuating relay in the delay circuit. We are thus able to use the attenuator-delay feature of the 110 mA current supply in conjunction with both scope and pen recorder.

A useful addition to the system is a time mark generator for calibrating sweep rates. This calibration should be performed for each sweep rate used. A calibration of the vertical axis is not so important, because only relative values are required and the voltage is plotted in arbitrary units. It is necessary, however, that the amplifier and recording devices be linear, in response to variations in signal level.

4.2 Specimen Probe Assembly

The specimen probe assembly, figure 5, consists of a specimen holder, a primary and secondary coil support, and a probe support to allow measurement within a cryogenic dewar. Two main goals directed the design of this assembly: first, to achieve interchangeability among a wide variety of primary and secondary coils of differing sizes and time constants and, second, to avoid the time consuming and wasteful transfer of liquid helium. The first set of probes (Series I) accepts specimens with diameters ranging up to 6 mm and fits into standard 25 to 50 liter liquid helium storage dewars. A second set of probes (Series II) accepts specimens up to 1.7 cm in diameter and fits into a specially modified storage dewar with a 2 cm ID neck. The third set of probes (Series III) accepts specimens up to 2.8 cm in diameter and is designed to be used with a conventional nitrogen shielded glass dewar with a 5 cm ID. The primary winding is placed in the nitrogen shield surrounding the inner dewar and the secondary is attached to the probe assembly in the same manner as Series I and II. The larger primary coils generally have longer characteristic time constants. This however presents no series decay interference problems as the specimen decay time also increases as the square of the specimen diameter. The probe

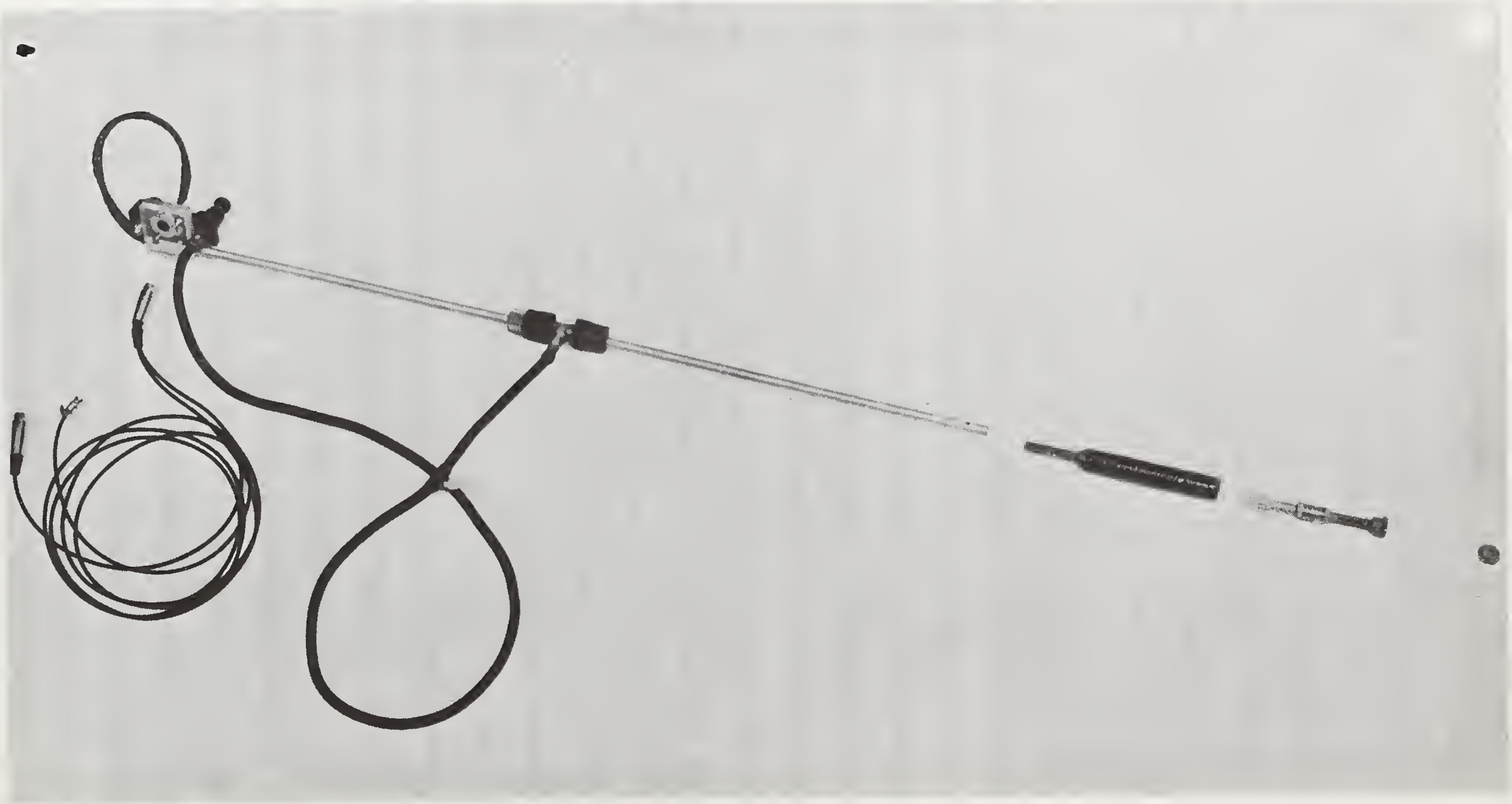


Figure 5. Eddy Current Probe System.

support is made to fit either Series I, II, or III probes. Series I and II are designed such that: the primary coil form plugs into a 5 pin connector mounted in the probe support, the secondary coil form plugs into a 3 pin connector mounted in the primary coil form, and the specimen fits into the secondary coil form. The specimen is held in place and the secondary is secured to the primary by an end cap and a wire that passes through all three parts. The wire is twisted together to prevent loss of the specimen. All secondaries of a given series are interchangeable. Several secondaries are available so as to match the size and eddy current decay time of various specimens. Figure 6 shows a collection of these probes.

