

Calorimetric measurements

Measurement of heat capacity

The goal of the measurement is:

- to deepen the knowledge of the students about specific heat;
- to acquaint students with two specific heat measurement methods.

To reach the aims set above,

- we summarize the knowledge about measuring the heat capacity, describe the specific heat measurement with blending calorimeter and using electrically heated calorimeter
- we measure the specific heat of some sample material

1. Theoretical summary

The internal energy (U) of a body can be changed by the macroscopic work (W) done on the substance (W) or by molecular level energy exchange (Q) in course of direct contact of another body.

This experience is summarized in the 1st law of thermodynamics

$$\Delta U = \Delta Q + \Delta W, \quad (1)$$

where ΔU is the change in internal energy U , ΔW is the macroscopic work done on the body ΔQ is the energy transferred by molecular mechanism in course of the direct contact with another body, often called **heat** or **amount of heat**.

If we transfer heat to a body (e.g. heat the body with electric radiator), its internal energy (and in most cases also its temperature) also change. Experience has shown that – in case of transferring only a moderate amount of heat –, the temperature change (Δt) is directly proportional to the heat transmitted (Q), is inversely proportional to the mass of the test substance (m) and also depends on the quality of the test substance:

$$\Delta t = \frac{Q}{cm}, \quad (2)$$

where the constant c , characteristic the material is called **the specific heat**.

The numerical value of the specific heat of a material shows how much heat is needed to change the temperature of 1 mass unit of the substance with 1 K. The unit of specific heat is $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$.

The heat taken up by the body, however, can not only be utilized to change the internal energy of the body, but can also be consumed to do work by the body.

$$\Delta Q = \Delta U - \Delta W$$

Therefore, the heat capacity:

$$c = \frac{1}{m} \frac{\Delta Q}{\Delta t} = \frac{1}{m} \frac{\Delta U}{\Delta t} - \frac{1}{m} \frac{\Delta W}{\Delta t}$$

Since the work will depend on the circumstances of the process, the heat capacity will only be determined clearly, if the heat transfer process is exactly specified.

Accordingly, in principle a wide range of heat capacities can be defined. However, in practice, only two of them are extensively used

- the constant volume (c_v) and
- the constant pressure (c_p) heat capacity.

The two types of heat capacity of gases are significantly different, but their numerical value for solid and liquid substances they are approximately the same.

The heat capacity, particularly at low temperatures, is also temperature dependant. In course of the present laboratory exercise we investigate solid substances for which the difference of the c_p and c_v is negligible. For the sake of simplicity we are talking about and referred to simply as specific heat c without using the index mark. (Strictly speaking, we measure c_p , assuming that the atmospheric pressure does not change during the measurement).

In the engineering practice, one of the decisive factors in sizing refrigeration and heating equipment and thermal behaviour of boundary structures is the heat capacity of the materials used. In material science, some changes in the structure of the material - e.g. phase changes – can be traced.

The determination of heat capacity is based on equation (2).

Weighting the mass of the test substance, the amount of heat absorbed or emitted by the test substance, and the temperature change, the heat capacity of the substance can be calculated. In such cases, instead of specific heat, the **heat capacity of the substance**, C is used, where $C = mc$

Equation (2) can be reformulated as $\Delta t = Q/C$.

Specific heat measurement

Two widely used method of heat transfer to the substance are

- blending (mixing) of 2 substances having different temperatures
- heat transfer to the test substance by electric radiators.

The basics of these two methods are presented below.

1.1 Specific heat measurement by blending (mixing)

The sample material characterized by known weight m , temperature t and unknown specific heat is mixed (blended) with a material with known parameters $((c)_i, (m)_i, (t)_i)$, - mostly with a liquid usually not chemically reacting with the sample material to be measured. We measure the common equilibrium temperature (t_k) .

Provided that during mixing only heat transfer occurs between the two materials and there is no heat loss, the heat taken up (or emitted) by the test sample is equal to the heat emitted (or taken up) by the other material with known parameter, therefore

$$cm(t - t_k) = c_i m_i (t_k - t_i), \quad (3)$$

on the basis of which the unknown heat capacity (c) can be determined.

