NBS MEASUREMENT SERVICES: STANDARD CELL CALIBRATIONS

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PREFACE

Calibrations and related measurement services of the National Bureau of
Standards provide the means for makers and users of measuring tools to achieve
levels of measurement accuracy that are necessary to attain quality,
productivity and competitiveness. These requirements include the highest
levels of accuracy that are possible on the basis of the most modern advances
in science and technology as well as the levels of accuracy that are necessary
in the routine production of goods and services. More than 300 different
calibrations, measurement assurance services and special tests are available
from NBS to support the activities of public and private organizations. These
services enable users to link their measurements to the reference standards
maintained by NBS and, thereby, to the measurement systems of other countries
throughout the world. NBS Special Publication 250, NBS Calibration Services
Users Guide, describes the calibrations and related services that are offered,
provides essential information for placing orders for these services and
identifies expert persons to be contacted for technical assistance.

NBS Special Publication 250 has recently been expanded by the addition of
supplementary publications that provide detailed technical descriptions of
specific NBS calibration services and, together with the NBS Calibration
Services Users Guide, they constitute a topical series. Each technical
supplement on a particular calibration service includes:

o   specifications for the service

o   design philosophy and theory

o   description of the NBS measurement system

o   NBS operational procedures

o   measurement uncertainty assessment
         error budget
         systematic errors
         random errors

o   NBS internal quality control procedures

The new publications will present more technical detail than the information
that can be included in NBS Reports of Calibration. In general they will also
provide more detail than past publications in the scientific and technical
literature; such publications, when they exist, tend to focus upon a
particular element of the topic and related elements may have been published in
different places at different times. The new series will integrate the
description of NBS calibration technologies in a form that is more readily
accessible and more useful to the technical user.

The present publication, SP 250-24, NBS Measurement Services: Standard Cell
Calibrations, by Bruce F. Field, is one of approximately 20 documents in the
new series published or in preparation by the Center for Basic Standards. It
describes calibration technology and procedures utilized in connection with NBS
Service Identification Numbers from 53110 to 53150 listed in the NBS

Calibration Services Users Guide. Inquiries concerning the contents of these documents may be directed to the author or to one of the technical contact persons identified in the Users Guide (SP-250).

Suggestions for improving the effectiveness and usefulness of the new series would be very much appreciated at NBS. Likewise, suggestions concerning the need for new calibration services, special tests and measurement assurance programs are always welcome.

Joe Simmons, Acting Chief
Office of Physical Measurement Services

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Center for Basic Standards

Table of Contents

Table of Contents (cont.)

List of Figures

List of Tables

NBS MEASUREMENT SERVICES: STANDARD CELL CALIBRATIONS

Bruce F. Field

Abstract - This document describes the procedures used at NBS to calibrate standard cells in terms of the U.S. Legal Volt. The two calibration services that are offered by the Electricity Division are discussed; Regular Calibration of client standards at NBS; and the Volt Transfer Program which is a process to determine the difference between the U.S. Legal Volt and the volt as maintained by a client laboratory. The operational procedures used to compare standard cells and to maintain the U.S. Legal Volt via the ac Josephson effect are discussed in detail.

1. Introduction

To maintain a unit of electromotive force (emf), standards laboratories typically use one or more groups of electrochemical cells called standard cells. Standard cells are physical representations of the unit of emf and are used as standards against which the emf of other cells and systems are compared. At present, saturated cadmium-sulfate-type (Weston) cells are used when high accuracy, 1 ppm or less, is required in maintaining a unit traceable to NBS.

Standard cells are electrochemical systems composed of two dissimilar electrodes immersed in an electrolytic solution. They are not intended to supply electric current and, therefore, are of different design from those electrochemical systems which are intended for such purpose. The stability of the emf of the cell depends on the chemical equilibrium within the cell. Although the emf of a cell is highly reproducible and generally exhibits a fairly constant emf, it must be periodically recalibrated to eliminate the effects of long term drift. The frequency with which recalibrations are required is a function of the accuracy requirement, the number of cells used to maintain the volt, and the stability of the individual cells. This must be determined by the client laboratory using the cells.

Calibration of cells in terms of the U.S. Legal (or NBS) Volt is accomplished via two services offered by the Electricity Division of the NBS.

Regular Calibration

Clients may send cells to NBS for direct comparison to NBS standards which are in turn calibrated in terms of the NBS Volt. At the conclusion of the test a report is issued with a statement of the values of the emfs of the cells and estimated uncertainties for the emf values, while the cells were at NBS. No additional

uncertainty is included for transportation effects, long term drifts of the emfs of the cells, or measurement errors in the client's laboratory.

Volt Transfer Program

The Volt Transfer Program (VTP) is a measurement assurance program designed to determine the difference in the unit of voltage maintained by a client laboratory using standard cells and the NBS Volt as maintained by NBS. In this program, a group of NBS-owned cells in a thermoregulated enclosure is measured at NBS, shipped to the client laboratory, compared to the client cell group, and returned to NBS for final measurements. The measurements to be made at the client laboratory are specified by NBS and the data is reduced and reviewed by NBS. A report is issued containing the difference of the client unit of voltage from the NBS Volt and specifying an uncertainty of that difference observed during the time of the test. In this experiment the uncertainty in the transportation of the standard cells is estimated and included in the final uncertainty.

2. Description of Service

Regular Calibration

NBS offers a voltage calibration service for saturated and unsaturated standard cells of the Weston type. All cells are compared to NBS standards which are calibrated in terms of the U.S. Legal Volt defined via the ac Josephson effect. Cells accepted for test include shippable or unshippable saturated cells that are either designed for immersion in an oil bath or that are housed in a thermoregulated enclosure. NBS maintains two oil baths, one at 28 °C and one at 30 °C, for testing immersible-type cells.

Routine calibrations of standard cells involve the following considerations:

1) Unsaturated cells require approximately 3 weeks for a complete calibration. The emfs of such cells are read daily for a period of 10 days. If the measured emfs fluctuate unduly or are unusually low, or if the cells show abnormal indications, the report of calibration will reflect these circumstances. Unsaturated cells are not likely to be injured by normal transportation (mail or express) if they are packed carefully. Because of the possible hazard from freezing, shipment during very cold weather should be avoided.

2) Saturated standard cells of the unshippable type should always be transported by messenger because such cells should never be tipped from an upright position by more than 45 degrees in any direction. Unshippable saturated cells contained in portable, temperature-regulated enclosures

2

should also be transported by messenger, and with the enclosure activated or under power if possible.

3) Saturated standard cells of the shippable type housed in portable thermoregulated enclosures should be packed carefully and shipped under power if possible. Liquid-in-glass thermometers normally mounted in such devices should be removed and provided with additional rigid packing for protection against breakage. Enclosures having a nominal cell temperature of 28 °C or lower should not be transported during the summer due to the danger of over heating. To prevent overheating, enclosures should not be energized by the ac power line while they are packed in shipping containers. When an enclosure is shipped under temperature control, arrangements should be made by the client to have it promptly delivered to and picked up from the airport (if shipping by air freight) to avoid exceeding the capacity of the batteries powering the enclosure.

4) Saturated standard cells which arrive having been maintained continuously at their nominal temperature of use will, workload permitting, undergo test immediately upon receipt for a period not to exceed 4 weeks, unless other arrangements are made. If such cells perform abnormally with respect to the typical performance of like cells in similar environments, the owner will be notified. Arrangements for further testing may be made at that time if desired. Cells will be returned as soon as possible after calibration.

5) Saturated cells arriving at a temperature other than their nominal temperature of use will be brought to their use temperature as soon as possible after receipt. Starting one month after they are initially brought to temperature, daily readings will be taken to observe the stability of the cells. When the cells stabilize, 10 daily readings will be taken and used to assign values to them. This process will not exceed 90 days unless special arrangements are made.

6) Prior to each daily reading of the cell emfs the temperature of the enclosure (or the oil bath) will be read using the temperature measuring device included in the enclosure, or special arrangements can be made to have the temperature monitored by a calibrated NBS platinum resistance thermometer. A calibrated platinum resistance thermometer is always used to monitor the temperature of the oil bath with the temperature reported relative to the International Practical Temperature Scale (IPTS-68).

Volt Transfer Program

The Volt Transfer Program experiment consists of four phases.

1) Preliminary Laboratory Study. During this phase NBS personnel will discuss with client laboratory personnel various aspects of the experiment, suggest experiments to evaluate the measurement process, and establish a tentative shipment and measurement schedule. If necessary NBS personnel may visit the laboratory. NBS may restrict participation in the Volt Transfer Program to those clients who use quality-control procedures to monitor their representation of the volt. Guidelines for setting up control chart procedures can be found in VTP Control Chart Requirements [40].

2) Shipment of an NBS Transport Standard. An NBS transport standard, a group of 4 cells (usually) in a thermoregulated enclosure with a battery pack, is shipped via air freight to the client laboratory. The success of the experiment depends on keeping the transport standard under power continuously and expediting its transport. Detailed instructions for transport are given to the client.

3) Measurement of the Transport Standard in the Client Laboratory. Measurements comparing the cell emfs of the transport standard to the emfs of the client laboratory cells are done in accordance with NBS specified procedures. Usually measurements are made daily over a two to three week period. Data is sent to NBS immediately after each measurement for reduction and review. The conclusion of this phase is determined by NBS after review of the client data; in some cases additional measurements may be required.

4) Analysis of the Data and Issuance of a Final Report. Upon return to NBS the transport standard will be remeasured to determine if it changed during the experiment. After sufficient measurements have been made the data is analyzed to determine the difference between the units of voltage at NBS and the client laboratory (V_{LAB} - V_{NBS}) and its uncertainty. If the difference exceeds the estimated uncertainty, new emf values for the client cells will be recommended to reduce the difference to zero.

3. Calibration Apparatus and Measurement Approach

Voltage Difference Measurements

All cells at NBS are calibrated by comparing them directly to NBS owned standard cells which are in turn calibrated in terms of the U.S. Legal Volt. All comparisons use redundant measurement designs and a series opposition method, as described in NBS Technical Note 430 [16]. Figure 1 shows a simplified schematic of the measuring circuit.
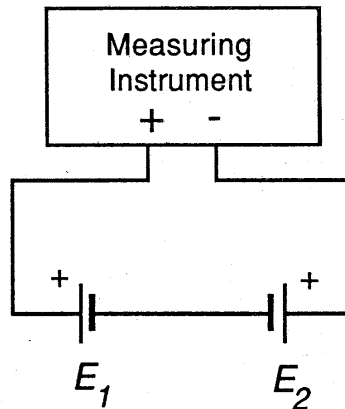
Fig. 1. Simplified measuring circuit.

