HEAT CAPACITY

REFERENCE Noakes, *Textbook of Heat*. Copies of the relevant sections are available at the Resource Centre.

INTRODUCTION



Definitions

The purpose of this experiment is to determine the specific heat of two metal blocks.

In one of these measurements you will also investigate the use of *Newton's Law of Cooling* to calculate a cooling correction.

When a body of mass M at temperature T_1 receives an amount of heat (or energy) Q, its temperature may increase from T_1 to T_2 .

The *heat capacity C* of a body is the amount of heat required to raise its temperature by one (Kelvin) degree:

$$C = \frac{Q}{(T_2 - T_1)}$$
(1)

By dividing out the mass, one gets *the specific heat capacity c* or simply *the specific heat*:

$$c = \frac{C}{M} = \frac{Q}{M(T_2 - T_1)}$$
(1')

The units of specific heat in SI are J / kg °C.

Historically, "specific" means "referred to water" and the measurements done in this experiment are referred to the specific heat of water. Thus, in this experiment we use as the unit of heat, not the conventional SI unit of energy, but rather **the calorie**. The calorie is defined as the heat required to increase the temperature of 1 gram of water from 14.5°C to 15.5°C. This definition makes the specific heat capacity of water equal to unity.

THE METHOD

To determine the specific heat capacity of a substance, *the method of mixtures* is often used. A vessel, called **calorimeter**, of known specific heat capacity S_c and mass m_c is partially filled with a mass m_w of water at a temperature T_1 and then mounted in a suitable manner so that it is thermally insulated from the outside world.

A mass M of the substance of unknown specific heat capacity c is heated to a higher temperature T_b (usually in boiling water) and then quickly transferred to the calorimeter. The temperature of the calorimeter and the water contained quickly rises to a value T_2 . It then slowly begins to fall as heat is lost to the room. If all the masses are measured in grams, the temperatures in degrees

HEAT CAPACITY

Celsius and the specific heat capacities in calories per gram per degree Celsius, the block of substance has thus given $Mc(T_b - T_2)$ calories of heat to the calorimeter and the contained water. If no losses occur, this must be equal to the heat gained by them, which is $(m_cS_c + m_w)(T_2 - T_1)$.

Thus:

 $Mc(T_{b} - T_{2}) = (m_{c}S_{c} + m_{w})(T_{2} - T_{1})$ (2)

and the specific heat *c* can be determined.

The calorimeter is made of copper and $S_c = 0.093$ cal g⁻¹ °C⁻¹.

Experiment 1

Arrange the calorimeter with the inner vessel filled with enough water to cover the metal block. Try it before you heat the block. Measure the initial temperature T_1 . Do not add anything between the inner and the outer vessels. The outer vessel acts as a thermal shield. The air between the two is the insulator.

Heat a metal block in boiling water (temperature T_b) and transfer it quickly to the calorimeter. The final temperature will be T_2 .

Consider carefully the systematic errors present in this experiment.

Determine the specific heat of one of the metal blocks, using Equation 2.

What temperature, or temperature range, does your value correspond to?

Experiment 2 - The cooling correction

In the second part of the experiment you will measure the specific heat of the second block by using the same method, but this time you will allow the cooling effect to be large enough to study. The derivation in (2) above neglects the heat lost to the surroundings when the temperature of the calorimeter + water + metal block rises above room temperature. The method is based on Newton's Law of Cooling, which assumes that the rate of loss of heat to the surroundings is proportional to the temperature excess above the surroundings:

$$\frac{dQ}{dt} = k \left(T - T_{room} \right) \tag{3}$$

where Q is the quantity of heat,

 \tilde{t} is the time,

dQ/dt is the rate of heat loss (how much heat is lost per unit time),

T and T_{room} are the temperatures of the cooling body and of the surroundings, and k is a constant of proportionality.

The experiment should be performed using the method of mixtures, under conditions where *heat* exchange with the room is deliberately made large, so that the cooling correction will be fairly conspicuous. This is achieved by placing the inner part of the calorimeter out in the open to increase heat losses to the air around it.

Measure the temperature of the calorimeter at the time of transfer, t_1 .

Read the temperature at frequent intervals; regular 15 sec intervals are recommended. These measurements should be continued until a maximum in the temperature has been passed and the temperature has fallen again about 1°C.