This method is primarily used for the specific heat determination of solids and liquids, but applicable also to constant pressure heat capacity measurement of gases. In this case, the sample gas is flowing in a spiral tube through the liquid. Knowing the mass and the temperature change of the gas, as well as all the data of the measurement liquid, the constant pressure specific heat of the gas (c_p) can be calculated.

With the possession of the heat capacity at constant pressure, the constant volume heat capacity (c_v) of the gas can also be determined (for example, by using sound velocity measurement technique).

1.2 Specific heat measurement using electric heating

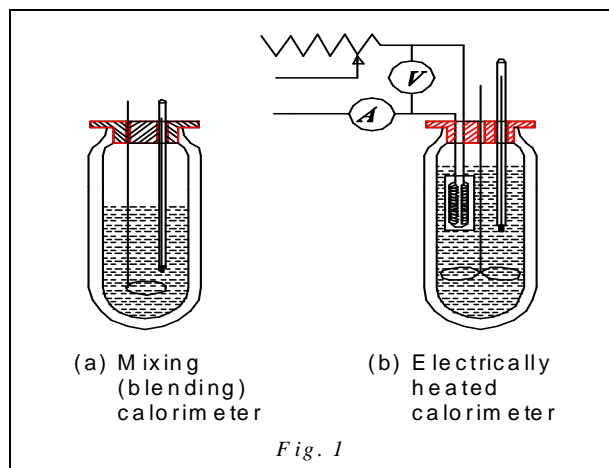
In this method the temperature of the test sample (characterized by specific heat c and mass m) is elevated using an electric heating by Δt .

Provided that all the energy given off by the radiator is utilized by elevating the internal energy of the sample:

$$UI\tau = cm\Delta t, \quad (4)$$

knowing the value of the heating power UI , the heating time τ , the sample mass m , and the temperature change Δt of the sample, the heat capacity c can be determined.

The method is particularly suitable for the determination of specific heat of liquids. However, it can also be used for solid substances if the sample is immersed in a liquid heated electrically together with the sample.



1.3 Heat capacity of the calorimeter and the temperature correction

In using mixing or electric calorimeter for measuring the heat capacity, until now we supposed that there was no heat exchange with the environment. To ensure this condition the heat transfer is executed in well heat isolated containers. (Fig.1. depicts the sketch of a mixing and an electric calorimeter.) However, the measurements cannot be performed without some heat loss to the environment, primarily

on two basic reasons: even the temperature of the vessel changes during the measurement, and anyway, there is always some heat loss to the environment even if we apply the best heat isolation available.

This two causes (errors) can be compensated (reduced) by taking into account the heat loss caused by the heat capacity of the vessel and the temperature correction.

1.3.1 Heat capacity of the calorimeter vessel

If we knew the mass and the specific heat of the different parts of the vessel and their temperature rise, the energy used to heat them during the measurement could be calculated. However, this condition is practically not feasible. Instead, we measure directly the C heat capacity of the calorimeter. Taking into account the heat capacity of the calorimeter, equation (3) and (4) take the form:

$$cm(t - t_k) = c_i m_i (t_k - t_i) + C(t_k - t_i) \quad (5)$$

$$U I \tau = cm\Delta t + C\Delta t \quad (6)$$

The determination of the heat capacity of the calorimeter happens using Eq. 5 and 6 by applying materials with known specific heat, mostly water.

1.3.2 Temperature correction

The heat exchange between the inside of the calorimeter and the environment is caused by the temperature difference between the temperature t_b of the inner space and the temperature t_0 of the environment. Although the energy loss caused by the temperature difference can be reduced by heat isolation and by selecting close t_b and t_0 values, there is some heat loss. This can be taken into account by applying temperature correction. The execution of the graphical temperature correction is presented below.

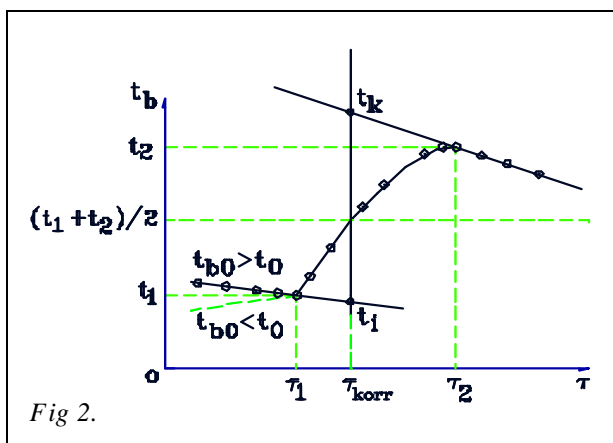


Fig 2.