Two cells are connected in series opposition (one unknown, one reference) and the small voltage difference is read using a digital voltmeter (DVM). In an ideal situation the difference in emf as measured by the voltmeter is:

$$E = E_1 - E_2$$

where E_1 and E_2 are the emfs of the two cells being compared. However, in the real situation there may be spurious emfs in the circuit. In general these can be classified into two categories:

1. Those emfs that remain constant, or relatively so, in relation to the interval over which a complete set of measurements is made.

2. Those emfs that vary rapidly (referenced to the interval over which a complete set of measurements is made).

If the emfs are of the second type they will have the effect of decreasing the precision of the process. On the other hand, if they are of the first type they will have the effect of introducing a systematic error into the measurement result such that

$$E = E_1 - E_2 + P$$

where P is the constant, and as yet unknown, emf. It is possible to estimate P by taking a second measurement E' as shown in Fig. 2, where

$$E' = E_2 - E_1 + P.$$

Taking the difference between the two expressions gives

$$E - E' = 2(E_1 - E_2),$$

thus yielding an estimate of $E_1 - E_2$ free of P. The pair of measurements are said to be "left-right" balanced. That is, if there is a positional effect it is balanced out of the final result. This technique is analogous to that used to eliminate the inequality of balance arms in precision weighing on a two-pan equal-arm balance. In order to designate the cell positions from the operational point of view, they are frequently designated as unknown and reference (or left and right) relative to the input terminals of the measuring instrument.
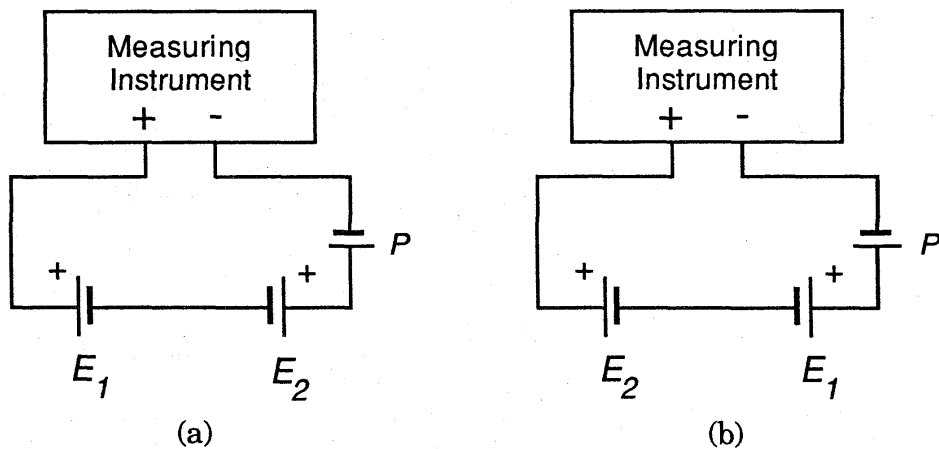
Fig. 2. Two measurement configurations to eliminate positional errors (P).

With classical potentiometers the left-right effect P does not vary significantly over the time of the measurements and it is sufficient to require that the total design be left-right balanced, i.e., each cell appears on the left side and right side of the measuring system an equal number of times irrespective of their order of appearance in the design. Digital voltmeters, however, have been found to introduce a small time-varying dc offset that must be eliminated by immediately reading every cell pair twice, once in the normal mode and once with the polarity of the input reversed. The algebraic difference of these two measurements divided by two is considered to be a single measure of the cell difference with the DVM offset eliminated.

Measurement Apparatus

Two voltage measuring systems are currently in use at NBS for cell comparisons. Except for the switching systems, they are identical. One system (System VTP) is used for comparison of NBS primary standards with NBS working standards and for comparison of the working standards to VTP transport standards. The second system (System REG) is used for comparison of NBS working standards to client cells sent in for regular calibration. Figure 3 is a block diagram of the measurement apparatus of the systems.

Cell emf inputs

	1000 µV source
Crossbar Scanner	Digital Voltmeter
Relay Controller	
	Printer
to other computers	Desktop Computer
File Server & 16MB Hard Disk	
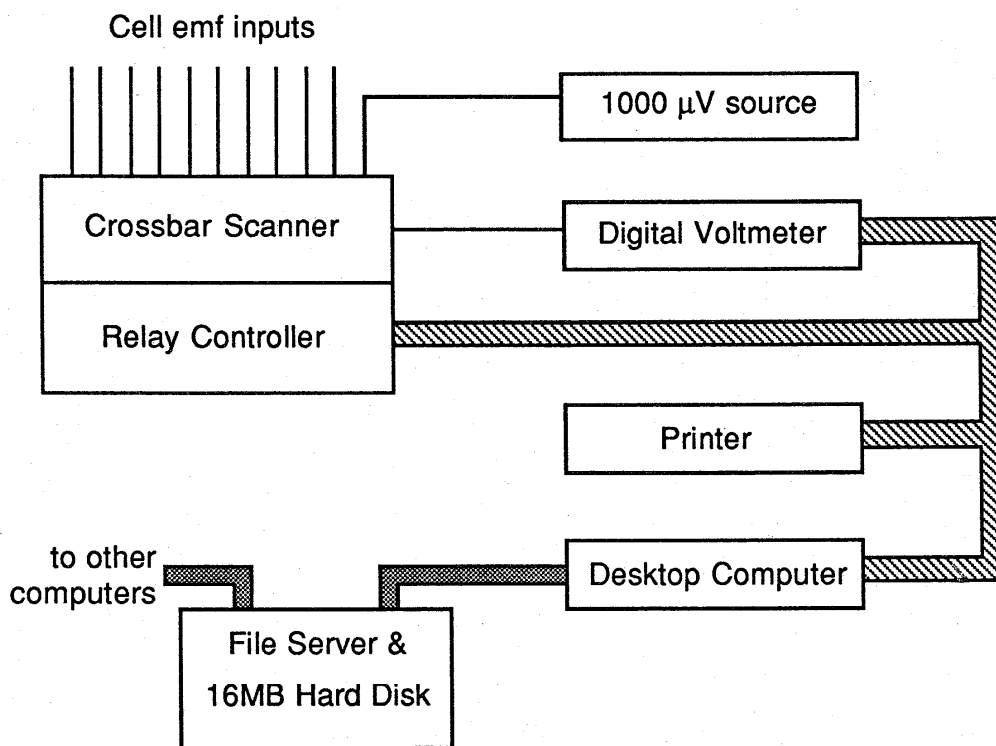
Fig. 3. Block diagram of the two measurement systems used for comparison of pairs of standard cells.

Using a measurement design, the computer commands the crossbar scanner to connect two cells in series opposition to the DVM; the DVM takes a number of readings of the voltage difference (usually three); the crossbar scanner reconnects the cells with reversed polarity; and the DVM takes three more readings. The computer records the readings, and when the experimental design is complete, it calculates the estimates of the cell differences using a least-squares method and records the cell emfs on the hard disk and on a floppy disk for backup. The hard disk is shared among several desktop computers to permit the data from both measurement systems to be stored in one location,

and to permit access to the data from other machines even while measurements are being made. A summary of the basic statistics is printed after each measurement set.

The digital voltmeters used to make the difference measurements are 6-1/2 digit high-resolution voltmeters. Two performance parameters of the voltmeters are critical to this application: low input bias current and small random measurement error. The design of the saturated standard cell is such that the emf stability depends on electrochemical equilibrium within the cell. Small charging or discharging currents that may be present at the input of the DVM will produce changes in the cell emf that may be significant. The voltmeters used at NBS have a measured input bias current of 12 pA which contributes a negligible error to the measurement. On the lowest voltage range of the voltmeter the standard deviation of a single measurement is 0.034 µV with an integration time of 18 seconds. The integration time was chosen specifically to obtain a measurement standard deviation of less than 0.04 µV. Since only small voltage differences are being measured (the worst case is about 600 µV when comparing cells at 37 °C to cells at 30 °C), only a modest DVM reading accuracy of 17 ppm (parts-per-million) is required for 0.01 µV accuracy in the voltage differences. (Unless otherwise specified, all uncertainties in this document are meant to correspond to a one standard deviation estimate.) To ensure that the voltmeter is within the required accuracy, it is checked every day by reading a calibrated 1000 µV source.

A commercial Zener standard that produces 1000 µV is connected to one input of the scanner switch, and a piece of copper wire (to provide a low-thermal short) is connected to a second input. Connecting the first input minus the second input presents the 1000 µV source to the DVM. Actually, two Zener standards and two copper wires are used, one set for each measuring system. Each 1000 µV source is read daily with the DVM to perform a one point calibration on the gain accuracy of the DVM. The sources are periodically calibrated using a resistive divider and a standard cell.

Pairs of cells are connected to the digital voltmeters by one of three low-thermal switching systems. The first system consists of a 10x10 matrix crossbar switch with latching solenoids. This switch is used to connect up to 80 VTP transport cells to measuring system VTP. A second modular switching system is also used to connect NBS reference cells to measuring system VTP. This system consists of up to five switch modules each capable of connecting one or two of ten cells to a common 4-wire signal bus [27]. The output of this bus is connected to the DVM of measuring system VTP. The third system, consisting of two 10x10 matrix crossbar switches with latching solenoids and a 2x5 selector switch, is used to connect up to 300 client cells to measuring system REG.

All the switching systems are based on a low-thermal crossbar switch; however, each system is constructed somewhat differently with capabilities for switching different numbers of cells. Common to all three systems is the capability to randomly select any two cells under computer control and connect them in

series opposition to the DVM in "normal" or "reversed" polarity. The matrix crossbar switches are actuated by momentarily energizing the switch solenoids, and then permanent magnets within the switches latch the contacts closed until a second release solenoid is energized. This momentary action is designed to minimize the heat input to the switch which in turn would produce thermal gradients and generate large thermal emfs in the switch. The uncompensated thermal emfs in these switching systems have been measured and found to be less than 20 nV. The solenoids in the modular switch system (used for intercomparison of NBS reference cells) are continuously energized during contact closure, but the switch has been modified to locate the solenoids outside the chamber containing the switch contacts to minimize the heat input to the contacts. The uncompensated thermal emfs have been determined to be less than 6 nV.

