Specific Heat of MCE materials

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Measurement and interpretation of specific-heat data around magnetic transitions

Presentation IMR, ShenYang & IMNU, Hohhot China June 2008
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What is MCE

• If we apply a magnetic field, B, at constant temperature, T, the magnetization generally increases. That means a lower rate of spin disorder (from scheme 1 to scheme 2).

• Lower disorder means however a lower entropy, S. To keep T constant we have to change S !!

• If we keep S constant (adiabatic field change), the T will change according to the spin state in the final field.

• These effects are called the "Magneto-Caloric Effect" or MCE.

Spin states for two different fields at the same temperature:

\( T_1 = T_2, \text{ but } S_1 > S_2 \)
MCE: two aspects

Conclusion: the Magneto-Caloric Effect (MCE) has two aspects:

- entropy change on isothermal (de)magnetisation $\Delta S_T$
- temperature change on adiabatic (de)magnetisation $\Delta T_{ad}$

These two aspects are closely related, and can be studied by magnetization measurements as a function of temperature, as well as by specific-heat measurements in magnetic field.
MCE: formula

• The basic formula for MCE is one of the so-called Maxwell relations under constant pressure:

\[( \frac{dS}{dB} )_T = ( \frac{dM}{dT} )_B \]

• This formula directly gives the obtained entropy change for an isothermal process:

\[\Delta S_T = \int ( \frac{dM}{dT} )_B \ dB\]

• It is clear that the largest values for \( \Delta S_T \) are found where \( ( \frac{dM}{dT} )_B \) is large.
MCE and phase transitions

Large values for \((dM/dT)_B\) are in particular found at magnetic phase transitions: the Curie point of ferro-(or ferri-)magnetic materials.

Only there (a few exceptions*) the magnetization drops sufficiently fast with \(T\) to generate significant effects.

That means that MCE only can be applied in a relatively small region around the transition.

* most important exceptions are paramagnets at \(T< 1K\).

Typical curve for the saturation magnetization of a ferromagnet.

MCE only shows significant effects in the box-region.
MCE relations: $\Delta S$

For the entropy holds the general formula:

$$S(T_p) = \int \frac{dQ}{T} = \int \frac{(C/T)}{dT}.$$

In this formula, where $C$ is the heat capacity, the integral has to be taken from $T=0$ up to the process temperature $T_p$.

For the entropy shift in field, we have to determine this entropy in both fields, the initial, as well as the final magnetic field:

$$\Delta S_T = \Delta \int \frac{dQ}{T} = \int \frac{(C(B_f)/T)}{dT} - \int \frac{(C(B_i)/T)}{dT}$$

The value for $\Delta S_T$ follows from the difference between two large, and nearly equal, values.

This method results, by consequence, in rather big uncertainties.
Another way of measuring $\Delta S_T$ is by use of the Maxwell relation, as already given some slides ago:

$$\Delta S_T = \int (\frac{dM(B,T)}{dT})_B dB.$$ 

We have to do the following:

- measure a series of isothermal $M(B)$ curves at adjacent constant temperatures (steps of, for instance, 2K, the smaller the better);
- determine numerically values for $\left(\frac{dM(B,T)}{dT}\right)_B$ along the curve of the wanted process temperature (with the help of values in adjacent curves, see next slide) with small steps of $B$ between initial and final field;
- perform a numerical integration from the initial to the final magnetic field.

This method yields reliable values for $\Delta S_T$ which are in sufficient agreement with calorimetric data.
MCE relations: \((dM/dT)_B\)

Values for \((dM/dT)_B\) for the various \((B,T)\) points can be found as given in the figure: 
\((dM/dT)_B\) at \(T_2\) and the given \(B\) follows from:

\[
(M(B,T_3) - M(B,T_1)) / (T_3 - T_1).
\]

NB: \(T_2 = (T_1 + T_3) / 2\).
MCE relations: $\Delta T$

For the adiabatic process, all spin entropy obtained from a field change is used for a change in temperature of the system itself:

$$\Delta T_{ad} = \int \frac{T}{C} \, dS = \int \left(\frac{T}{C}\right) \left(\frac{dM}{dT}\right)_B \, dB$$

This follows from $C \cdot \Delta T = T \cdot \Delta S$, where $C$ is the heat capacity of the whole system: magnetic, electronic and lattice contributions.

Both $C$ and $S$ are strongly dependent on temperature and magnetic field around a magnetic transition.

To determine $\Delta T_{ad}$ in this way sufficiently accurate, we need accurate data on $M$ as well as $C$.

For the latter, we need specific-heat measurements.
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Cooling cycle

In order to make practical applications around room temperature, we have to look for ferromagnetic materials with a high saturation magnetization and a Curie point in the neighbourhood of 290 K.

This material has to be magnetized and demagnetized successively in a repeating process, with appropriate heat exchange steps between the field changes.

This working mode in cooling cycles puts some limiting conditions on the physical properties of the candidates.

Some of them we will discuss here shortly.
Cooling cycle

In the figure, the cooling cycle is given in M(B) format.