Fig 2 shows the temperature change of the calorimeter during the calorimetric measurement as a function of time. The curve can be divided into 3 sections with regard to the different processes characteristic of the sections.

a) Start-up period: The temperature equilibration process between the fluids (oil, water) placed into the calorimeter and the vessel itself, as well as the temperature equilibration process between the fluid and its environment. Depending on the temperatures of the calorimeter vessel and the fluid, in this period the inner temperature decreases if $t_{b0} > t_0$ or raises if $t_{b0} < t_0$ (t_{b0} is the initial temperature of the inner space at the beginning). Because of the small temperature difference, in this section the temperature - time relationship is nearly linear.

b) Main period: The start-up period is followed by the main energy exchange process, starting with mixing of the material or with switching in the electric heating. In the main period the t_b temperature of the inner space rises. This is the period when the energy exchange between the materials mixed or between the material in the calorimeter and the heater happens. Since the inner temperature rises above the temperature of the environment, there is some heat loss to the environment. Because of this heat loss the temperature of the inner space cannot reach the expected t_k equilibrium temperature in case of perfect heat isolation. However, by analyzing graphical representation of temperature - time relationship of the terminal period following the main period, this value can be estimated.

c) Termination period: In this section $t_b > t_0$ and because of the imperfect heat isolation the inner temperature of the calorimeter slowly decreases. The temperature decrease can be regarded as linear again.

Obviously the process differs from being ideal, mainly because of the errors resulting from the imperfect heat isolation. The temperature - time graph gives some help in correcting the errors. The practical implementation of this temperature correction is explained on Fig 2.

We depict the temperature - time graph, and fit straight lines onto the start-up and terminal periods.

Let co-ordinates of the last tangential points of the straight line fitted to the start-up period τ_1, t_1 , and the co-ordinates of the last tangential points of the straight line fitted to the terminal period τ_2, t_2 . After determining these two points we draw a line parallel with the time axis at $t = (t_1 + t_2)/2$. We draw a paral-

lel straight line with the temperature axis through the intersection point of this straight line and the graph of the main period. We regard the intersection point of this parallel line with the line fitted to the start-up period as the initial temperature t_1 , and its intersection with the line fitted to the terminal period as the common temperature t_k of the system (the calorimeter and the measuring liquid).

The correction described above is based on the following considerations: Because of the energy exchange with the environment the temperature in the calorimeter continuously changes, equilibrium temperature can never be reached therefore, neither the initial, nor the final temperature can be directly measured. The straight line fitted to the start up period shows how would the temperature change within the calorimeter if no energy exchange stated in the main period.

With the help of the straight line fitted to the termination period one can estimate the would-be temperature of the calorimeter in case of ideal heat isolation.

A high quality calorimeter has small heat capacity and good heat isolation, therefore has negligible heat exchange with the environment. In such a case the temperature is near constant in the start-up and termination periods.

2. The measurement rig

Measuring instruments:

- 1 litre capacity stainless steel vacuum flask 2 pc., with Platinum resistive thermometers
- electric cattle (boiler)
- resistive heater with 10 Ω resistance and 50 W maximal power
- Multimeter HAMEG, power supply for the resistive heater
- for each measurement rig 1 pc. Aluminium and 1 pc. plastic test-piece (Please, check carefully which test-piece is used in the measurement!)
- ice
- measuring cylinder
- calibrated mercury thermometer, 1 pc.

Measurement tasks:

Attention! Boiling water may cause serious burning injuries, pay attention not to overspill the boiling water, and not to touch the hot metal test-piece! Utmost care and attention should be paid to these dangers during the measurements.

1. Thermometer calibration

Pt 1000 standard thin-layer resistive thermometer is used with 1000 Ω resistance at 0 $^{\circ}\text{C}$ -on. During heating its resistance rises with a rate of 3.92 $\Omega/^{\circ}\text{C}$. However, because of the finite resistance of the wires, slices and banana-plugs there appears a constant (temperature independent) serial resistance, necessitating temperature correction.

The thermometers of both vacuum flasks should be calibrated using Mercury thermometers in cold tap water. Let's determine the values of the serial resistance and the resulting temperature correction!