Redundant Measurement Designs

Redundant measurement designs are used to compare cell emfs because they provide diagnostic information about potential errors or problems with the measuring system. Two important parameters are estimated by the designs: the within-day standard deviation and the left-right (positional) effect in the measuring system. The within-day standard deviation permits laboratory personnel to estimate the quality of the measurements and, if necessary, to eliminate anomalous observations from the measurement design and re-compute the cell emfs with little loss in accuracy.

Two specific designs are generally used, one for comparison of two groups of four cells, and one for comparison of one group of six cells to one group of four cells. These designs are described in detail in Appendix A. On occasion additional designs are required for groups with varying numbers of cells; these are constructed similarly to the ones in the Appendix. The cell emfs are estimated from the cell difference measurements by solving the overdetermined set of equations using the least-squares method and including the constraint that the mean emf of a given group of cells (i.e., the reference group) is known. This results in assigning individual emf values to all the cells in terms of the mean emf of the reference group. This calculation is performed by the computer program READBOX which is discussed in Appendix D.

Temperature Measurements

All saturated standard cells exhibit an emf change with temperature and must be maintained at a constant temperature. Cells sent to NBS for calibration are either housed in portable thermoregulated enclosures, or are immersed in NBS-provided constant-temperature oil baths. Thermoregulated enclosures generally contain a temperature sensing element which can be used to monitor the temperature variations within the cell enclosure. Typical devices are mercury-in-glass thermometers, thermistor bridges, and platinum resistance thermometers. NBS follows the manufacturer's recommended procedure for

monitoring the temperature using these devices. The temperature scale embodied in the temperature device is taken as correct, primarily because accurate knowledge of the temperature is unnecessary. Cell emfs are corrected only for small *changes* in temperature, referenced to a nominal temperature as established by the temperature device.

For cells housed in the NBS oil baths, calibrated platinum resistance thermometers and an ac resistance thermometer bridge are used to measure the temperature. The temperature of the oil bath is stable and uniform to at least 0.001 °C. The estimated uncertainty of the temperature measurement with respect to the International Practical Temperature Scale (IPTS-68) is 0.005 °C (3 standard deviation estimate), and includes uncertainty for the power dissipation in the thermometer, errors in the determination of the triple point of water, and errors in the drift of the calibration constants between calibrations.

Cell emfs are corrected for small day-to-day temperature changes by monitoring the temperature as described above and applying an emf correction based on the International (or Wolff) Temperature Formula [13]:

$$E_T = E_{20} - 0.00004060(T-20) - 0.000000950(T-20)^2 + 0.000000010(T-20)^3$$

in volts where E_T is the emf at temperature T and E_{20} is the emf at 20 °C. This equation is used to correct the cell emfs to any arbitrary nominal temperature by computing the correction for the actual temperature with respect to 20 °C and subtracting the correction for the nominal temperature with respect to 20 °C. The formula is an approximation and is not exact for all cells although it provides reasonable accuracy (better than 0.1 µV) if the total correction is less than 1 µV.

4. Maintenance of the Volt

The ac Josephson Effect

The U.S. Legal (or NBS) Volt is presently defined in terms of the atomic constants h (the Planck constant) and e (the elementary charge) via the ac Josephson effect [26]. Critical to this definition is the role played by a Josephson junction which may be regarded as a frequency-to-voltage converter, where the frequency-to-voltage ratio is precisely equal to the combination of physical constants 2e/h. The current value of 2e/h used for maintaining the NBS Volt is 483593.420 GHz/V_{NBS}. The U.S. Legal Unit of voltage is known to be smaller than the SI unit by about (9 ±1) ppm (3σ) [41]. (The dominant system of units used throughout the world to express the results of physical measurements is *Le Systèm International d'Unités* or International System of Units, abbreviated SI.)

When two weakly coupled superconductors are irradiated with microwave energy, the assembly (a Josephson junction) can be used to produce precise voltages described by the following equation:

$$E = nf/(2e/h)$$

where n is an integer and f is the frequency of the irradiating microwave energy. A variety of experimental tests (for material dependence, temperature dependence, etc.) and theoretical investigations of the Josephson relation have been made which indicate that for ordinary Josephson devices (particularly tunnel junctions) with conventional current-voltage lead configurations the ratio is exact to at least a few parts in 10^8 [23]. In practice, frequency measurements of the microwave energizing signal are based on the NBS unit of time interval, the atomic second.

The Josephson Array

Arrays consisting of from 1500 to 2076 Josephson junctions have been used to produce a total voltage of up to 1.2 V [42,43]. These arrays do not require individual control of the bias currents as is usual, but avoid the multiple bias problem by using constant-voltage steps which cross the zero current axis of the junction I-V curve. This arrangement allows a large array of junctions to share a common current bias at or near zero. The arrays are fabricated using niobium and lead alloys and are stable at room temperature.

Microwave Apparatus

The microwave radiation applied to the Josephson array is supplied by a 60 mW Gunn diode oscillator at 94 GHz which is frequency-stabilized by a frequency locking counter containing a quartz-crystal oscillator. The short term frequency stability of the microwave radiation (15 min) is about 1 part in 10^9. The frequency is measured by the frequency counter with a resolution of 1 part in 10^{10}. The accuracy of the counter time base is regularly checked against the U.S. frequency standard by comparing the counter time base to a 100 kHz high-stability oscillator which is simultaneously compared to the signal from WWVB using a VLF comparator.

DC Measurement Apparatus

Figure 4 shows some of the dc measurement apparatus used to compare the array voltage at 1.018 V to a 1.018 V Zener reference standard. (Not shown is a low-thermal-emf crossbar selector switch used to connect one of three Zener references to the measurement system.) To measure the voltage of the Zener reference, the array is adjusted to produce a voltage nearly equal to the Zener reference by (a) adjustment of the bias current and microwave power to select a voltage step, and (b) adjustment of the microwave frequency to fine-tune the step voltage. The step is observed on the oscilloscope to check for any abnormalities.

The difference between the array and Zener reference is then measured by averaging several readings (E_1) of the digital voltmeter. Low-thermal-emf reversing switch A is reversed and several more readings (E_2) are taken to eliminate offsets in the digital voltmeter. The bias current to the array is reversed and adjusted to produce -1.018 V and reversing switch B is switched. Two more sets of readings $(E_3$ and E_4 respectively) are taken with switch A in its normal and reversed positions. This action is required to eliminate thermal emfs in the leads from the array to the reversing switches. The Zener voltage is calculated as $(E_1 - E_2 - E_3 + E_4)/4 + nf/(2e/h)$ where n is the integer step number, f is the microwave frequency, and 2e/h is as defined above. This measurement sequence is repeated five times for each Zener reference, with a typical standard deviation of 0.009 µV for the five measurements, and takes about 12 minutes.

A final check is made on the thermal emfs in the leads from the Zener reference to reversing switch B by replacing the Zener reference with a short and adjusting the array to operate on the zero-voltage-step with the microwave power set to zero. The same measurement sequence is run as for the 1.018 volt measurement. The residual thermal emfs thus determined are subtracted from the 1.018 volt measurements. (The Zener references are connected to one of the modular crossbar switches described in section 3. The output of this switch is considered to be the output of the Zener references as all measurements of these references are made through the switch. Any stable thermal emfs within the switch, or between the switch and the Zener reference, are cancelled as they add equally to both the 2e/h measurements and the cell comparisons.)
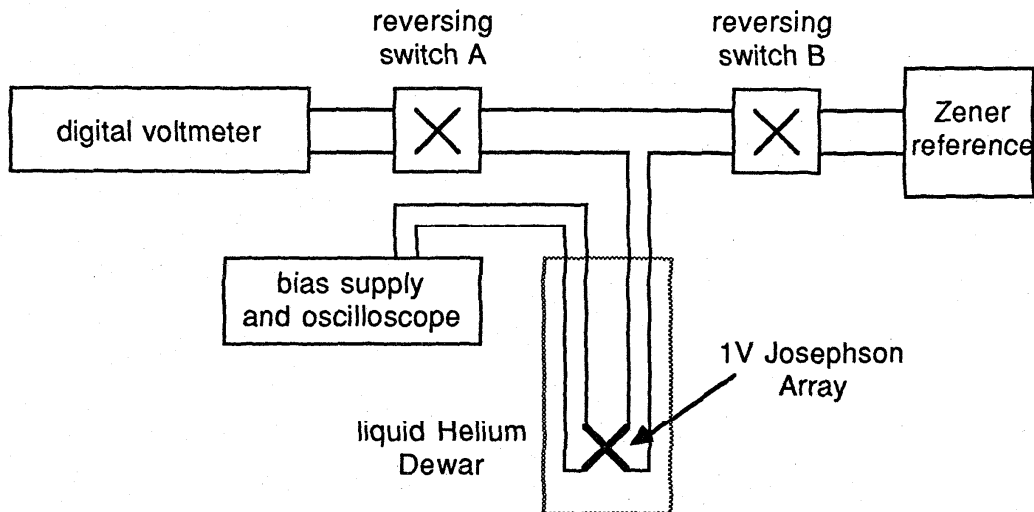
Fig. 4. Simplified diagram of the measurement system used for calibration of three Zener references.

Standard Cell Comparisons

Two standard cell groups (consisting of 10 cells total and considered to be the NBS primary groups) are calibrated in terms of 2e/h at weekly intervals. The calibrations consist of making cell comparison measurements (using redundant measurement designs) between the primary groups of cells and a group of three Zener reference standards each producing 1.018 V. The pattern of group comparisons currently in use is shown in Fig. 5. A first set of cell-Zener comparisons are made and then the three Zener standards are each calibrated in turn by the Josephson Array. After the Array calibrations the cell comparisons are repeated to determine if the Zener standards changed during the measurements.