Plot **temperature** *vs.* **time** on graph paper. On the graph (indicated in Figure 1), select a time t_2 at which you would expect the metal block and the liquid in the calorimeter to have more or less reached thermal equilibrium so that the whole system is then cooling as a unit.

The amount of heat loss between t_2 and t_3 ($t_3 > t_2$) can be determined by integrating Equation (3) to yield:

$$Q = k \int_{t_2}^{t_3} (T - T_{room}) dt$$
 (4)

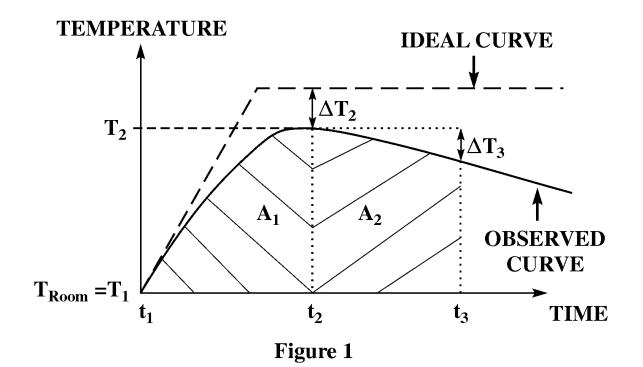
The right hand side of this equation is just the area under the curve of $(T - T_{room})$ versus t, denoted by A_2 in Figure 1.

The left hand side (Q), the heat lost by cooling in the interval $(t_3 - t_2)$, is proportional to ΔT_3 , the drop in temperature during this time interval. Remember that Q is equal to the product of the specific heat capacity of the cooling body, its mass, and the drop in temperature. Thus we obtain $\Delta T_3 = k' A_2$, where k' is another constant.

Similarly, the drop in temperature due to cooling in the time interval between $t = t_1$ and $t = t_2$, is given by $\Delta T_2 = k' A_1$ (note that, since the mechanism by which cooling takes place is the same for times between t_1 and t_2 and between t_2 and t_3 , the constant of proportionality will be the same for both regions).

Finally we have: $\Delta T_2 / \Delta T_3 = A_1 / A_2$.

Thus, if T_2 is the temperature observed at time t_2 , the temperature which the calorimeter and its contents would have reached had no heat been lost by cooling is $T_2 + \Delta T_2$, and equation (2) should be correspondingly corrected. A_1 and A_2 are most conveniently measured by counting squares on graph paper.



HEAT CAPACITY

Correction for the heat capacity of the thermometer:

The thermometer you use in this experiment is a partial immersion model. Insert it exactly to the line. The liquid this thermometer uses is kerosene.

If the specific heat capacities of kerosene and of glass are expressed as calories per cm³ per °C, they are: 0.57 cal/(cm³ °C) for kerosene and 0.45 cal/(cm³ °C) for glass.

Assume that the thermometer's bulb is mainly kerosene and has a volume V_1 . The column (up to the line) is mainly glass and has a volume V_2 .

Measure V_1 with the aid of a 10 cm³ graduated cylinder, by measuring the water volume the bulb displaces.

Measure the column diameter and length (up to the line) and calculate V₂.

The amount of heat absorbed by the thermometer when immersed in the calorimeter can now be expressed as:

 $Q_t = 0.57V_1(T_2 - T_1) + 0.45V_2(T_2 - T_1)$ (5)

This quantity of heat (Q_t) will also correct equation (2).



Please dispose of any water in the sink!

(Revised: Ruxandra M. Serbanescu – 2004. Previous versions of this guide sheet were written by Tony Key in 1995 -1998)

Preparatory Questions

- **Note:** We hope that the following questions will guide you in your preparation for the experiment you are about to perform. They are not meant to be particularly testing, nor do they contain any "tricks". Once you have answered them, you should be in a good position to embark on the experiment.
- 1. The SI unit of heat is the Joule. How is that related to the calorie?
- 2. What is your best estimate of the reading error in the thermometer you will use?
- 3. You read on the package of your favorite junk food that it contains 250 calories per serving. Are these the same kind of calories that you will be measuring in this experiment?
- 4. The derivation of equation (2) assumes that there was no heat loss in the transfer of the heated block to the cooler water. If this equation were used to analyze the data from an experiment in which the heat losses were, in fact, significant, what would be the value of the specific heat obtained?
- 5. Two bodies, made of different materials and having different specific heats, but of equal mass and identical shape, are heated up. They are then allowed to cool down. Assuming that the constant *k* is independent of the material the bodies are made of, which body would you expect to cool down more quickly?