The probe support is a thin walled stainless steel tube which contains the primary and secondary coil leads and has a connector mounted at each end. The upper connector is a 4 pin panel plug mounted on a plastic plug. The lower connector is recessed within the tube, and the primary coil form slides into the tube to mate with this connector. The recessed plug is secured to the probe support tube with a screw. To prevent loss of the primary coil form in a dewar, a screw fastens the coil form to the support tube. In addition, we have found it advisable to cut a few small holes in the stainless steel tubing above the recessed plug to control thermal oscillations. This also reduces the time required to insert the probe into a dewar, and helps save liquid helium.

To maintain a positive pressure within the dewar during insertion and withdrawal of the probe, the simple device shown in figure 7 is used. The probe can be held at any depth by tightening the O-ring fitting. The vacuum hose insures an air-tight fit on the neck of the dewar, while the rubber tubing allows one to pressurize the dewar with He gas. The latter is useful in preventing entry of air when the probe is repeatedly

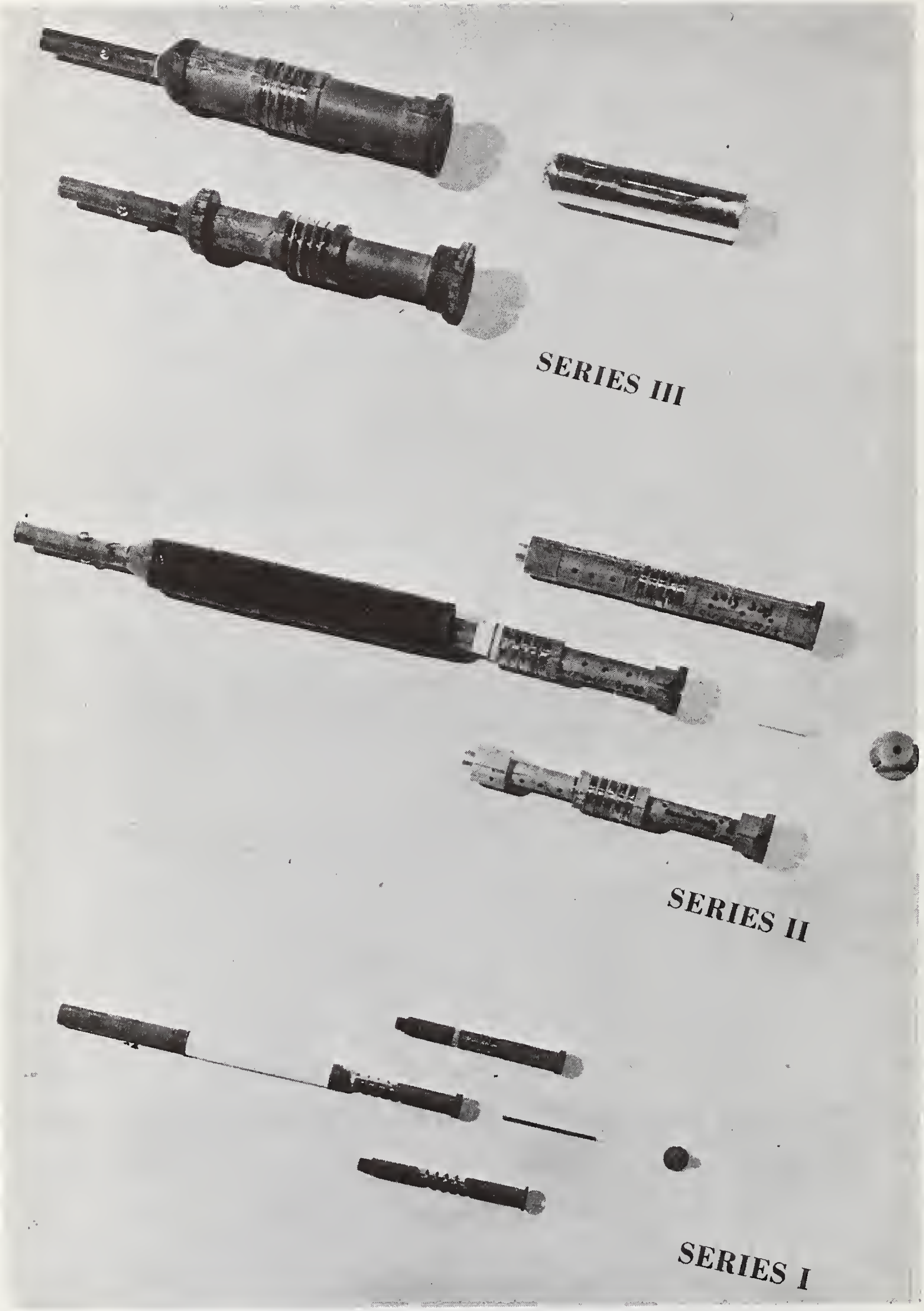


Figure 6. Primaries and Secondaries for Probe System.