Only Zener standards are compared to the Array because the Array voltage occasionally and unpredictably jumps abruptly to a slightly different voltage step. If the Array were being compared to a cell while this shift occurred, a small charging or discharging current would be introduced into the cell, slightly changing it's emf. Zener standards, however, are not significantly affected by this type of current pulse.
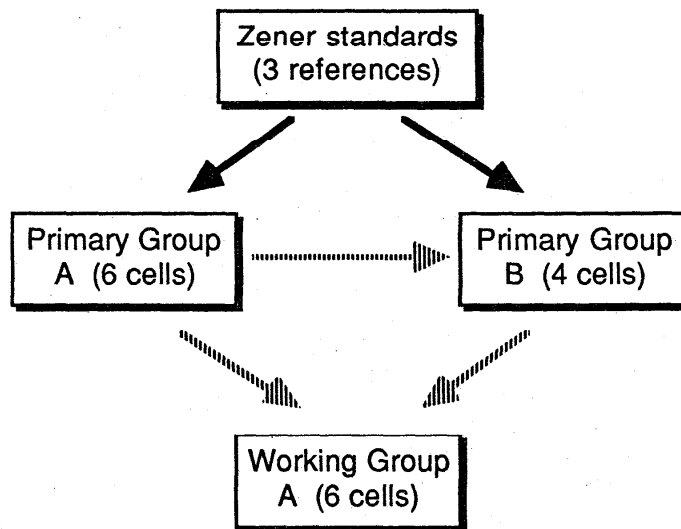
Fig. 5.   Measurement sequence used to assign values to the primary groups based on 2e/h measurements.

TABLE I

UNCERTAINTIES IN THE ASSIGNMENT OF THE MEAN EMFS OF THE PRIMARY GROUPS

Source of uncertainty	1 std. dev. estimate (ppm)
Microwave frequency	0.005
Assignment of Zener reference group using Array	0.007
Random uncertainty of comparison of Zener reference group to the mean of Primary Group A	0.009
Change in the Zener reference group during the 2e/h measurement	0.019
Uncompensated thermal emfs in the cell switches	0.005

RSS total	**0.023**

Uncertainty

Table I summarizes the sources of uncertainty in assigning a value to the mean emf of Primary Group A at the time of a 2e/h measurement. The microwave frequency is measured by a frequency counter which is calibrated in terms of WWVB. An uncertainty is included for measurement uncertainty and drift of the oscillator frequency.

For each daily 2e/h measurement each Zener reference is compared to the Array five times. The pooled standard deviation of the mean calculated from individual comparisons is 0.0042 μV (60 degrees of freedom). This value, divided by the square root of three (0.0024 μV, 0.002 ppm), is used as the limit of the random component of uncertainty in comparing the mean of the three Zener standards to the Josephson Array. The thermal emfs in the leads to the Zener reference are measured and subtracted from the Zener values. The uncertainty of determining the thermal emfs is 0.0042 μV (0.004 ppm). All other known sources of systematic error are negligible.

The random component of uncertainty in comparing the Zener standards to the primary group is determined from the 0.034 μV pooled standard deviation of a

single cell-Zener comparison. Because of the redundant measurements of the measurement design, the uncertainty of the difference of the mean of the Zener reference group to the mean of the primary group is 0.012 μV. Two measurement designs are made for Primary Group A (before and after the 2e/h measurements); thus, the uncertainty of it's mean emf is reduced by the square root of two for a total uncertainty of 0.009 μV (0.009 ppm).

The difference of the mean Zener group emf minus the mean primary group emf typically shows a change of (0.008±0.011) μV in the before and after comparisons described above. These appear to be caused by small random shifts in the Zener references emfs. Taking a conservative approach, we assign an uncertainty of 0.019 ppm (0.008+0.011) for changes in the mean Zener group emf during the measurements.

Modular low-thermal switches (described in Section 3) are used to connect the various cells to the measuring system. The thermal emfs in these switches that do not cancel on cell reversal have been measured to be 0.005 μV (0.005 ppm).

The Root-Sum-Square (RSS) total is an estimate of the uncertainty in assigning a value to the mean emf of Primary Group A based on one 2e/h measurement. This is an estimate of how well the present system would agree with another totally independent 2e/h system. Based on data from actual 2e/h measurements (see Fig. 6, for example) the reproducibility with which the mean emf of a single group of standard cells can be determined using the present Josephson apparatus is about 0.020 ppm.

5. Operational Procedures

Calibration of the Laboratory Primary Cells

Standard cell emfs drift with time so the use of a simple time invariant model for the cell emf can lead to unacceptably large step changes in the disseminated volt each time the volt is reassigned from Josephson Array comparisons (2e/h measurements). In addition, it is desirable to "average" several 2e/h measurements to reduce the random error of the measurements. Thus, we use a model for the primary cell group emfs that predicts a linear drift with time and new model coefficients calculated after every fourth 2e/h measurement.

2e/h measurements are made at approximately weekly intervals. For every fourth measurement (a cardinal measurement) additional cell comparisons between the primary and working cell groups are made. These data are used to reassign the emfs of all the primary cell groups. In general, least-squares lines are fit to the last five or so cardinal measurements and these lines are used to predict weekly values for the means of the cell emf groups for the coming month. The exact number of measurements chosen for the fitted lines depends on (a) how well the cell emfs fit a linear model, and (b) the random scatter in the 2e/h measurements of the cell emfs. The judgement and experience of the

laboratory staff are used to determine the models. Figure 6 shows the typical behavior of the mean emf of six cells in Primary Group A plotted against time. The line plotted in Fig. 6 is the least-squares fitted line to the data; the residual standard deviation of the fitted points about the line is 0.020 μV.

The three 2e/h measurements made on "off-weeks" each month are used to check the prediction of the assignment of the cells. The collection of cell groups that constitute the primary groups changes as cells need replacement or enclosures need repair. In general, the primary groups consist of two or three groups of four to six cells each, with about 10 to 12 cells total. Generally, these standard cell emfs drift with time; drift rates of the different cells range from +0.1 to -0.7 ppm/year.
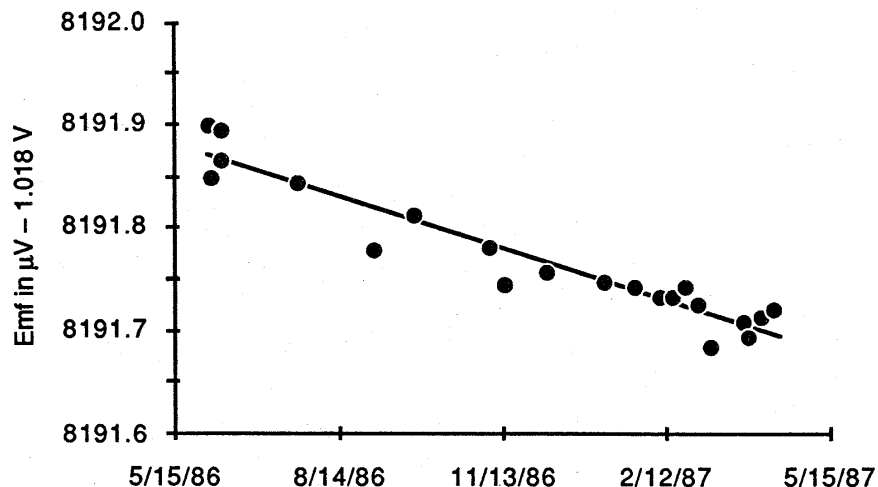
Fig. 6.   Mean emf of Primary Group A as determined from 2e/h measurements.

The primary cell groups also serve as a check standard for the 2e/h measurements. If an individual 2e/h measurement assigns values to the primary cells that are inconsistent with the predicted values, all the measurement systems are investigated to determine the source of the inconsistency. If the problem cannot be resolved, the 2e/h measurement is usually repeated. In the exceptional circumstance where later 2e/h measurements confirm the deviation from the predicted model (usually more than 0.07 ppm) appropriate past workload data are corrected to reflect the change.

Note: Prior to February 1987 two series-connected Josephson junctions producing 10 mV were used as the basis for the U.S. Legal Volt. The small voltage produced by the junctions was "stepped-up" to 1.019 V by special

potentiometers and compared to unsaturated standard cells. These unsaturated cells were compared to the primary cells using a manual potentiometer. Because of the difficulty of these measurements they were made only monthly and they are described in detail in reference 26. Some data (particularly figures 8 and 13) are based on these older measurements. The use of the Josephson Array has reduced the total uncertainty of Table I from 0.036 ppm for the old system to 0.023 ppm for the Array.

Calibration of Working Cell Groups

To minimize the possibility of disturbing the primary cells, the client cells are not compared directly to the primary cells. Instead, as shown in Fig. 7, the primary cells are used to calibrate working groups of cells once each day, immediately before calibration of the client cells or the NBS transport standards for the Volt Transfer Program. The working cell emfs are determined from the predicted values of the primary cells, and are used for that day. The working cells are then compared to client cells and the NBS transport standards. This is feasible because of the small within-day uncertainty of 0.004 to 0.007 ppm which is introduced by the intercomparison of standard cells. Measurements are made using redundant designs and the VTP automated measuring system.
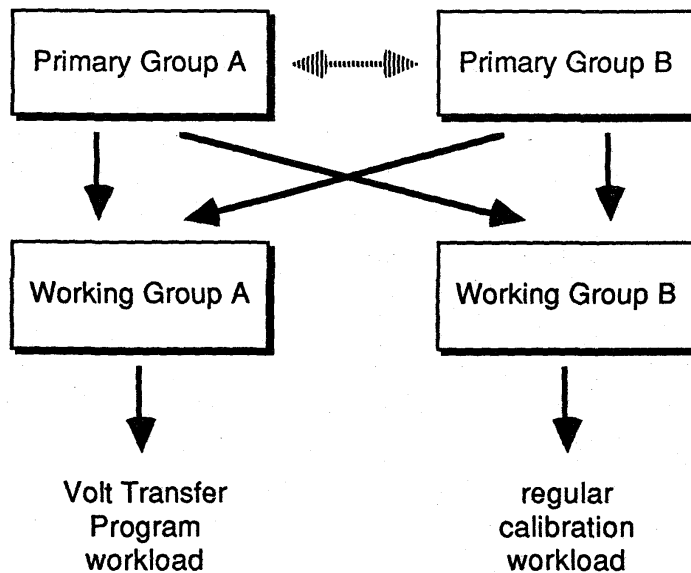
Fig. 7.   Measurement sequence used to compare the Regular
Calibration and VTP workload to NBS working groups.