(Attention! The equilibrium temperature should be reached before the final reading, and to facilitate this use a mixer!)

2. Measuring the heat loss of the vacuum flask

Fill up the vacuum flask with boiling water, and wait until the system takes up the heat. Thereafter, because of the imperfect heat isolation, the vacuum flask releases some heat to the environment, causing slow temperature decrease. Estimate the rate of heat loss, and determine how the heat loss influenced the measured values during the measurements further on. (Measure the heat loss at least for 5 minutes!)

3. Estimating the heat capacity of the vacuum flask

Measure the mass of the stainless steel flask. The specific heat of the stainless steel is 500 J/kg $^{\circ}\text{C}$, the thickness of the inner and outer wall of the vacuum flask are identical. Estimate the heat capacity of the vacuum flask!

4. Measuring the heat capacity of water

Fill 0.8 l cold water into one of the vacuum flasks. Immerse the heating resistance into the flask, and measure the temperature rise of the water for 12 minutes using 50W power supply. Determine the specific heat of water from the heat released by the heater and the temperature change! (The heat capacity of the vacuum flask can be taken into account as estimated in *Exercise 3* above)

5. Measuring the heat capacity of the vacuum flask using the mixing (blending) method

Boil up 0.5 l of water, and fill it into one of the vacuum flasks. Fill up the other vacuum flask

with 0,5 l cold tap water. The mass of the water filled into the flasks should be determined by weighting the boiler before and after. Wait until equilibrium temperatures are reached. Pour the water from the cold water vacuum flask into the hot water flask, and applying continuous mixing, wait until equilibrium is reached. Determine the heat capacity of the vacuum flasks using the measured temperature changes and the masses of the hot and cold water. Compare the measured values with that of the estimated heat capacities in exercise 3!

(Note: The hot water vacuum flask should always be fixed to the rig to prevent any accidental tilt.

6. Measuring melting heat of ice

Boil up 0,6 l of water, and pour the hot water into one of the a vacuum flasks. The mass of water should be determined by repeatedly weighting the boiler (before and after pouring the water). Wait until equilibrium temperatures are reached. Fill-up the vacuum flask with melting ice, wait until the ice is completely melted and an equilibrium temperature develops. Measure the volume of water in the vacuum flask, determine the amount of ice filled into the vacuum flask from this volume. Determine the melting heat of ice.

7. Measuring the specific heat of Aluminum

Measure the volume of the Aluminum test-piece. Pour as much hot water into the vacuum flask that immersing the test piece into the flask, the resulting total volume remain less than 1 l. Fill up the other vacuum flask with cold water. Immerse the Aluminum test rig into the cold water and wait until equilibrium temperatures develop in both vacuum flasks. Then re-locate the Aluminum test-piece into the hot water, and again wait until the common temperature develops. Determine the specific heat of Aluminum on the basis of the temperature changes.

8. Measuring specific heat of plastics

Repeat exercise 7 using the plastic test-piece!

Evaluate the results during the measurements! Repeat the measurements 4-8 if possible. If substantial differences occur between measurements, or if the results substantially differ from the reference values in the literature, try to find the reason and make the

necessary measures to eliminate the measurement errors.

Since we measure the resistance of the Platinum temperature sensor to determine its temperature, to facilitate the interpretation of the resistance values to be read, it is favorable to calculate some data in advance.. The temperature dependence of the platinum thermometer can be described by the following formula:

$$R(t) = 1000\Omega \cdot \left[1 + 3,92 \cdot 10^{-3} \frac{1}{^\circ C} (t - 0^\circ C) \right]$$

Calculate, what resistance change will be caused by a temperature change of $1^\circ C$. Determine the resistance of the thermometer at temperatures $10^\circ C$, $20^\circ C$ $100^\circ C$.

Heat of solution

There are many materials in the construction industries that evolve or consume heat when solved in water. Examples are the solution of calcium-oxide (lime), calcium-sulphate (gypsum) and cement (in making concrete). In planning the individual operations, the evolving heat should be taken account or rather utilised.