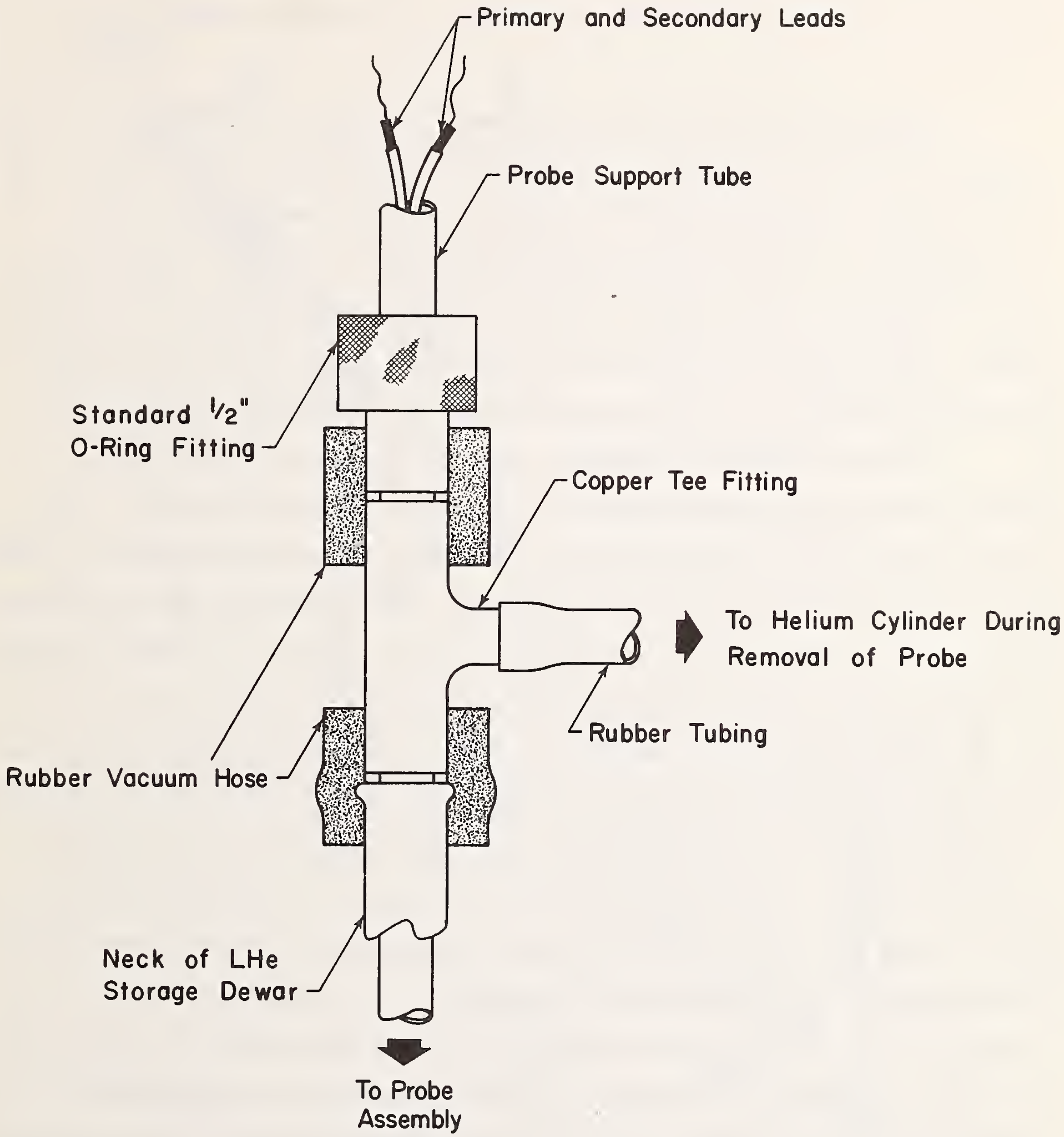


Figure 7. Storage Dewar Fitting for Probe System.

inserted and withdrawn from the dewar. A small rubber balloon can be attached at a tee fitting in the tubing and thus provide a visual check on pressure. The balloon also helps control thermal oscillations in the dewar.

During repeated thermal cycling, the plastic casing on most coaxial cable tends to shatter. If the shields of adjacent cables touch, ground loops may form that will increase noise in the circuit. To prevent this, we lay each cable down the middle of a long strip of cloth tape. The tape is then folded over the cable so that the sticky surfaces meet. Cloth tape is little affected by thermal shock, and will provide adequate insulation. These taped leads are fed down the support tube.

We have provided detailed drawings in figure 8 and 9 and assembly instructions (Appendix C) for a Series I probe assembly. For larger speciments, one can simply scale up the given dimensions. There are two limiting factors to be considered. If the larger probe assembly does not fit into the neck of the largest dewar available or, if the amount of liquid helium boiled off by the extra mass of the larger primary coil and windings becomes excessive, the best solution is to build a primary coil large enough to encircle a double walled nitrogen shielded cryostat. The inner dewar would contain the secondary coil form, the specimen and the cryogen. The primary could be immersed in liquid nitrogen both to cool the primary and provide a heat shield for the inner cryogen. Unfortunately, the advantages of the dip-probe assembly are lost, because cryogens must be transferred into the inner dewar. The Series III probes are built in this way. All the secondaries are wound with resistance wire to reduce the resistance change between room temperature and cryogenic temperatures. Copper wire, for instance, has a resistance ratio of about 8 between room temperature and 76 K, and a ratio of 100 between room temperature and 4 K. If the coil resistance