17

This procedure is modified as necessary when cells show erratic behavior or temperature-regulated enclosures fail. At present the primary cells consist of two groups, in different thermoregulated enclosures, that are independently compared to each of the working groups. This results in two assigned values to each working group. In an ideal situation the two values should agree; the difference is a measure of the error of the predicted values for the primary cells. Figure 8 shows the typical behavior of this difference. If the assigned values disagree by more than 0.08 μV (as they occasionally do in Fig. 8), direct comparisons are made between the two primary groups to try and resolve the disagreement. In many cases the disagreement can be traced to abnormal behavior of the temperature controller of one of the enclosures, or a rapidly changing cell emf.
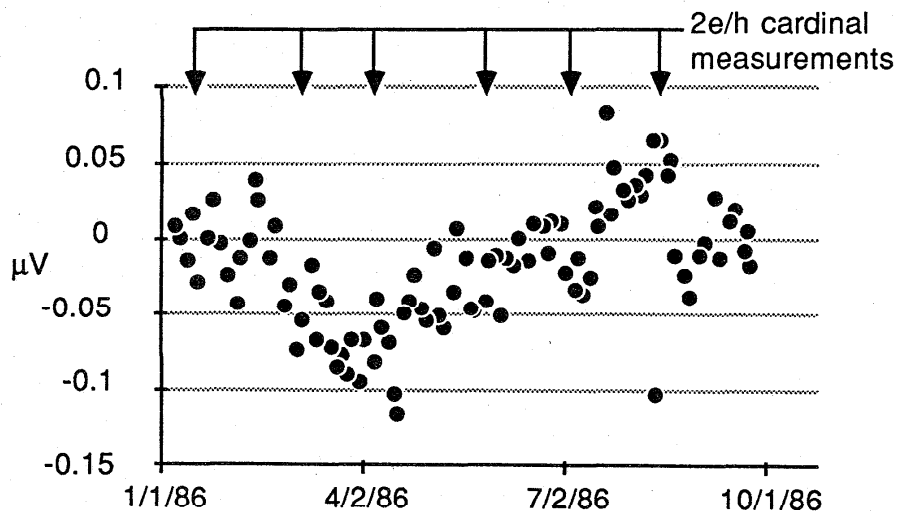
Fig. 8. The difference between the two daily values assigned to
Working group A from the two Primary groups. The arrows
indicate dates on which the cell emfs were reassigned based
on 2e/h measurements.

If the lines fit to the emfs of the primary groups are poor predictors of the emfs, it would be expected that the difference would be nearly zero immediately after a 2e/h measurement and gradually diverge thereafter. The data of Fig. 8 do not indicate this. The data do show correlation with changes in room temperature, even after correcting for the indicated cell temperatures [29]. This appears to be related to less than optimum temperature control of Primary Group B, which is a commercial enclosure. Plans are underway to replace this enclosure with an NBS-designed enclosure similar to the one for Primary Group A [29].

TABLE II

UNCERTAINTIES IN THE ASSIGNMENT OF THE
MEAN EMF OF THE WORKING GROUP

Source of uncertainty	1 std. dev. estimate (ppm)
Assignment of primary group (from Table I)	0.023
Day-to-day fluctuation of primary groups	0.028
DVM scale error	0.005
Random uncertainty in comparison of primary group to working group	0.004
Uncompensated thermal emfs in cell switches	0.015

Uncertainty of assignment to working group RSS total	**0.040**

Table II summarizes the uncertainties in assigning a daily value to the mean emf of the working groups. Although several 2e/h measurements are combined to predict values for the primary groups, the uncertainty of the primary group assignment is not reduced from the value quoted in Table I because part of the uncertainty may be systematic to all the 2e/h measurements. An uncertainty is included for the day-to-day fluctuation of the primary groups and the additional uncertainty due to predicting the values of the primary groups up to one month ahead. This is estimated by taking the standard deviation of the difference of the two assigned values to a working group, calculated from the daily comparisons with the primary groups (see Fig. 8).

The DVM scale error is estimated based on readings of the calibrated 1000 μV source which show a scale error of 70 ppm and a maximum cell difference of 64 μV. The random uncertainty of the cell comparisons is estimated from the redundant measurement designs as before with a pooled standard deviation of a single measurement of 0.034 μV.

Low-thermal switches connected to measuring system VTP (described in Section 3) are used to connect the various cells to the measuring system. The

19

thermal emfs in these switches that do not cancel on cell reversal have been measured to be 0.015 μV (0.015 ppm).

The RSS total uncertainty in assigning a value to the mean emf of either working group is estimated to be 0.040 ppm.

Regular Calibration

Calibration of Client Saturated Standard Cells

Cells received for calibration may be subjected to a stabilization period before measurements are begun. The length of the stabilization period depends on whether the cells were shipped to NBS under constant temperature control and may be as long as 4 weeks. If space is available on the measuring system, and cells have been shipped under temperature control, they are generally connected to the measuring system immediately. However, later review of the data may result in these early measurements being discarded.

Three types of saturated standard cells are calibrated: cells in oil at 28 °C or 30 °C and groups of cells in temperature-controlled enclosures. The first two types are placed in oil baths whose temperature is stable and uniform to at least 0.001 °C and whose temperatures are determined using NBS-owned platinum resistance thermometers. Temperature-controlled standard cell enclosures are tested under the following ambient conditions:

Temperature	(23 ± 1) °C
Relative Humidity	50% or less

The operating temperature of the cells in temperature-regulated enclosures is determined using the temperature measuring device supplied with the enclosure. If the enclosure has a temperature indicating bridge, an NBS owned null detector is used to make the readings to within the resolution of the bridge, usually 0.001 °C. An NBS or customer owned platinum resistance thermometer may be used if requested. Temperature measurements are made each day before the cell emf measurements are started.

Assignment of the Final Value

Client cells are compared to NBS working cells for a minimum of one measurement design per day for ten working days. The cell emfs are plotted and the data is reviewed by two staff members who decide if the cell emfs exhibit sufficient stability for a report to be issued. If so, the means of the ten measurements are used as the final assigned values of emf of the cells. If the cells show excessive drift or other unusual behavior, additional measurements may be taken.

20

TABLE III

UNCERTAINTIES IN THE ASSIGNMENT OF THE MEAN EMF OF A CLIENT CELL

Source of uncertainty	1 std. dev. estimate (ppm)
Uncertainty of assignment to working group	0.040
Change in working group during the day	0.040
DVM scale error	0.010
Random uncertainty of comparison of working group to Client cell	0.007
Uncompensated thermal emfs in the cell switches	0.030
Uncertainty of assignment to Client cell (not including temperature measurement errors; see text)	
RSS total	**0.065**

Table III summarizes the sources of uncertainty in calibrating a client cell in terms of the U.S. Legal Volt.

The DVM scale error is calculated as described for Table I, except cell differences as large as 120 μV may be measured. The random measurement uncertainty of the working group - client cell comparison is estimated from the redundant measurement design as before.

No allowance for temperature has been included in the above uncertainties. Fluctuations in cell emfs due to inexact measurement and correction of temperature changes of the primary and working groups are included in the day-to-day fluctuation of the primary groups, and the within-day fluctuation of the working groups. The uncertainty of the cell emfs due to the imprecision of the temperature monitoring device is estimated by calculating the change in cell emf (according to the International Temperature formula) for a change of one least count of the temperature monitoring device. In the case of cells in enclosures containing internal thermistor bridges, where a least count of 0.001 °C is possible, an additional uncertainty of approximately 0.05 ppm is

included. Enclosures monitored by mercury-in-glass thermometers are assigned an uncertainty equivalent to half the smallest graduation marked on the thermometer, approximately 0.5 ppm for a resolution of 0.01 °C. For cells calibrated in NBS oil baths an emf uncertainty equivalent to a temperature uncertainty of 0.005 °C is used to account for possible calibration errors in the platinum resistance thermometers used at NBS.

The day-to-day random component of the uncertainty of the client cell emf is determined by calculating the standard deviation of the measured emfs of the cell from the ten daily measurement designs and comparing it, at the 99% confidence interval (CI) using an F-test, with the pooled standard deviation of a large population of measurements of similar standards (0.135 - 0.188 μV, depending on the type of enclosure). If the statistic is determined to belong to that population, then the population standard deviation of the mean is used as the estimate of the limit of the random component. If not, the computed standard deviation of the mean is used as the estimate.

The final reported uncertainty is the direct sum of this random component, the total assignment uncertainty from Table III, and the temperature uncertainty, multiplied by a factor of three.

The calibration service has recently been extensively modified, with completely new automated measuring systems and new quality control procedures. The values quoted in the tables above are estimates of the uncertainties of the new system. Until a complete evaluation is completed, the following (previously determined) uncertainties are being used. The client cell assignment uncertainty is taken as 0.075 ppm, the pooled standard deviation for random error is 0.135 μV, and the temperature uncertainty is the same as described.

The reported uncertainty contains no allowance for long term drift of the cells under test. Long term behavior must be determined by the client by analysis of the history of each individual standard. In addition, no allowances are made for the possible effects of transporting the standard between laboratories or the possible existence of a gross temperature dependence on ambient (room) temperature of a standard cell enclosure.

Volt Transfer Program

The Volt Transfer Program involves sending an NBS owned transport voltage standard to the client laboratory. The transport cells are compared to NBS working standards at NBS before and after shipment to the client laboratory, and to the client reference group of standard cells while at the client laboratory. The process is described in more detail below.

Measurement of the Transport Standard at NBS

The transport standard consists of a commercial thermoregulated enclosure usually containing 4 saturated shippable standard cells, operating at an internal temperature of 30 °C or 32 °C. The temperature is measured using the internal temperature bridge and an external null detector to provide 0.001 °C resolution. Corrections to the cell emfs are applied according to the discussion given in Section 3. Transport standard cells are compared daily to Working Group A using redundant measurement designs and the VTP measurement system (Fig. 7). Before shipment to a client laboratory, the cell emfs are plotted and examined for stability. In any case, at least 15 daily measurements are required after the enclosure's return to NBS and before it is shipped to another laboratory.

Upon receipt of a purchase order NBS schedules the shipment of a transport standard to the client laboratory. The transport standard is shipped with an external power supply containing a battery to power the standard during shipping, and in a special container designed to provide physical shock protection and temperature lagging. The battery supply can maintain temperature control of the standard for about 24 hours during normal ambient shipping conditions. Since the temperature control system cannot supply cooling to the enclosure, shipment to warmer locations is avoided during extremely hot weather to prevent the enclosure from overheating. Shipment is normally via air freight with special delivery service from NBS to the airport just in time for the scheduled flight. The delivery service may also be able to arrange, with an affiliated service, for pickup and delivery of the enclosure to the client laboratory. If not, client laboratory personnel are notified of the time of arrival of the standard and are expected to provide transportation from the airport to their laboratory within the 24 hour lifetime of the batteries.