THERMAL EXPANSION OF A SOLID

The complete, interactive guide sheet of this experiment can be found at http://faraday.physics.utoronto.ca/IYearLab/Intros/ThermalExpans/ThermalExpans.html

ABSTRACT

Everybody knows that liquid thermometers make use of thermal expansion. The volume of a liquid increases as temperature increases. Thermal expansion plays an important role in numerous applications: joints included in buildings, highways, railroad tracks, and bridges compensate changes in dimensions with temperature variations.

Most solids expand on heating because atomic motion becomes larger and the average separation between atoms or molecules changes. Suppose an object has an initial length L_i along some direction at some temperature. The length increases by ΔL for a change in temperature ΔT . When ΔT is small enough, ΔL is proportional to ΔT and L_i

$\Delta L = \alpha L_i \Delta T$

The proportionality constant α is called average coefficient of linear expansion.

In this experiment, you will investigate the thermal expansion for two metal rods. You will prove that thermal expansion is a linear phenomenon and calculate the average coefficient α for the two metals.

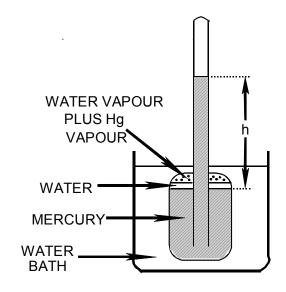
VAPOUR PRESSURE OF WATER

REFERENCES

G.R. Noakes. New Intermediate Physics. Copies are available at the Resource Centre.

THE EXPERIMENT





The purpose of this experiment is to study the variation of the vapour pressure of water between about 300K and 373K. The apparatus is shown schematically in the figure. The bulb in which the water vapour is contained has been evacuated of all gases and then filled with mercury and pure water. The pressure of the water vapour causes the mercury to rise up in the tube. (The height h of the column of mercury is a convenient unit for the vapour pressure, though, of course, it needs some units conversion to be expressed in SI units.) The bulb is immersed in a water bath whose temperature can be varied and measured.

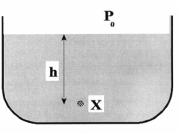
The procedure is simply to measure the height h as a function of the temperature T of the *water in the bulb*. This temperature can be quite different from the temperature of the water bath unless a) they are in good thermal contact, and b) sufficient time is allowed for the

system to reach thermal equilibrium. Therefore it is very important that the water in the water bath completely covers the bulb, and that thermal equilibrium has been reached *before* h and T are measured. How can you tell when thermal equilibrium has been reached?

The measurement of h requires some thought. There is a scale against which the top of the mercury column can be measured. However, the scale does not extend down to the level of the mercury in the bulb. In addition this lower point of the mercury column is not fixed, but will change slightly as the height h changes. Study the apparatus and be sure you know how to measure h correctly and as precisely as possible. Then check with your demonstrator that your method is the best available. The analysis of the data of vapour pressure as a function of temperature is not based on any exact theory. But a reasonable approximation is provided by integrating the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\ell}{T(V_v - V_\ell)}$$

where T is the temperature **in Kelvin**, dp is a small change in the vapour pressure due to a temperature change dT (*i.e.*, the slope of the vapour pressure - temperature curve), V_v is the volume per mole



of the vapour phase, v_{ℓ} is the volume per mole of the liquid phase, so that $(V_v - V_{\ell})$ is the change in the volume per mole when water evaporates into a vapour, and ℓ is the latent heat per mole (also called the Enthalpy or Heat of Vapourisation) in the transition from a liquid phase to a vapour phase, *i.e.*, the heat per mole absorbed in that transition.