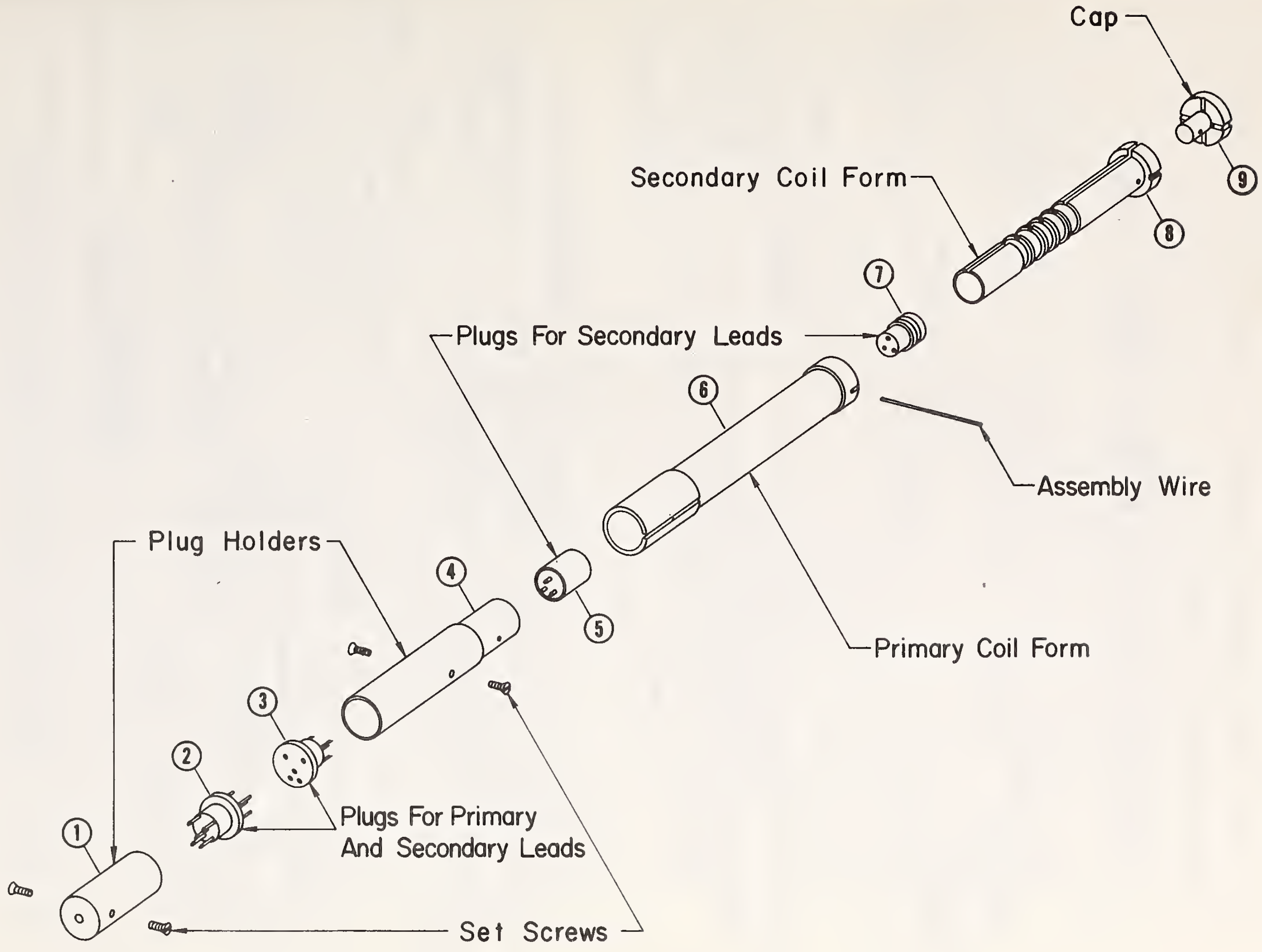
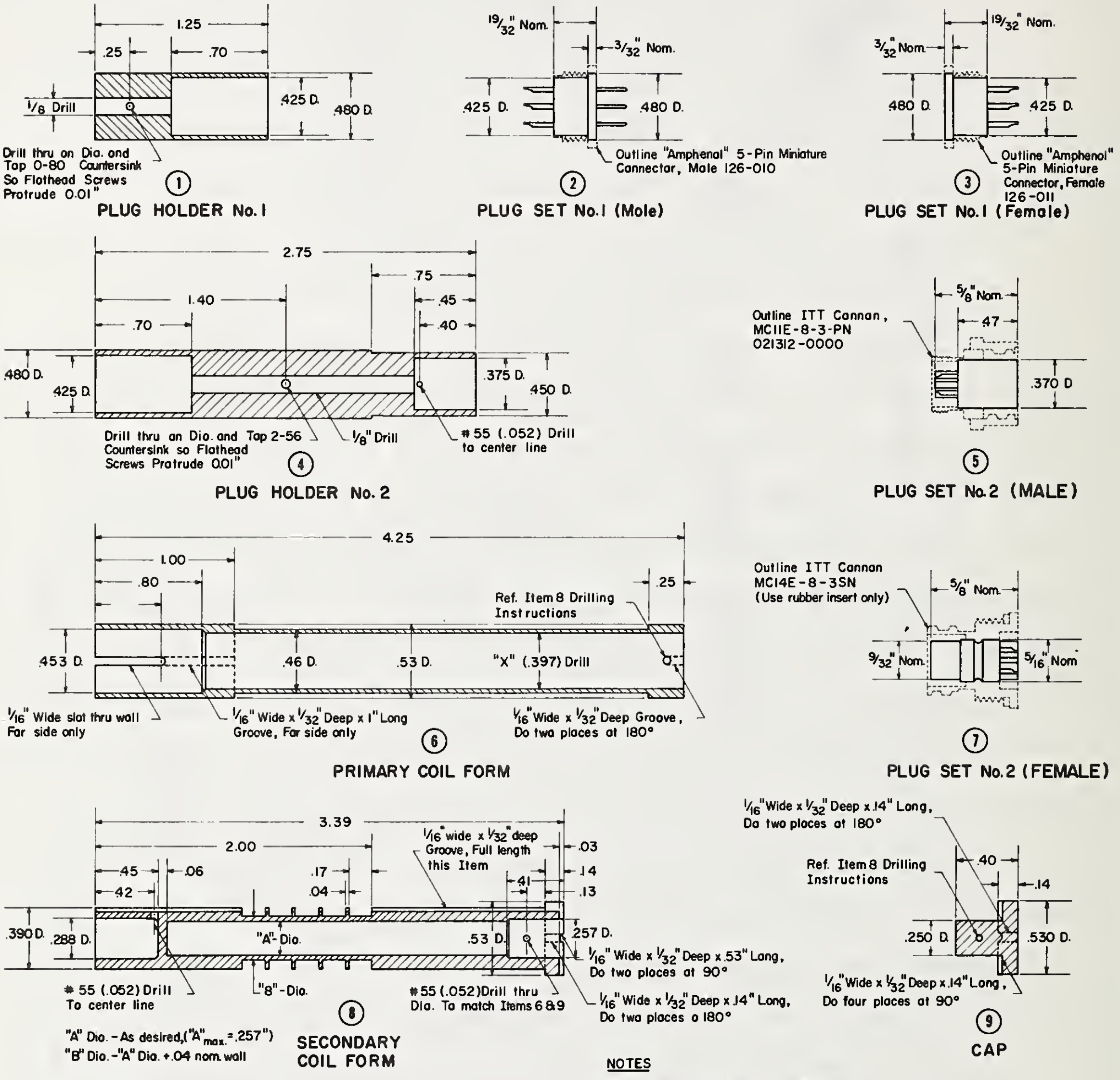


Figure 8. Plug Assemblies for Probe System.