Comparison of the NBS Transport Standard to the Client Standard

Each laboratory participating in the Volt Transfer Program must identify a group of saturated standard cells that are considered to be the "laboratory reference group" and constitute the "laboratory volt". The transport standard cells are compared to the cells of the laboratory reference using redundant measurement designs similar to the ones used at NBS. Each laboratory uses its own measuring equipment in the manner it would normally use to calibrate saturated cells, except for the requirement that an NBS-specified measurement design be used. NBS provides data sheets to record the measurements which are returned to NBS where the cell comparison observations are reduced to determine the cell emfs in terms of the client laboratory volt. Laboratories are required to make daily design measurements and the data is reviewed by NBS, as it is taken, to determine when sufficient data has been obtained to permit shipment of the standard back to NBS. A minimum of 10 measurement designs over 10 days is required for the transfer; however, the number is more typically in the range from twelve to twenty. In addition, the within-day standard deviation and left-right components from the measurement designs are checked

to see if they are statistically in control with respect to the expected values determined from measurements at NBS and other laboratories.

Upon its return to NBS, the standard is again compared to Working Group A as before and, when the standard has stabilized and sufficient data has been taken, a final report is issued. Typical measurement data is shown in Fig. 9 where the mean emf of a transport standard over the period of one transfer is plotted. The emf in the figure is expressed in microvolts with 1.01 volts subtracted from the total cell emf.
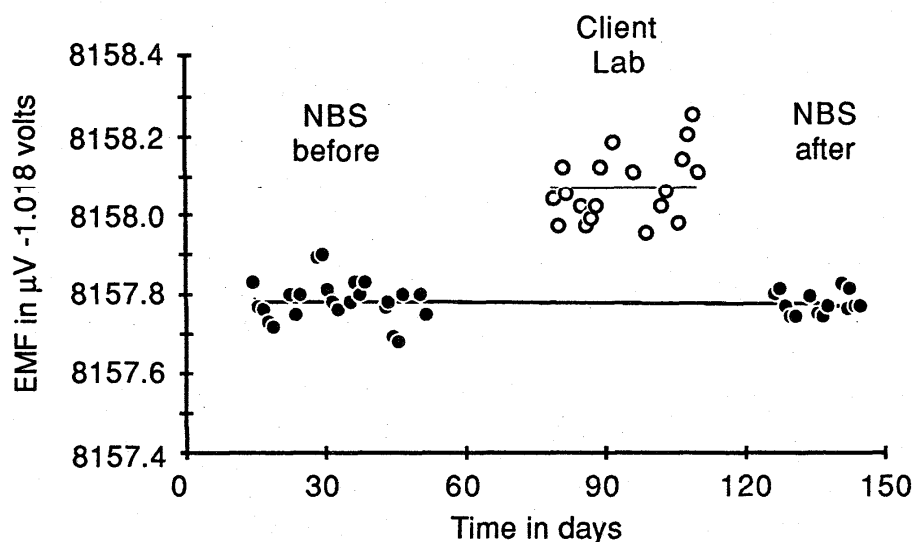
Fig. 9. Mean emf of a typical transport standard as measured at NBS and a client laboratory.

Assignment of Final Value

Emf assignments at NBS and the client laboratory for each cell of the transport standard are plotted as in Fig. 9 above. Data showing cell emf changes due to shipment or other effects are removed from the analysis; often the first measurement after shipment is anomalous. The data are also reviewed for abnormal temperature readings and to determine if the data reasonably conform to a linear model. As the before and after NBS data do not usually exactly agree, a least-squares line is fitted to the NBS data for each transport cell, and values are predicted for each of the times the cell was compared to the client laboratory cells. V_{LAB}-V_{NBS} is determined using each cell in the transport enclosure by subtracting the NBS predicted values of the transport cell from the respective client laboratory emf assignments, and taking the mean of these differences.

Although the difference in the units as determined from each of the four cells in the transport standard should agree, on occasion some cells show abnormal behavior, usually excessive drift, or excessively long recovery from physical shock or electrical disturbance. The judgement and experience of the laboratory staff are used to determine when to exclude a cell from the analysis or, on rare occasions, use only the NBS data taken before or after the transfer.

TABLE IV

UNCERTAINTIES IN THE DETERMINATION OF V_{LAB} - V_{NBS}

Source of uncertainty	1 std. dev. estimate (ppm)
Uncertainty of NBS assignment to transport group	0.061
Correlated temperature effects of the transport	0.050
Temperature resolution	0.050
Random component due to individual cell assignments and changes during transport	0.093
Uncertainty of V_{LAB} - V_{NBS} determination using a four cell transport enclosure	
RSS total	**0.132**

Table IV summarizes the sources of uncertainty in the determination of V_{LAB}-V_{NBS}.

The uncertainty in assigning a value to the transport standard while at NBS is obtained through an analysis identical to Table III, except the switches used for the VTP transport standards have somewhat lower uncompensated thermal emfs (0.020 µV as opposed to the 0.030 µV shown in Table III).

The transport standards used for the Volt Transfer Program all contain thermistor bridges with 0.001 °C resolution; an uncertainty for the cell emf equivalent to this temperature change is included. In addition, the cell temperature within the enclosures changes slightly with changes in room

temperature. The thermistor bridge does not properly reflect the change of the temperature of the cell in this case, probably due to a temperature sensitive component of the bridge circuitry that is at room temperature. An uncertainty estimate of 0.05 ppm is included to account for a difference between the client laboratory ambient temperature and the NBS laboratory ambient temperature.

Each of the four cells in the transport standard is used to determine a value for the difference in laboratory units, V_{LAB} - V_{NBS}. The standard deviation of these four values includes an uncertainty in predicting the cell emfs while at the client laboratory, an uncertainty in comparing the client laboratory reference to the transport standard, and an uncertainty for random changes in the cell emfs due to shipment. A pooled standard deviation of 0.19 μV has been computed from 50 transfers and is used as the population standard deviation. The calculated standard deviation for each new transfer is compared to the population standard deviation at the 99% confidence interval using an F-test. If the statistic is determined to belong to that population, then the population standard deviation of the mean is used as the uncertainty estimate; if not, the actual standard deviation of the mean is used. Thus the uncertainty estimate for a four cell transport standard, based on the population standard deviation, is (0.19 μV)/2 or 0.095 μV (0.093 ppm).

If the difference V_{LAB} - V_{NBS} exceeds 0.20 ppm (1.5 times the uncertainty based on the population standard deviation), the report will recommend adjusting the assigned values of the client reference cell emfs to reduce the difference to zero. Adjusted values for the cell emfs are calculated based the measurements made in the client laboratory comparing the client reference group to the NBS transport standard. Each comparison results in a determination of the difference of each client reference cell emf from the mean emf of the client reference group. The average difference for each cell, over all the comparisons, is added to the newly determined mean emf of the reference group to calculate the new values for each of the client reference cells.

6. Quality Control Procedures

Measurement System Verification

Potential sources of error in the cell measurement systems include scaling or gain errors in the digital voltmeters, uncompensated thermal emfs in the crossbar switches and cell leads, leakage currents to ground from the measurement apparatus, and circulating ground currents. Several quality control procedures are periodically performed to estimate or eliminate these uncertainties.
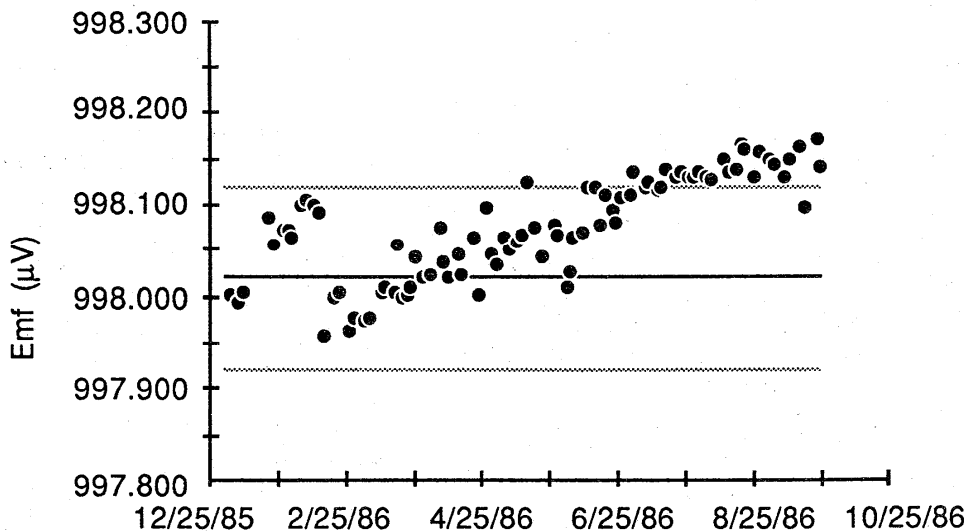
Fig. 10.   Daily DVM readings of the 1000 μV Zener source.

Before each daily set of cell comparisons the measurement system reads the output of a 1000 μV Zener source to monitor the gain error of the 0.1 volt range of the digital voltmeter. All voltmeter measurements are taken with the applied voltage in the normal polarity and again with the polarity reversed by the crossbar switch to eliminate any uncertainty due to zero offset of the voltmeter and thermal emfs in the leads to the voltmeter. The daily measured values of the 1000 μV source are plotted on a control chart and compared to predetermined limits. Figure 10 is a plot of the voltage of the Zener source that is connected to measuring system REG. The control limits correspond to a worst case cell comparison uncertainty of approximately 0.01 ppm. If the limits are exceeded, the reason for the out-of-tolerance condition is investigated by laboratory personnel. Usually the problem is found to be that the voltage of the 1000 μV Zener source has drifted (as it has in Fig. 10), and the source is recalibrated.