In order to get a more quantitative feeling for the parameters in the cooling process, we present in the next slide a schematic picture of this process in S(T) as well as M(T) format.

A cooling cycle consists of 4 steps:
- application of B
- thermal exchange with external coolant
- removal of B
- thermal exchange with medium to be cooled.

Cooling cycle in M versus B format. $T_1 < T_2$. None of the cycle steps is an isotherm!

In the next slide we will follow the cycle in detail.
Scheme of cooling cycle

In higher field the transition shifts to higher T.
So, lower S-curve and higher M-curve is the higher-field curve.
NB: field change is taken adiabatically.

Cooling Cycle:
1 -> 2  application of B
2 -> 3  thermal exchange (*) with external coolant
3 -> 4  removal of B
4 -> 1  thermal exchange (*) with medium to be cooled
Again the cycle in $M(B)$ format, now with all 4 relevant curves given.

The area within the loop is the energy of one cycle.

If the B-step is given, this area is determined by the vertical step, which, in turn, is depending directly on $(dM / dT)_B$.

In fact, for high MCE, the magnetic isotherms have to be S-shaped, as in the next slide.
Scheme of cooling cycle

The cycle in case the transition shifts under increase of $B$ to a higher temperature, as is the situation in the $S(T)$ and $M(T)$ plots two slides before. The area within the loop has been increased remarkably.
High lattice heat capacity

In case the heat capacity, $C$, is large compared with the contribution $\Delta S$ of the transition, as in this figure, the real temperature shift decreases according to:

$$\Delta T_{ad} = \left(\frac{T}{C}\right) \Delta S$$

NB: if $\Delta S$ is mainly determined by the latent heat of a first order transition, $\Delta S = L/T$, it follows that in realistic approximation:

$$\Delta T_{ad} = \frac{L}{C}$$
Conclusions from diagrams

• For heat exchange with external coolant as well as with medium to be cooled, it is very important to know $\Delta T_{ad}$. However, it is difficult to obtain this value correctly from magnetization data only.

• Direct measurement of the shift of the $S(T)$ curve as a function of $B$ around the magnetic transition yields a good indication for the (upper limit of the) adiabatic temperature change.

=> Direct measurement of the heat capacity around the transition in the relevant magnetic fields may result in important data, in particular on the adiabatic temperature change.
Some additional remarks

• Heat exchange with external coolant and medium to be cooled has to take place sufficiently easy.

• This implies that the materials should have a relatively high heat conduction.

• By consequence, we are generally restricted to metallic materials.

• However, Eddy currents may not disturb the picture. This puts restrictions on electrical conductivity and dB/dt.

• The heat conduction should not be destroyed by powderizing caused by structural changes in first order magnetic transitions. (*)

• Because MCE is a bulk property, for practical applications the (starting) materials have to be worldwide sufficiently abundant.
Some additional remarks

- Application of a magnetic field by the change of the current through a coil is in general too slow for practical situations.

- Moreover, the use of small permanent magnets is preferred.

- In that case, field changes take place by removing the material from the field (or the field from the material).

- In doing so, appreciable forces are exerted on the material, which has to be resistant to that.

- These forces are at least two orders of magnitude larger than the gravitational force...

- Magnetic and thermal hysteresis may cause serious problems in the application of MCE. The latter is shortly discussed in a following section.
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Hysteresis

If a strong magneto-elastic coupling causes the transition to be first order:
- the entropy change will increase;
- the active interval will decrease;
- thermal hysteresis may give problems.

To elucidate the thermal hysteresis problems, let us look to the following schemes.
Cooling cycle with and without hysteresis

The effectiveness of the cycle is greatly reduced by thermal hysteresis. This follows from the reduced area within the cycle in the above picture, and, thus, in the S(T) picture too.

The same holds for more realistic M(T) curves.
Conclusions from hysteresis diagrams

The thermal hysteresis has to be much smaller than the shift of the transition by the applied magnetic field.

*Order of magnitude of the shift: $\sim 3 \, \text{K/T}$. Field in permanent magnet: $< 2 \, \text{T}$.*

$\Rightarrow$ *Thermal hysteresis has to be $< 2 \, \text{K}$.***
### 1st or 2nd order?

<table>
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<th>Property</th>
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<th>2nd order</th>
</tr>
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<td>moderate</td>
</tr>
<tr>
<td>Active range</td>
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<td>moderate</td>
</tr>
<tr>
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<td>no problem</td>
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<tr>
<td>Powderizing</td>
<td>problem</td>
<td>no problem</td>
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<tr>
<td>Heat conduction</td>
<td>low if cracks</td>
<td>in general no problem</td>
</tr>
<tr>
<td>Tunability</td>
<td>necessary</td>
<td>not necessary</td>
</tr>
<tr>
<td>.....</td>
<td>.....</td>
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</tbody>
</table>
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Specific-Heat measurements

• Traditionally, two methods are available:
  - relaxation method;
  - (semi-)adiabatic method.

• The first is recommended if thermal isolation of the sample is poor.

• The second is recommended if thermal isolation of the sample is good.
Thermal isolation

What means “poor” and “good”?

The task is to detect the T-effect of a heat pulse.