FABRICATION DETAILS OF AN EDDY CURRENT PROBE



NOTES

All tolerances to provide a smooth sliding fit on mating pieces.

All items (except plugs) to be made from linen rod.

Figure 9. Fabrication Details of an Eddy Current Probe.

remains high at all temperatures, a critically damped coil with a minimal time constant is easier to maintain. Resistance wire works well because its resistance is not strongly dependent upon temperature. To increase the winding density, the wire should be insulated with a minimum thickness of enamel. A thin insulation is also less likely to crack under thermal shock. A high resistance wire should not be used to wind the primary since the I^2 R heating may create temperature disturbances on the specimen as well as cause excessive liquid helium boil off.

The secondary coil form is divided by thin walls into several segments. Each segment is wound so as to produce several small coils connected in series, all wound in the same direction. This reduces inter-turn capacitance, thus reducing the coil time constant. A similar design would improve the characteristics of the primaries, but would make machining and winding the coils more tedious.

5. Typical Experiment

This apparatus has been used extensively to study homogeneity and purity of metals considered for use as standard reference specimens. Measurements have been performed on several hundred specimens of zinc, copper, silver, tin and other metals as part of the characterization prior to the issue of a certificate of analysis by NBS-OSRM on a standard reference metal. To illustrate the general procedures involved in the eddy current analysis of an actual specimen, we will describe how the series of tin specimens was prepared and analyzed. About 60 specimens were machined out of a large supply of high purity material that had been analyzed for impurities by various other techniques. The objective was to detect local variations in purity within the bulk material by comparing the RRR of specimens selected from various parts of the lot. Each of the specimens was a cylinder 3 cm long by 1 cm in diameter.

Earlier work with similar material indicated that the surface layers of these specimens were badly contaminated. An electrolytic etch recommended by Teggart[11] was, therefore, used to remove up to 2 mm from the diameter of each specimen. Four specimens were etched at a time, and good uniformity was obtained by bubbling nitrogen over the tin during the etch. Also, better results were obtained by using a large electrolytic cathode of tin placed concentrically about the specimens. The large cathode seemed to reduce the development of surface irregularities. The etch required about 30 minutes. The specimens were then thoroughly washed with water and ethanol.

To minimize the effect of physical imperfections the specimens were annealed. To insure uniformity of treatment all 60 specimens were annealed at the same time. The anneal took place in a vacuum at 200°C for one hour. The oven was allowed to cool very slowly to room temperature.

The specimens were rather large, so we used a Series II probe assembly (figure 6) and the modified large neck helium dewar. Each specimen was centered in the secondary coil and supported by an insulating rod. To remove ice blocks and prevent the probe from freezing in place, the neck of dewar was reamed with a close fitting brass rod before each measurement. The O-ring support (figure 11) was slid into place on the dewar neck and the assembly was lowered until the pressure increased. When the pressure droped again, the assembly was lowered in stages until the specimen was covered by liquid helium.

The delay-attenuator circuit was used, and the delay was set at about 5 seconds, based on earlier tin measurements. The primary current was turned on at about 100 mA for 10 to 15 seconds to allow the field to penetrate the specimen. Note that field penetration rate of the specimen is the same as the decay rate. The current must remain on long enough to assure essentially total penetration. This can be judged both from the amplitude of the signal and the measured decay relaxation time. Two decay traces and two signal base lines for each specimen were recorded on a single photograph. Each insertion boiled off about 0.1 liter of liquid helium.

The data were analyzed by measuring the height of the signal above the baseline at regular time intervals and plotting the log of this amplitude versus time. A typical plot is shown in figure 10. In general, the amplitude can be measured in arbitrary units as only the slope is necessary to obtain the relaxation time. The semilog plot was checked for linearity. Non-linearity may be caused by insufficient delay, baseline drift, incorrect allignment or placement of the baseline, or a variable specimen cross section. For the tin specimens, the time constant of the decay in liquid helium was about 2.1 s, while at 273 K the time constant was calculated to be 60 μs, which gives a residual resistivity ratio of 35,000. This value varied among the different specimens, presumably due to variations in purity. These samples have a length to diameter ratio of 3, which requires a form correction factor of about 1.07 according to figure 1. The revised RRR is then 37,000. To evaluate purity variations, one must use equations 5 and 9 and compare measured RRR with the RRR predicted from the quantitative impurity analysis. The statistical variation of the homogeneity, however, is immediately interpretable. A variation in electronic purity of about 20% from the mean was observed.