After each measurement design, the computer controlling the measurement system reduces the data using a least-squares technique and computes the standard deviation for a single measurement for that design. This standard deviation is compared to a control limit based on the population standard deviation to determine if it is in statistical control. If it is out of control the measurement design may be repeated. Measuring system VTP will repeat the measurement design once if the standard deviation is out of control. If the standard deviation of the second design is also out of control the system does not repeat it again. Measuring system REG does not repeat the design under any

circumstances. The standard deviation is a function of the individual cell group being measured, and control limits for newly arrived client cell groups are not well known. Each day, a pooled standard deviation from all the measurement designs that are in control is calculated and plotted on a control chart for each of the measurement systems (REG and VTP). Figure 11 is the control chart for measurement system REG.
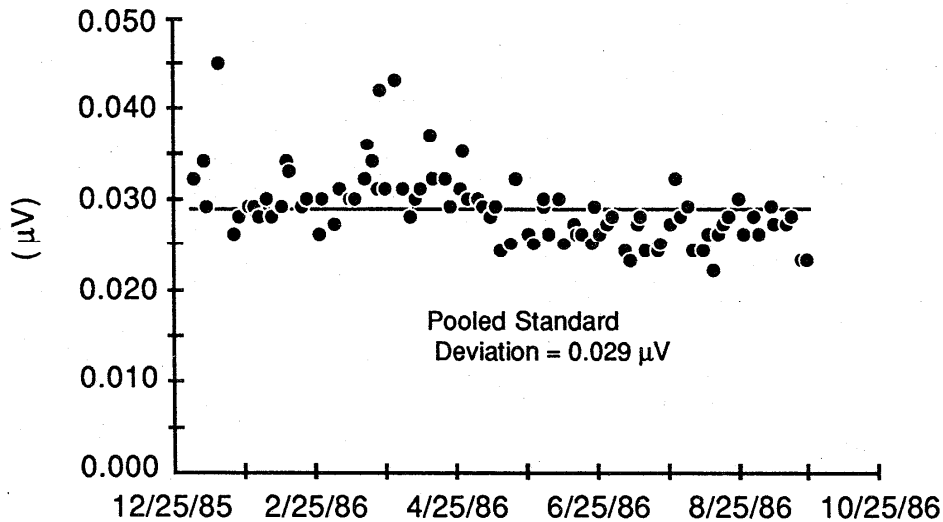
Fig. 11. Within-day standard deviations calculated from the redundant measurement designs.

Thermal emfs in the leads from the cell enclosures to the crossbar switch are evaluated regularly. The positive and negative leads are shorted together at the end where they would normally connect to the cells and a redundant measurement design is made between two sets of shorted leads. These thermal emf measurements are performed frequently, usually every two months or so as cell enclosures leave the laboratory and leads become free. Experience has shown that the thermal emfs are usually small and fairly constant (approximately 15 nV and 30 nV for measuring systems VTP and REG respectively).

Both measurement systems print out a daily log of the measurements performed by each system. Figure 12 is a typical example produced by the VTP measurement system. This log contains the measured value of the 1000 μV source, and a list of the groups of cells that were measured. The time of the measurement, the reference group used, the measured temperature of the group, the change in temperature correction, the change in the group mean emf, the standard deviation of the redundant design, and the measured DVM

offset voltage are printed for each cell group measured. The change in group temperature correction and mean emf are calculated by subtracting the values obtained for the previous day's readings from the current day's readings. If any of the values exceed predefined limits the measurements are flagged on the log and lab personnel investigate the problem. The limits are set at 0.1 μV for both the change in temperature correction and mean emf, and are based on laboratory personnel experience. The exact values are not overly important since they serve only to alert the operator to a potential problem.

VTP MEASUREMENT LOG FOR: 29 May 1986　　[1.4]　　　　　　WEEK: 8622

DVM check Zener measurement = 1000.014　(+/-　0.005) uV

Time	STD-ID	UNK-ID	UNK Temp (C)	Change T-corr (uV)	Change Mean (uV)	SD (uV)	DVM Offset (uV)	
10:20	18	2800	30.0070	-.113	.084	.020	-.251	T
10:31	18	19	29.9790	-.034	.028	.009	-.274	
10:42	18	2000	31.9965	-.030	-.000	.021	-.299	
10:53	18	1400	30.0080	-.038	.002	.029	-.271	
11:05	18	2100	32.0055	-.059	.007	.027	-.300	
		MEAN of daily runs:		-.053	.024		-.279	
		Standard deviation:		.036	.035	.022	.021	

Some runs were marked for exceeding predefined limits.
The letters in the right hand column mean:

T -　　the temperature correction changed by more than .1 uV
M -　　the mean of the unknown group changed by more than .1 uV
S -　　the std. dev. exceeded 1.4 time the accepted std. dev.
D -　　the magnitude of the dvm offset exceeded 2 uV

ALL CALCULATIONS COMPLETED AND SRM UPDATED

Fig. 12.　Typical daily log printout from the VTP measuring system.

As discussed earlier, two working groups of cells are calibrated daily in terms of the primary groups. Cell emf values are predicted for these working groups at the same time predictions are made for the primary cell groups, i.e., once every 4 weeks when 2e/h measurements are made. Occasional problems with temperature regulated enclosures, oil baths, and unstable cells have made long term predictions of either the primary or working groups meaningless. However values for up to one month ahead are predicted for the primary and

working groups based on four or more months of data. Each day the values of the working groups are calculated based on the daily intercomparisons of the primary groups against the working groups and the predicted values of the primary groups. The measurements or measurement systems are scrutinized whenever there is significant (0.08 ppm) disagreement between the directly predicted values of the working groups and the values assigned through the primary groups. Figure 13 is a plot of the difference between the daily values assigned to Working Group A and the predicted values.
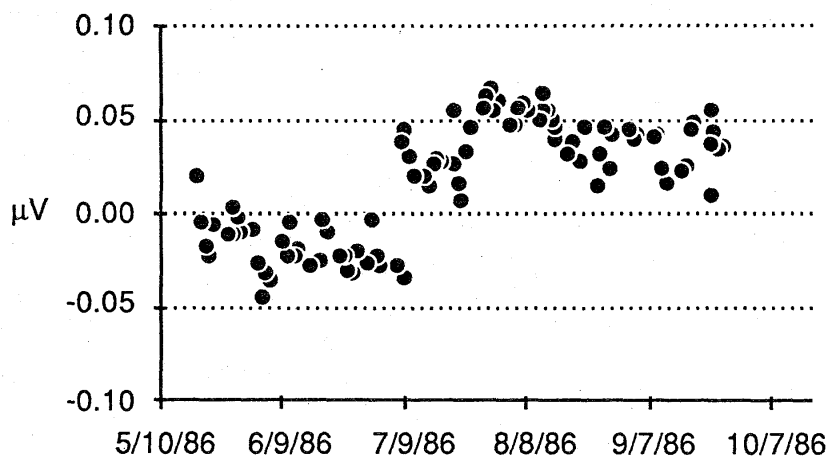
Fig. 13. The difference between the daily value assigned to the mean emf of Working Group A from the two Primary groups, and from the predicted value of the Working Group.

An enclosure that can be used exclusively as a long term check standard is not available because of a shortage of good quality enclosures and cells. Instead, the average of the changes in emfs of the workload from the previous day's measurements is calculated daily and noted by laboratory personnel.

Occasional additional tests are performed on the automated systems. Selected cell enclosures are calibrated with both systems to ensure that their results agree, and the automated systems are compared to a calibrated millivolt potentiometer . Measurements of the insulation/leakage resistance of the measuring systems are done occasionally and recorded in laboratory notebooks. Closure experiments are done monthly (at least) to detect systematic errors due to leakage resistance. Closure experiments consist of redundantly comparing three cell enclosures with the pattern, A-B, B-C, and C-A. Summing the three mean emf differences should yield a value of zero; the disagreement of the actual value is an indication of measurement error. Using twenty-four such experiments performed on different enclosures between July 17, 1986 and

October 1, 1986, the mean closure error was -0.0009 μV with a standard deviation of the mean of 0.0017 μV.

Measurement Assurance for Client Standards

Standards shipped to NBS in temperature regulated enclosures under power are hand carried from the Building 301 Receiving Room as soon as Electricity Division personnel are notified. The temperature is checked by qualified laboratory technicians and the enclosure is brought to the Volt Facility Laboratory. Laboratory personnel within the Volt Facility connect and disconnect the standards to the measuring systems to minimize the possibility of incorrect connections.

After stabilization and measurement of the standard, the data are plotted for each standard cell emf in the enclosure. These data are reviewed by laboratory personnel and anomalous data usually related to stabilization are removed. The remaining data are used to generate a calibration report. The final calibration report and intermediate emf plots are also reviewed by the leader of the Electricity Division Dissemination Services Group.

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Appendix A - Redundant Measurement Designs

Redundant measurement designs are used for all standard cell comparisons as they are efficient in providing the maximum amount of information per measurement and provide information about possible systematic effects in the measuring system. The designs are used to provide estimates of:

1) the cell emfs with respect to a group mean emf,
2) the within-day standard deviation of a single observation,
3) the left-right (positional) effect,
4) the standard deviations of the cell emfs,
5) and the deviations of individual observations from the predicted values.

In general, when comparing two or more cell groups, a "full" design is used where all possible pair differences that involve two cells from different groups are measured. The 4x6 design and 4x4 design below illustrate this process. For intercomparison of cells within a single group the appropriate design from NBS Technical Note 430 is used [16].

On occasion an anomalous reading may be discovered during the data reduction of the cell comparison data. Since some redundancy is provided by the design it is possible to remove one or two observations and recalculate with little loss in accuracy in determining the cell emfs with respect to the group mean.

For the examples below, the cells in the groups are designated R1 - R4 (R for reference) and X1 - X4 or X1 - X6 (X for unknown) depending on the design. The voltage difference measured is "left cell" - "right cell".

4x4 Design - 16 observations

Observation number	Left cell	Right cell	Observation number	Left cell	Right cell
1	R1	X1	9	X3	R4
2	R1	X3	10	X1	R4
3	R2	X2	11	X4	R3
4	R2	X4	12	X2	R3
5	R3	X1	13	X3	R2
6	R3	X3	14	X1	R2
7	R4	X2	15	X4	R1
8	R4	X4	16	X2	R1

4x6 Design - 24 observations

Observation number	Left cell	Right cell	Observation number	Left cell	Right cell
1	R1	X1	13	X5	R4
2	R1	X3	14	X3	R4
3	R1	X5	15	X1	R4
4	R2	X2	16	X6	R3
5	R2	X4	17	X4	R3
6	R2	X6	18	X2	R3
7	R3	X1	19	X5	R2
8	R3	X3	20	X3	R2
9	R3	X5	21	X1	R2
10	R4	X2	22	X6	R1
11	R4	X4	23	X4	R1
12	R4	X6	24	X2	R1

U. S. Department of Commerce
NATIONAL BUREAU OF STANDARDS
National Measurement Laboratory
Gaithersburg, MD 20899

REPORT OF CALIBRATION
DC Voltage Standard

Description of Standard:
Standard Cell Enclosure
Model XXXXXXXXXXXXXXXXXX
Containing 4 Saturated Standard Cells

Submitted By:
XXXXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXXXX

This standard cell enclosure was received 21 Mar 1986, not under power with an internal temperature far below its normal operating temperature.