The solution heat determination is illustrated by the determination of the heat of solution of a common compound, calcium chloride. Calcium-chloride ($CaCl_2$) intensively releases heat when solved, therefore can also be used to melt ice. When spilled on roads it efficiently melts the ice, and is less harmful to the plants than Sodium-chloride and can also be used at lower temperatures. In concrete mixtures it accelerates the solidification process (however, being corrosive, it cannot be used in reinforced concrete). _It is also used in some highways to reduce the flying dust: sprayed on the road it absorbs water from air, develops a this water layers on the road surface that adheres the dust.

Measuring instruments, reagents

- thermo cup with cap, 1 pc
- Cup fixing rig 1 pc
- digital thermometer 1 pc
- measuring cylinder 300 cm³ capacity for measuring the distilled water 1 pc.
- distilled water;
- digital scale
- crystal-water free modification of calcium-chloride crystals.

Performing the measurement:

1. Rinse the cup with distilled water and pour the amount of water determined by the instructor into the cup (200 ml)
2. Immerse the thermometer into it and wait until the temperature stabilizes.
3. Read the temperature value.
4. Scale in the amount of salt determined by the instructor. (3 g)
5. Applying cautious continuous mixing wait until the temperature stabilizes, and read the temperature value.

Evaluation of the data

1. Calculate the heat evolved :

$$Q = m_{\text{water}} \cdot c_{\text{water}} \cdot \Delta t$$

2. Knowing the weight of the salt calculate the molar solution heat. The mol mass of the salt can be taken from standard molar weight tables.

Sun-collector testing

This measurement was originally part of the 3rd round of the Physics National Secondary School Contest of 2005.

Introduction

The energy demand of manhood is mostly ensured using fossil fuels. However, fossil fuels are a limited resource, and burning of fossil fuels cause serious environmental damages. The flue gases represent air pollution (causing different diseases, like allergic diseases, different type of tumors, etc. The evolving carbon-dioxide is responsible for the glass-house effect, resulting in rising temperature and climatic changes.

The present practice of energy-economy is not sustainable.

The energy demand can only be ensured on the long run by environmentally friendly methods, parallel with applying energy saving technologies and extensive use of renewable energy sources.

The application of renewable energies does not change the natural energy equilibrium of the earth. Basically, the renewable energy sources utilize the direct or indirect effect of the sunbeam and the energy of the soil. Indirect use of the Sun encompasses the use of the energy of water, the wind, and

the bio-mass, the direct use is possible with using solar cells or sun-collectors

This exercise is an introduction to the use of sun-collectors

Measurement tasks

1. Determine the dependence of the power gained from the sun-collector illuminated with a spotlight (reflector) from the flow-rate of the water circulating in the system, measured by a rota-meter. Depict the results in a graph. Explain the results.

To perform the measurement, locate the spotlight (substituting the Sun) centrally, opposite to the collector, at a distance of 30 cm.

3. Determine the efficiency of the collector by which it utilizes the absorbed energy of the beam, at different flow rates. One might suppose that the surface of the collector absorbs 204 W energy from the light beam of the spotlight. List the possible factors not taken into account when determining the efficiency. How would these factors modify the efficiency?

Measuring instruments and materials

1. Model-collector with coupled system (detailed description see later)
2. Halogen spotlight (500 W) with rig
3. Digital thermometer with alternating switch
15. Thermometer

The model-collector and the coupled system

The task of the sun-collector is to absorb the possible maximum amount of radiation of the Sun reaching the Earth, and warm-up the fluid circulating in the system as much as possible.

One of the most important elements of the collector model is a copper sheet of 1.5 mm thickness. A copper coil is soldered on one side of the sheet, the other side of the sheet is painted black to absorb as much amount of radiation reaching the surface as possible. To reduce the heat loss, the back side of the sheet and the coil and the edges are covered with a polystyrene heat isolation of a thickness of 20 mm.

Fig 1 shows the experimental rig with the model sun-collector.