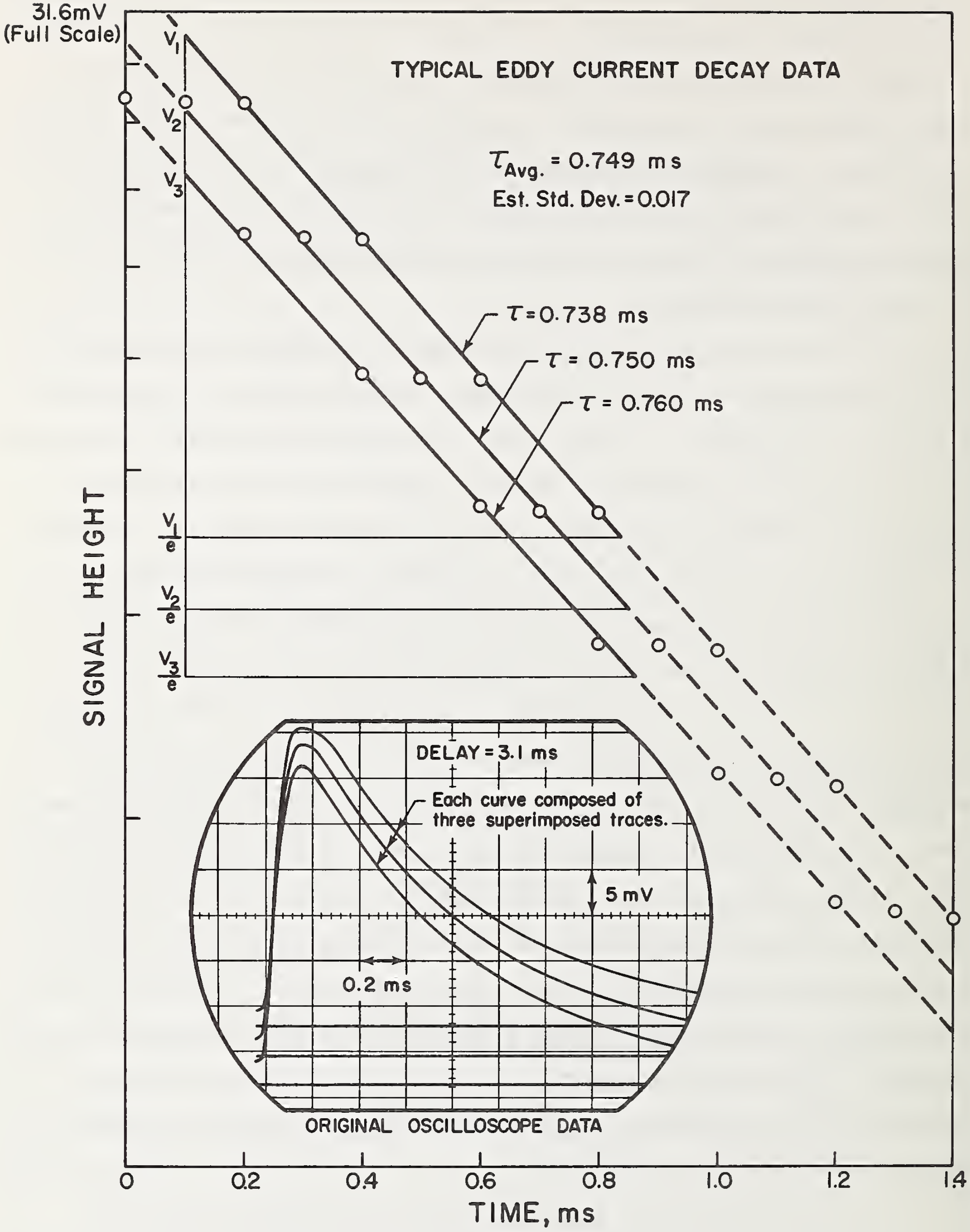


Figure 10. Typical Eddy Current Decay Data.

6. Precision and Accuracy

As described earlier, one may determine either resistivity or residual resistivity ratio with this apparatus. The precision of these measurements, generally, is dependent on the measurement of the temperature, specimen dimensions, and decay time constant. The accuracy of the measured resistivity values is dependent on the accuracy of these variables, and is also dependent on the accuracy of the model relating eddy current decay and resistivity.

The imprecision and inaccuracy of the temperature measurement are generally negligible. Usually the temperatures are based on the use of fixed point baths, such as: ice-water, boiling liquid nitrogen, and boiling liquid helium. If reasonable care is taken, the temperatures of these fixed points are easily reproduced within 0.1%.

Generally, specimen dimensions are sufficiently uniform and large that the imprecision and inaccuracy of measurements are less than 1%. In other instances the measurement uncertainty is determined by the specific specimen in question; in any case, the errors are readily estimated.

The imprecision and inaccuracy associated with the determination of the time constant of decay is strongly dependent upon the nature of the recording equipment and the amount of time spent by the operator in analyzing the data. We have chosen equipment and a procedure consistent with an imprecision and inaccuracy of less than 1%. At this level of uncertainty the cost of equipment is reasonable and the recording-analyzing time is of the order of a few minutes per specimen. If the need arises this precision and accuracy can by improved at the expense of equipment cost and measurement time.

The most difficult variable to assess from the standpoint of accuracy is the model relating decay time and resistivity. Probably the best estimates of this uncertainty come from direct comparison with resistivity measurements from potentiometric methods. We have made a few such comparisons but unfortunately such comparisons can be made only in the overlap region of the two methods. In this region neither method is at its best; therefore, these estimates are probably somewhat higher than typical. The results of these comparisons are listed in table 1. Based on these results we estimate total uncertainty, including model uncertainty, to be about 3% for residual resistivity ratio and 5% for resistivity.

It is to be noted that, depending on the nature of the experiment, the uncertainty in some of the variables, although present, becomes unimportant. For example, if the residual resistivity ratio is desired, such as for homogeneity studies, the specimen dimensions need not be measured. The model inaccuracy, if it is constant with temperature, also becomes less important. If measurements are done to determine the effect of various heat treatments on a single specimen, both the specimen dimension and the model errors are unimportant since they are constant.

The development of a usable system and practical techniques was greatly facilitated by the work of J. C. Moulder and M. B. Kasen. The electronic circuit components designed and built in our laboratory were primarily the work of J. C. Jellison. The financial support and samples provided by R. Michaelis and the Office of Standard Reference Materials, NBS, Washington greatly aided and encouraged our work.