By making two reasonable approximations,

(i) $(V_v - V_\ell) \simeq V_v$ the volume per mole of the vapour; and (ii) $pV_v = pV/n = RT$ (ideal gas law)

we obtain
$$\frac{dp}{dT} = \frac{\ell}{\underline{RT}^2}$$
 or $\frac{dp}{p} = \frac{\ell}{RT^2} dT$

If we now make the important approximation that l is independent of temperature, this equation can be integrated immediately to give:

$$p = p_o \exp\left(\frac{-\ell}{RT}\right)$$

where p_0 is a constant of integration and R is the gas constant. This equation should be valid in the temperature range this experiment is performed. Thus a plot of ln (*p*) versus 1/T will be a straight line, the slope of which will give a value for ℓ . Remember that *T* should be in Kelvin! You should compare your value with that given in the *Handbook of Chemistry and Physics*.

In determining the error in your value of ℓ , it is important to consider the possible systematic errors this experiment contains. For example:

- Is it necessary to correct for the pressure due to the liquid water in the bulb which rests on top of the mercury surface in the bulb?
- Is the water vapour at the same temperature as the water bath? Or does the mercury column conduct heat from the bulb at a significant rate?
- Should the values of *h* be corrected for the thermal expansion of the mercury and glass*?
 - * The coefficient of volume expansion of mercury, $\alpha \approx 0.181 \times 10^{-3} \text{ deg}^{-1}$ The coefficient of volume expansion of glass, $\beta \approx 8.5 \times 10^{-6} \text{ deg}^{-1}$.
- Does the vapour pressure of mercury produce a significant error?

As in any other experiment, an effort should be made to estimate these errors *quantitatively* in order to decide whether any of them are significant. (revised jbv - 89; tk - 96)

VAPOUR PRESSURE

Preparatory Questions.

- **Note:** We hope that the following questions will guide you in your preparation for the experiment you are about to perform. They are not meant to be particularly testing, nor do they contain any "tricks". Once you have answered them, you should be in a good position to embark on the experiment.
- 1. Write down the equation for the pressure, P, at a point X, situated a distance of h below the surface of a liquid of density ρ if the surface of the liquid is at zero pressure. *Hint for those who haven't seen this before: the pressure is a force per unit area. Calculate the force that a column of height* h *and cross sectional area* A *would exert at point X due to its weight; then divide by* A *to get the pressure.*
- 2. What might be the effect on your experimental results if the water in the water bath does not completely cover the water and vapour mixture in the bulb?
- 3. As the pressure increases, the mercury will rise up the tube and the level of the reservoir will drop. How will you ensure that you measure the correct value of *h*, the height between the meniscus of the mercury in the tube and the top of the reservoir?
- 4. For the experimental results to make sense, the temperature of the water and its vapour, the mercury and the water bath must be all the same when a measurement is taken. Suggest a procedure that will ensure that this is actually the case.
- 5. If the experimental error in the temperature, **T**, is Δ **T**, what it the error in 1/**T**? If the error in your value of pressure is Δp , what is the value of the error in ln(p)?

ABSOLUTE ZERO

INTRODUCTION



As you may know, for an ideal gas at constant volume, the relation between its pressure p and its temperature t, measured in ${}^{0}C$, is given by:

$$t = m \, p + b \tag{1}$$

Thus a plot of *t* versus *p* will be a straight line with slope *m* and intercept *b*.

This relation, called *Charles' Law*, is

approximately true for all gases provided the pressure is reasonably small.

Different gases will have different values for the slope. However, the extrapolated value of the temperature when the pressure is zero, the intercept, turns out to be the same for all gases. Since the pressure cannot have a value less than zero, this temperature is the minimum value any gas (or any object) may have, and is called *Absolute Zero*. This in turn defines an absolute temperature scale, the *Kelvin*.

$$Kelvin \equiv t(^{\circ}C) + |Absolute Zero|$$
(2)

In this experiment you will find the value of Absolute Zero by taking temperature, pressure data for a fixed quantity of gas held at constant volume in a Pyrex glass bulb.

In everything that follows, temperatures measured in Kelvin are given the symbol T, while temperatures in Celsius are indicated by t.

THE EXPERIMENT

You will measure the pressure and temperature of the gas in the bulb for temperatures from 0 $^{\circ}C$ to about 100 $^{\circ}C$. Note that the volume of the gas is at least approximately constant; the constancy of the volume is explored further in the **ANALYSIS** section below.

The bulb is placed in a bath of water, whose temperature is controlled by adding ice to the bath or heating it with the hot plate. The temperature of the bath is measured with the supplied thermometer.