The data from which the values in the table below are computed are the result of ten daily measurements of the differences between the EMF's of the cells under test and those of NBS working standards during the period between 5 May 1986 and 16 May 1986.

POSITION NUMBER	EMF (volts)	UNCERTAINTY (microvolts)	EMF (volts)	UNCERTAINTY (microvolts)
1	1.0181270	0.27	1.0181269	0.27
2	1.0181271	0.27	1.0181270	0.27
3	1.0181272	0.27	1.0181271	0.27
4	1.0181268	0.27	1.0181267	0.27

The electromotive forces on the left above were corrected to nominal temperature (30.0 degrees Celsius) using the International Temperature formula proposed by F.A. Wolff. The electromotive forces on the right are at the mean operating temperature during the test (30.0019 degrees C) as determined by use of a temperature deviation measuring device mounted in the enclosure.

The above uncertainties include components for random fluctuations in the cell under test and in NBS equipment and standards, for a systematic error of 0.076 ppm in the measurements of NBS working standards in terms of the Josephson effect, and for the systematic error in transfer due to the finite resolution of the apparatus used to determine the temperature of the cells under test. In the case of standard cells tested in NBS oil baths, the latter uncertainty is replaced by the EMF equivalent of 0.005 degrees Celsius which is the uncertainty of the temperature measurements in this laboratory. The random error component is computed from the standard deviation of the mean EMF and is at the three sigma level.

These uncertainty figures contain no allowance for the effects of transportation upon this standard. The minimum uncertainty due to such effects under very carefully controlled transport conditions has been seen to be 0.42 ppm (3 sigma). Any valid uncertainty statement applying to the above values when the standard has been moved from the NBS Volt Facility must contain such a component of error. If data from which to estimate the transport error are not available, one part-per-million is not an unreasonable value. Also not included in the above uncertainties is an allowance for long term drift of the values of the outputs of this standard. This must be determined from historical data on a case by case basis.

A summary and analysis of the data upon which the above values are based is appended. A complete explanation of the uncertainty statements given above as well as additional information regarding NBS calibration of such voltage standards is also included.

For the Director
National Measurement Laboratory

Norman B. Belecki, Physicist
Center for Basic Standards
Electricity Division

Test No. XXXXXXXX
Date: 21 May 1986

U. S. Department of Commerce
NATIONAL BUREAU OF STANDARDS
National Measurement Laboratory
Gaithersburg, MD 20899

REPORT OF CALIBRATION
DC Voltage Standard

Description of Standard:
          Unsaturated Standard Cell
          Model No. XXXXXXXXXXXX
          Serial No. XXXXXXXXXXX

Submitted By:
          XXXXXXXXXXXXXXXXXXXXXXXX
          XXXXXXXXXXXXXXXXXXXXXXXX
          XXXXXXXXXXXXXXXXXXXXXXXX

The electromotive force of this cell at 22.4 degrees Celsius was, at the time of test, 1.01923 volts. This value, correct to 0.005 percent, is the mean of a series of measurements concluded 24 Apr 1986. The stated uncertainty (0.005%) includes allowance of plus or minus 50 microvolts for variability in the EMF of the cell during test.

This is an unsaturated cell of the cadmium sulfate type, suitable for work requiring no greater accuracy than 0.005 percent. Such cells have a temperature coefficient that is negligible within the ordinary range of room temperature. Rapid changes in temperature may, however, produce temporary alterations of several hundredths of one percent in the electromotive force.

Precautions in using standard cells: (1) the cell should not be exposed to temperatures below 4 degrees Celsius, (2) abrupt changes in temperature should be avoided, (3) all parts of the cell should be at the same temperature, (4) current in excess of 0.0001 ampere should never pass through the cell, (5) unsaturated cells should be recalibrated at intervals of a year or two because the electromotive force of an unsaturated cell usually decreases with time.

                    For the Director
                    National Measurement Laboratory

                    Norman B. Belecki, Physicist
                    Center for Basic Standards
                    Electricity Division

Test No. XXXXXXXX
Date: 1 May 1986

U. S. Department of Commerce
N A T I O N A L   B U R E A U   O F   S T A N D A R D S
National Measurement Laboratory
Gaithersburg, MD   20899

R E P O R T   OF   T E S T

Determination of $V_{TSCC} - V_{NBS}$

Laboratory: (LAB)
XXXXXXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXXXXXX
XXXXXXXXXXXXXXXXXXXXXXXXX
Reference No. XXXXXXXXX

Reference Cells:
      5403   5404   5402
      5406

The difference between the unit of electromotive force
maintained by the above laboratory and the U.S. Legal Volt, as
maintained by the National Bureau of Standards (NBS), was
experimentally determined during the period between November
11, 1985 and February 28, 1986.   The results, given in the
equation below, are based on the previously-assigned mean emf
of the reference cells listed above.

$$V_{LAB} - V_{NBS} = 0.15 \times 10^{-6} V_{NBS}$$

The above number is based upon the experiment described in
Appendix A and the data summarized in Appendix B of this
report.

The uncertainty of this difference, $V_{LAB} - V_{NBS}$, is 0.15
microvolts at the 99% confidence level.   It was determined by
combining in quadrature random error components resulting from
variations among the cells in the transport standard due to the
transfer, day-to-day fluctuations in the results of NBS
measurements of the transport standard, and day-to-day
variations in the difference between the results of the
client's measurements and the corresponding NBS-predicted
values of the emf's of the cells in the transport standard. As
far as is presently know, systematic effects are negligible.
The pertinent data and their reduction are given in Appendix B,
along with plots of all data taken both at NBS and in the
client laboratory.

Test No.. XXXXXXXX

Page 2

This uncertainty, the difference cited above, and the results of any adjustments made to the values of the reference cells whose numbers are given above are valid only under conditions approximating those under which this experiment was performed. In particular, the operating temperature of the reference cells must be within 0.05 degree C of that measured during the course of the experiment. This condition must be met in order that errors in the algorithm used to compute temperature corrections not affect the experimental uncertainty.

On July 1, 1972, NBS changed from using saturated standard cells to maintain the U.S. Legal Volt to the use of the ac Josephson effect. Based upon data taken to date, it is estimated that the U.S. Legal Volt is constant, with respect to time to at least 0.1 ppm. This figure is not included in the above uncertainty. As further data are obtained, the uncertainty for this type of experiment will be refined to take into account the improved method for maintaining the volt.

If the measured difference between the unit of voltage as disseminated by this laboratory and the U.S. Legal Unit of voltage is greater in magnitude than the characteristic standard deviation of a measurement of this type (0.20 ppm), it is recommended that the assigned mean value of the laboratory's reference group be adjusted so that $V_{LAB} - V_{NBS} = 0$. Appendix C has be included in this report to facilitate recommended adjustments.

For the Director
National Measurement Laboratory

Norman B. Belecki, Physicist
Center for Basic Standards
Electricity Division

Test No. XXXXXXXX
Date: May 14, 1986

Appendix D - SOFTWARE

All software for controlling the measurement systems, reducing the cell data, and producing test reports, was written in-house specifically for the intended application. At present the software is in transition; a minicomputer used to do data reduction is in the process of being replaced by a number of dedicated desktop computers. Software has been completed for these computers to make standard cell comparisons and calculate the cell emfs from the cell difference observations. These data are stored on a shared hard disk. Existing software for the minicomputer to maintain a data base of cell emfs of NBS and client standards, produce control charts, and produce test reports is currently being converted to run on a new, more modern, minicomputer. This is only an interim step since these programs need to be substantially rewritten to provide better quality control charts and easier access to the data base.

The following programs are complete and operate on the desktop computers.

READBOX - This program intercompares standard cell voltages using a redundant measurement design, reduces the data to determine the cell emfs, and saves the data to disk. The actual voltage differences are measured with measuring system VTP, using the digital voltmeter, with the cells connected to the voltmeter by a crossbar switch. The data collected by the program is stored on a floppy disk in drive 0 and optionally on the Shared Resource Management (SRM) hard disk. The files on the floppy disk are designed to hold approximately one week's worth of data. A printed log is generated for each day's measurements listing the boxes compared, the standard deviation of the measurements, the change from the previous day's measurements, and the DVM offset. At the end of all the measurements, the above quantities are summarized.

READCAL - This program is a slight modification of READBOX to run on measuring system REG. The crossbar switch used with system REG is a 300 position switch rather than the 80 position switch used with system VTP, and is addressed slightly differently by the computer.

STDCEL - This program is contained within READBOX (and READCAL) and is used to reduce standard cell difference observations to standard cell emfs. This program is used when individual cell difference observations, within a measurement design, are out of control. It permits the operator to remove selectively those suspect observations from the design and store the corrected cell emfs on floppy and hard disks.

EDIT - This program is a general purpose text (ASCII) file editing program and is used to create or modify an existing "runfile". The "runfile" contains a list of standards and their temperatures that are to be read by READBOX. This file is updated daily using EDIT to contain the current enclosure temperatures, cell identification numbers, and crossbar circuit numbers.

This program can also be used to view or modify any of the data files containing cell difference observations or cell emfs.

The following programs operate on the old minicomputer and are in the process of being converted to run on the new minicomputer.

VFORMAT - This program takes data in the format produced by READBOX and converts it to "Analysis" format for the program described below.

ANALYSIS - This program (and a number of variants created for special purposes) produces control charts of cell emfs and cell temperatures on a line printer. The program also performs a linear fit to the cell emf and can be used to predict the emf of cells at a given time. This is used for calculating V_{LAB} - V_{NBS} from the Volt Transfer Program transport cells.

REPORT - This program in conjunction with ANALYSIS above is used to produce a final VTP report. This program performs text formatting, combining the test report text with the values obtained from ANALYSIS.

BFORMAT - This program converts the READBOX data into a format compatible with EMF below. This is necessary as EMF was originally written for operation with an entirely different measurement system. When completely converted to the new minicomputer, BFORMAT will be bound with EMF to produce one program.

EMF - This program compiles standard cell emf data for the regular calibration service. The data are printed out, statistical tests are applied to determine if the data are sufficiently stable and if the temperature correction is reasonable, and a calibration uncertainty is calculated.

CELL REPORT - This program in conjunction with EMF produces the final calibration report for the regular calibration service.