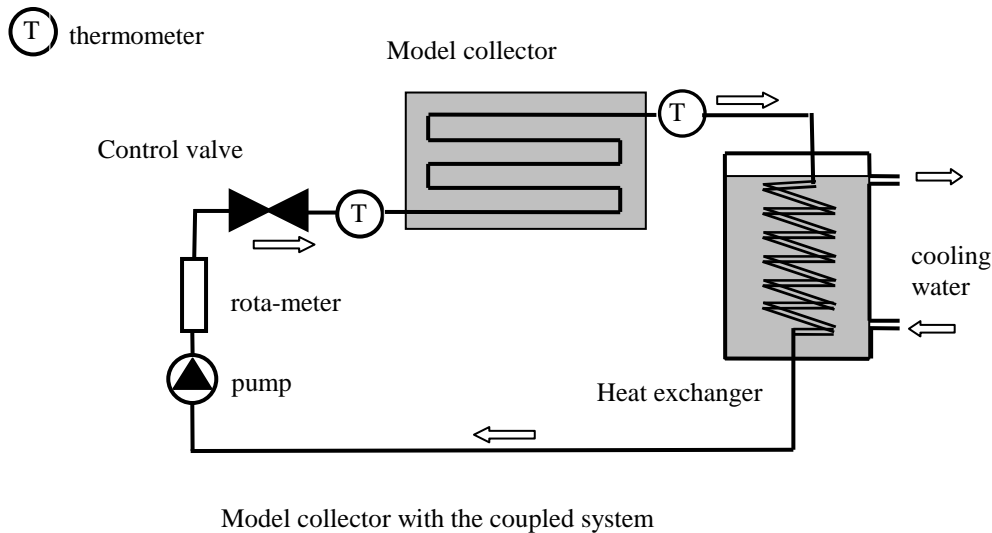


Fig 1.

The water is circulated in the system using an aquarist pump. The flow is measured with a rotameter and controlled with a control valve. The rotameter is calibrated in cm^3/min units. (The set flow value can be read at the upper edge of the rotameter swimmer. The scale in the rotameter corresponds to the fact that the rotameter was calibrated at

60°C -using water. For water temperatures different from 60°C the table below can be used to determine the flow rate.

A precondition of the correct functioning of the system is that it should be free of air bubbles – de-aerating is essential.

Water flow rates (cm^3/min) at different temperatures						
Mark in the rotameter	10°C	20°C	30°C	40°C	50°C	60°C
20	7.21	10.36	13.28	15.84	18.07	20.00
40	19.13	24.88	29.74	33.80	37.18	40.00
60	33.86	41.49	47.65	52.62	56.67	60.00
80	49.80	58.95	66.11	71.76	76.30	80.00
100	66.32	76.73	84.74	90.97	95.95	100.00
120	82.96	94.56	103.37	110.20	115.61	120.00
140	99.80	112.50	122.06	129.43	135.27	140.00
160	117.47	131.01	141.12	148.89	155.03	160.00
180	135.09	149.48	160.16	168.33	174.78	180.00
200	152.67	167.90	179.15	187.75	194.52	200.00
Water densities (kg/m^3) at different temperatures						
	999.73	998.23	995.68	992.25	988.07	983.24

The temperature of the water entering and leaving the collector is measured by two thermistors (temperature dependant resistances, denoted by T in Fig. 1) The thermistors can be connected to the digital display (readable with a precision of 0.1°C) through an alternating switch. The water warmed up in the collector releases the heat in a water cooler.

Thermocouple and its use

The functioning of the thermometer is based on the contact-potential evolving when two different metals get into contact. The contact potential depends on the material of the metals in contact as well as on the temperature. Copper – isothan thermocouples are used in the competition in a circuitry depicted in Fig. 2.

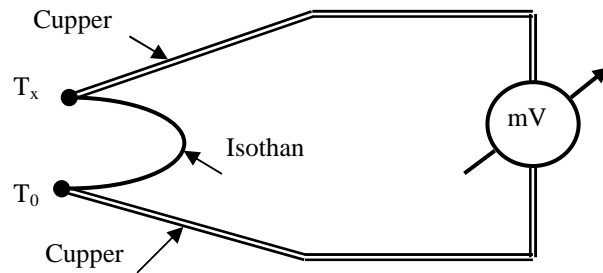


Fig. 2

Holding the copper-isotherm contact points at T_0 and T_x , respectively, the milli-volt meter measures a potential proportional with the temperature difference. If T_0 is known (set using melting ice to produce 0°C), temperature T_x can be determined from the measured potential. In calibrating the thermo-couple

we concluded that the potential produced by the thermo-couple is $39.6 \mu\text{V}/^\circ\text{C}$.

Note that to ensure a good thermic coupling between the red copper sheet and the thermocouple, instead of using a wire, the copper sheet was directly coupled to the volt-meter.