The thermometer is a *Partial Immersion* type, which means that it will give accurate readings only if it is immersed in the bath to the line indicated on the stem near the bulb, with the stem remaining at room temperature. Pay particular attention to the measured temperatures when the bath is a mixture of water and melting ice and when the water in the bath is boiling.

The manometer you will use to measure the pressure of the gas in the glass bulb has a specified accuracy of " \pm 0.25% of the reading \pm 5 digits". The last part of the specification means that the last digit read is uncertain by \pm 5. For example, if the manometer reads:

737.6 mm of mercury (Torr)

then 0.25% of the reading is 1.8 Torr. Thus the total error of accuracy is 1.8 + 0.5 Torr, and the pressure is:

 737.6 ± 2.3 Torr

The most difficult part of the experimental procedure is manipulating the hot plate controls so that the temperature of the bath remains constant long enough for the temperature of the gas in the bulb to equal the temperature of the bath as measured by the thermometer. When equilibrium is achieved the pressure will be constant in time. The difficulty of achieving this condition will be one factor in determining the errors you should assign to your measurements.

There are three data points where thermal equilibrium is easy to achieve. One is when the bath is at room temperature, a second is when the bath is a mixture of water and melting ice, and the third is when the water in the bath is boiling.

Measure atmospheric pressure with the barometer in MP125 or MP126 when you begin to take data and again when you are finished. Note the room temperature with the thermometer beside the barometer for both measurements.

ANALYSIS

The first, most simple analysis of the data will involve fitting the temperature versus pressure data to a straight line. The intercept of the fit is your experimental value of Absolute Zero. As a first term *Core* experiment you should also calibrate the thermometer as described below.

As a second term experiment, *the other calibrations* described below may also be applied to your data.

Calibration of the Thermometer

You may calibrate the thermometer using the measured temperatures for boiling water and for a mixture of water and melting ice.

The boiling point of water goes down as atmospheric pressure decreases. Thus boiling water on a mountaintop has a lower temperature than boiling water at sea level. The boiling point t_B , in Celsius, at a given atmospheric pressure H_C is given by:

$$t_B = 100.0 + 0.037(H_C - 760) \tag{3}$$

 H_c is measured in mm of mercury (Torr) at 0 Celsius. This is the reading you obtained from the barometer adjusted to 0 Celsius using the table pasted alongside the barometer. The factor 0.037 is an experimentally determined number for the change in the boiling point of water per Torr difference in pressure between the observed pressure and the Standard Pressure.

You may assume that the actual temperature of the water and melting ice is 0 Celsius provided equilibrium has been achieved.

Is there an appreciable difference between the expected values of the boiling point and the freezing point of water, and the values you actually read on the thermometer? If so, you may need to correct your temperature values. It is reasonable to assume a linear correction and you should devise one that gives you the correct values at both calibration points.

Volume Measurement

In the experiment you will have noticed that not all of the trapped air is heated when you heat the water around the bulb. The air in the tubes connecting the bulb to the manometer presumably stays close to room temperature. To take this effect into account we do the following calculation.

Suppose there are *n* moles of trapped air, n_1 being in the heated region itself and n_2 being in the connecting tube, most of which is approximately at room temperature. As the air is heated, it becomes less dense in the bulb relative to the tube, and therefore n_1 decreases and n_2 increases, but *n* remains constant:

$$n = n_1 + n_2 \tag{4}$$

For the bulb, with volume V_1 :

$$pV_1 = n_1 RT \tag{5}$$

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whereas for the connecting volume V_2 :

$$pV_2 = n_2 R T_R \tag{6}$$

Here T_R is the room temperature in Kelvin. We eliminate n_1 and n_2 :

$$pV_1 + \frac{pV_2T}{T_R} = nRT \tag{7}$$

This looks like the normal ideal gas law except for the second term on the left hand side, which should be smaller than the other two terms.

Rearranging, we obtain:

$$\frac{1}{T} = \frac{nR}{V_1} \frac{1}{p} - \frac{V_2}{V_1 T_R}$$
(8)

However we must consider one more correction.

Expansion of the Pyrex Glass Bulb

Given the volume V_R at room temperature T_R , the coefficient of volume expansion β gives the volume V at temperature T according to:

$$V = V_R [1 + \beta (T - T_R)]$$
⁽⁹⁾

Using this to correct for the volume of the bulb V_1 , Equation 8 becomes

$$\frac{1}{T} = \frac{nR}{V_{1R}(1 - \beta T_R)} \frac{1}{p} - \frac{V_2 + \beta V_{1R} T_R}{V_{1R} T_R (1 - \beta T_R)}$$
(10)

Thus a plot of 1/T versus 1/p will be a straight line if the ideal gas law holds over the temperature range explored in this experiment.