Table 1. Comparison of Resistivity Measurements by Eddy Current Decay and Potentiometric Methods

Specimen Identification	Diameter mm	RRR[†]	Residual Resistivity, nΩ cm	
			Eddy Current	Potentiometric
Ag 923D-Y1)[*]	1.44	1330	13.1	11.1 ± 12%
Al (C1-3)[*]	2.38	356	9.75	9.46 ± 4%
Au (T-1-1)[*]	1.26	847	2.78	2.62 ± 5%
Cu (round robin #2)	6.04	100	15.4	15.4 ± 0.5%
Cu (OFHC-AFC)	6.05	100	15.5	14.9 ± 5%
Cu (Stock 5 - annealed)	3 × 3	3600	0.418	0.477 ± 0.1%
Cu (8A)	6.04	64	39.4	36.1 ± 7%
Cu (OFHC-O)[**]	1.6	580	2.59	2.56 ± 1%
Cu (OFHC-V)[**]	1.6	156	9.55	9.61 ± 1%
Cu (Stock 6K-O)[**]	1.6	5100	0.298	0.290 ± 1%
Cu (Stock 6K-V)[**]	1.6	3740	0.408	0.389 ± 1%
Cu (Stock 7G-O)[**]	1.6	5480	0.275	0.273 ± 1%
Cu (Stock 7G-V)[**]	1.6	1360	1.11	1.10 ± 1%
Mo (3)	6.28	83	55.9	51.9 ± 4%
W (I18-7)	3.03	74	71.1	69.0 ± 1%
W (1-2)	6.35	52	67.9	70.7 ± 3%

[†] RRR is the residual resistivity ratio $\rho_{273\ K}/\rho_{4\ K}$.

[*] These specimens were slightly bent during the potentiometric measurement. This would lower the resistivity and may be partly responsible for the differences observed between the two measurement methods.

[**] Size effect corrections have been performed on these data. The correction is greater for the eddy current method than the DC method. At a ratio of 5000 the eddy current correction is greater than the DC correction by about 7% for this diameter copper wire. Proportionately smaller corrections apply for the lower ratios.

7. References

1. Bean, C. P., DeBlois, R. W., and Nesbitt, L. B., J. Appl. Phys. 30, 1976 (1959).

2. Zimmerman, J. E., Thiene, P., and Harding, J. T., J. Appl. Phys. 41, 1572 (1970).

3. Kasen, M. B., Phil. Mag. 21, 599 (1970).

4. Neighbor, J. E., J. Appl. Phys. 40, 3078 (1969).

5. Arp, V. D., Kasen, M. B., and Reed, R. P., Technical Report AFAPL-TR-68-87, WPAFB, Ohio, February, 1969.

6. Moulder, J. C., Clark, A. F., and Gniewek, J. J., Measurement of Effective Electronic Purity by the Eddy Current Decay Method, Symposium on Trace Characterization - Chemical and Physical, October 3-7, 1966, NBS, Gaithersburg, Md. (unpublished).

7. LePage, J., Bernalte, A., and Lindholm, D. A., Rev. Sci. Instrum. 39, 1019 (1968).

8. Weinstein, M. A., J. Appl. Phys. 33, 762 (1962); also Weinstein, M. A., J. Appl. Phys. 37, 248 (1966); also Weinstein, M. A., J. Appl. Phys. 37, 2548 (1966).

9. Meaden, G. T., Electrical Resistivity of Metals, Plenum Press, New York (1965).

10. Metals Handbook, 8th Ed. Vol. 11, Amer. Soc. for Metals, Novelty, Ohio (1964).

11. Teggart, W. J. McG., The Electrolytic and Chemical Polishing of Metals, Pergamon Press, New York (1959).

12. Stern, R., Levy, M., Kagiwada, R., and Rudnick, I., Appl. Phys. Lett. 2, No. 4, 80-81 (1963).

13. The use of trade names of specific products is essential to the proper understanding of the work presented. Their use in no way implies any approval, endorsement, or recommendation by NBS.

14. Blatt, F. J., Physics of Electronic Conduction in Solids, McGraw-Hill, New York (1968).

Appendix A: Useful Formulae

I. To calculate the time constant τ in seconds of a uniform specimen, given the resistivity ρ in Ω cm and relative permeability μ.

A. Circular cross section

$$\tau(r, \rho) = (2.17 \cdot 10^{-9}) \frac{\mu r^2}{\rho}$$

where r = specimen radius in cm.

B. Rectangular cross section

$$\tau(a,b,\rho) = (1.27 \cdot 10^{-9}) \frac{\mu}{\rho} \frac{a^2 b^2}{a^2 + b^2}$$

where a, b are the dimensions of the cross section in cm.

C. Hollow Elliptical Cylinders

For a circular cylinder of $\mu = 1$, a = inner radius in cm.

b = outer radius in cm.

$$\tau(a,b,\rho) = 10^{-9} g(a/b) b^2 / \rho$$

g(a/b) is given in table below:

a/b	g	a/b	g	a/b	g	a/b	g
0.00	2.173	0.35	2.102	0.65	1.587	0.95	0.3011
0.05	2.173	0.40	2.059	0.70	1.431	0.96	0.2430
0.10	2.172	0.45	2.001	0.75	1.253	0.97	0.1838
0.15	2.170	0.50	1.926	0.80	1.052	0.98	0.1236
0.20	2.164	0.55	1.833	0.85	0.827	0.99	0.0623
0.25	2.153	0.60	1.720	0.90	0.576	1.00	0.000
0.30	2.133						

II. To correct a measured time constant for end effects, use figure 1 to find the L/D correction factor, C, for the given specimen

$$\tau_{\text{corrected}} = C\tau_{\text{measured}}$$

III. To calculate RRR from $\tau_{76\text{ K}}$ and $\tau_{4\text{ K}}$ determination

$$\text{RRR} = \frac{\rho_i(273\text{ K})[\tau(4\text{ K})/\tau(76\text{ K}) - 1]}{\rho_i(76\text{ K})} + 1$$