Further, the general form Equation 10 is:

$$\frac{1}{T} = \alpha \frac{1}{p} - \delta \tag{11}$$

where:

$$\alpha = \frac{nR}{V_{1R}(1 - \beta T_R)}$$
(12a)

$$\delta = \frac{V_2 + \beta V_{1R} T_R}{V_{1R} T_R (1 - \beta T_R)}$$
(12b)

This may be rewritten by rearranging and using a binomial expansion to get:

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$$T = \frac{p}{\alpha} \left[\frac{1}{1 - \delta p / \alpha} \right] = \frac{p}{\alpha} \left[1 + \frac{\delta}{\alpha} p + \left(\frac{\delta}{\alpha} p\right)^2 + \left(\frac{\delta}{\alpha} p\right)^3 + \dots \right]$$
(13)

If $\delta \ll \alpha$ this becomes:

$$T \cong \frac{1}{\alpha} p + \frac{\delta}{\alpha^2} p^2 \tag{14}$$

Since *T*, the absolute temperature, is the temperature *t* in Celsius minus the value of Absolute Zero, this equation can be written as:

$$t = \frac{1}{\alpha}p + \frac{\delta}{\alpha^2}p^2 + b$$
(15a)

or:

$$b = t - \left(\frac{1}{\alpha}p + \frac{\delta}{\alpha^2}p^2\right)$$
(15b)

where *b* is the value of Absolute Zero.

Fitting t versus p to a second order polynomial and using Equation 15a to find Absolute Zero is unlikely to give a good result. This is in part because the fitter will *fit* to values of $1/\alpha$ and α/δ^2 , although they are not free parameters but instead are numbers that you may calculate.

Thus, you should use Equation 15b to determine the value of b by:

- Estimating V_1 , V_2 , and *n* and calculating α and δ . Note that this will use your first, simple, determination for Absolute Zero in order to find T_R . You should be very careful about units for the pressure, the gas constant *R*, etc.
- Calculating *b* for each of your data points.
- Averaging the result of each calculation of *b* to give a final value of Absolute Zero.

CONSTANTS

Density of mercury at 0 $^{o}C = 13.5951 \text{ g/cm}^{3}$

Coefficient of volume expansion of Pyrex glass $\beta = 3.3 \times 10^{-6} \text{ deg}^{-1}$

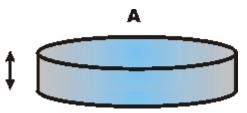
1 mole of any gas occupies 22.4 liters at STP (Standard Temperature and Pressure).

Universal gas constant R = 8.31 J/(mole K)

1 mole = 1 gram molecular weight = 10^{-3} kg molecular weight

PREPARATORY QUESTIONS

 Above we refer to pressures in units of Torr, which is the pressure exerted by a cylinder of mercury, as shown to the right, of height L = 1 mm. Assume the area A of the cylinder is 1 square meter. What is that pressure in units of Pascals =



Newton/meter² exerted by the column of mercury?

- 2. Does your answer to Question 1 depend on the area A of the column? Why? Does it depend on the column being circular? Why?
- 3. At what depth below the surface of a lake will you experience a pressure twice the pressure you experience on the surface?
- 4. If you are on top of a mountain where atmospheric pressure is 740 Torr, what is the boiling point of water? The answer to this question explains why you can't make a good cup of tea on top of a mountain.
- 5. The temperature of a gas is a measure of the average kinetic energy of the molecules of the gas. What is the average kinetic energy of the gas molecules when the temperature of the gas is 0 Kelvin?
- 6. Is it meaningful to talk about the temperature of a perfect vacuum? This is potentially a somewhat subtle question.

REFERENCE

Almost any first year university level physics textbook.

AUTHORS

This Guide Sheet was written by David M. Harrison, June 2001. The part on calibrations and corrections is based on material written by Derek A.L. in 1990. Milton From and Tony Key contributed to previous versions of the Guide Sheet in 1995 and 1996, 1998 respectively.