IV. To correct a measured RRR for size effect

$$\rho_{\text{measured}} \cong \rho_{\text{bulk}}(1 + \ell/d)$$

where ℓ is the electronic mean-free-path and d is the minimum sample dimension.[9]

V. To calculate the impurity contributions to resistivity, assuming Mathiessen's Rule, and given the specific resistivities of the impurities.

$$\rho_i = \sum_{i=1}^{n} R_i C_i$$

where R_i = specific resistivity of i^{th} impurity (see reference 14)

C_i = concentration of i^{th} impurity

n = number of impurity species

VI. To calculate various circuit parameters

A. Inductance, L in henries, of a solenoid of radius a in meters, length ℓ, in meters with n turns per meter and permeability, μ

$$L = \pi a^2 \mu n^2 [\sqrt{\ell^2 + a^2} - a]$$

B. Length of wire in an n layer, densely wound circular cylindrical solenoid of inner radius a, length ℓ and wire radius b

$$\text{length} = n\pi\ell\left[\frac{a}{b} + \frac{(n-1)\sqrt{3}}{2}\right]$$

It is assumed that b is much smaller than both ℓ and a.

C. Time constant of a pure L-R circuit

$$\tau = \frac{L}{R}$$

Appendix B: Tables of Typical Numerical Calculations

Table 1. Time Constant, τ in seconds, of circular rod vs. Resistivity and Diameter.

Resistivity (Ω cm)	Diameter (cm) .05	 1.0	 2.5
8×10^{-3}	1.7×10^{-8}	6.8×10^{-6}	4.2×10^{-5}
1.7×10^{-6}	8×10^{-7}	3.2×10^{-4}	2.0×10^{-3}
10^{-10}	1.4×10^{-2}	5.4	34

Table 2. Calculated resistivity and time constants of a 5 mm diameter aluminum cylinder as a function of temperature (assume RRR $\simeq$ 10,000).

temp. (K)	ρ ($\mu\Omega$ cm)	τ (μ s)
295	2.74	49.6
273	2.5	54.4
200	1.6	85.
80	0.25	544.
~4	0.00027	496,000

Appendix C: Assembly Instructions for Series I Probes

Figures 8 and 9 illustrate the details of a Series I probe assembly. The detailed fabrication procedure for this probe is given below. Numbers given in parenthesis refer to part numbers in figures 8 and 9.[13]

Primary: First assemble plug holder #2 (4). Teflon[13] insulated-36 gauge wires are soldered to the five pin plug (3). The wires are fed through the 1/8 inch hole in the holder (4) and two are passed through the #55 hole to be soldered to the primary leads. The remaining two leads are soldered to the male three pin plug (5). Both plugs (3, 5) are glued in place (in an arbitrarily selected but standarized orientation to insure interchangeability of probes) with plastic cement. The cement is thinned with acetone for easier handling.

Next, the plug holder (4) is inserted into the primary coil form (6) and the #55 hole is aligned with the lead groove. The plug holder (4) is glued in place with thinned cement. The wires are laid along the groove and soldered to the primary coil leads. These wires are held down with a thin layer of cement. Excessive cement here can break the wires as it dries or when it shrinks upon cooling. The latter problem frequently goes undetected at room temperature but exhibits itself as an open circuit upon cooling.

Probe Support: The primary and secondary leads are soldered to a four pin connector at the top of the support tube, and are then brought down the tube and connected to the internal recessed plug. These leads should be sufficiently long to pass completely through the tube. The excess is drawn up into a loop at the top, as the plug is recessed into the tube.

Insulated wires are soldered to the male five pin plug (2) and pushed through the 1/8 inch hole in the holder (1). To reduce noise pick-up, the pair of primary leads should be twisted together to form a tight double spiral. The secondary pair is similarly twisted. These wires are connected to the appropriate coaxial leads. Each wire should be insulated at the solder point by a bit of cloth tape or shrinkable tubing. Ordinary plastic tape does not hold well at low temperature. The plug (2) is aligned and glued with plastic cement. If a primary is plugged into the #1 holder (1), it is easy to slide the holder into place in the probe support tube, and align the screw holes. To standardize the holes in the probe support tube, a brass guide is made with a 1/2 inch ID to slide over the support tube, and the screw holes are drilled through appropriately placed holes in the wall of the guide.

Secondary: Teflon insulated #36 wires are soldered to the secondary plug (7) and twisted to reduce noise pickup. The leads are passed through the #55 hole and along the groove in the secondary coil form (8). The plug (7) is then aligned and glued in place. The leads from the secondary windings are brought along the groove and soldered to the plug (7) leads. Thin cement holds the leads at the bottom of the groove. If desired, the sense of the primary and secondary windings can be noted and leads attached so as to always give signals of the same polarity, no matter which coils are used. We have not done this as the banana plug input to the recording device is easily reversed.

FORM NBS-114A (1-71)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET**	1. PUBLICATION OR REPORT NO. NBS SP 260-39	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Standard Reference Materials:
The Eddy Current Decay Method for Resistivity
Characterization of High Purity Metals

5. Publication Date

May 1972

6. Performing Organization Code

7. AUTHOR(S)

A. F. Clark, V. A. Deason, J. G. Hust, and R. L. Powell

8. Performing Organization

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address

Same as item 9.

13. Type of Report & Period Covered

Final

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Characterization of high purity metals by resistivity measurements at low temperatures is discussed. In particular, the eddy current decay method of resistivity measurement is described in detail. The advantages and limitations are presented along with the theoretical basis of the method. Detailed instructions are given for constructing and operating the apparatus.

17. KEY WORDS (Alphabetical order, separated by semicolons)

Apparatus; characterization; eddy current decay; electrical resistivity; high purity metals; homogeneity; low temperature.

18. AVAILABILITY STATEMENT ☒ UNLIMITED. ☐ FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NTIS.	19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 53
	20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price 55 cents

USCOMM-DC 66244-P71

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