After the pulse, the sample temperature returns exponentially, with relaxation time $\tau$, back to the frame temperature.

In case of “poor” isolation, the relaxation time, $\tau$, is short (~10s).

For “good” isolation, the $\tau$ has to be $> 10$ min.
Relaxation method

A constant power $P$ raises $T$ from the frame temperature $T_f$ up to $T_h$, where $(T_h - T_f) = P / k$, with $k$ the heat link to the frame in [J/Ks].

The power is switched off at time $t = 0$.

Then $T(t) - T_f = (T_h - T_f) \exp(-t / \tau)$

with $\tau = C / k$.

From this, it follows for the heat capacity $C$:

$C = k \tau = \tau P / (T_h - T_f)$.

Characteristic $T(t)$ curve for the relaxation method.
Relaxation method

Problems:
- Switching $P$ may influence the frame temperature $T_f$.
- Method is time consuming: one point takes at least $10^\ast \tau$.
- $T_f$ has to be kept constant during measuring $T(t)$: you need a separate frame-temperature controller with high stability.
- Relaxation between sample and holder (with heater and thermometer) has to be much faster than between (sample+holder) and frame.

Characteristic $T(t)$ curve for the relaxation method.
(Semi-)adiabatic method

- A well defined heat pulse $\Delta Q$ is given to an only slowly $T$-drifting sample.

- The temperature step $\Delta T$ is determined by extrapolating both drift curves (before and after the heat pulse) to halfway the heat-pulse interval.

- The heat capacity follows from $C = \Delta Q / \Delta T$.

Typical $T(t)$ curve for the semi-adiabatic method.
The drift curves are supposed to be linear in time.
(Semi-\-)adiabatic method

In fact, both drift curves are exponentials, but the zero level (= the frame temperature) is far away, and the relaxation time is long.

By consequence, both drift curves are, in good approximation, linear in time.

If the slopes are not exactly identical, the most accurate value for $\Delta T$ is found halfway the heat pulse interval.
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The hybrid method

- In case the isolation of the sample is "intermediate" (τ is of the order of 1 min.) the relaxation method will take a rather long time for one point.

- To overcome this, and other drawbacks, we developed a hybrid method, which is much faster and showed to be at least as accurate.
The hybrid method

- Starting point: an only slowly drifting (frame and) sample temperature.
- A heat pulse is given to the sample, as in the (semi-)adiabatic method.
- After the pulse, T is going nearly exponentially back to the frame temperature, as in the relaxation method.
- The step is determined from an extrapolation of this latter exponential curve, to be discussed later in detail.
Time schedules

For the (semi-)adiabatic method, the schedule is simple.

• A repeating series of heat pulses increases the temperature of the sample step by step over the whole wanted range. The frame temperature is at large distance (most below $T_{sample}$).

• By monitoring the T-drift of the sample between the pulses, we can determine the value of the T-step, resulting in a heat-capacity value at each heat pulse.

• In doing so, one point takes about 2 minutes.

• The steps have to be large enough to overcompensate the (negative) T-drift.
For the **relaxation method** the time schedule is as follows:

- Install the wanted frame temperature and wait until it is constant (with high-stability controller, about 15 min).

- Switch on the power $P$ and wait until $T_{\text{sample}}$ is constant (> 5 relaxation times).

- Switch off $P$, and measure $T_{\text{sample}}$ until $T_{\text{sample}} = T_{\text{frame}}$ (> 5 relaxation times).

This all together will take $\sim (15 \text{ min}.+ 10^*\tau)$ per point, most of it taken by stabilizing $T_{\text{frame}}$.

For long relaxation times, the second contribution becomes dominant.
For the **hybrid method**, the time schedule is as follows:

- Install the wanted frame temperature and wait until it is nearly constant (with a simple heater only, a big mass of the frame is sufficient) and until $T_{\text{sample}}$ is about equal to $T_{\text{frame}}$.

- Give a heat pulse, just as in the (semi-)adiabatic method.

- Follow $T_{\text{sample}}$ after the pulse for about 1 minute.

- Go to the next wanted frame temperature.

This all together will take ~10 min. per point, not dependent on $\tau$. 

**Time schedules**
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Extrapolation time

• In the (semi-)adiabatic method, the T-step is, in general, taken by extrapolating the drift curves to halfway the heat pulse.

• If the slopes of the drift curves are not exactly the same (what, in general, is the case) this can be shown to be the best approximation.
Extrapolation time

- In the hybrid method, extrapolating to halfway the heat pulse is not correct.
- From a numerical simulation we learned that, if $t_0$ is halfway the heat pulse, for the $t_{\text{extrapol}}$ holds:

$$t_{\text{extrapol}} = t_0 + 0.0416 \times (\Delta t_{\text{pulse}})^2 / \tau.$$  

For instance, if the heat pulse takes 10s, and also $\tau = 10s$, the point of extrapolation shifts 0.416 seconds to the right, starting from $t_0$. 
Extrapolation time

A calculation of the correct extrapolation time is not difficult. Let us start the pulse with constant power $P$ at $t = 0$ and end at $t = t_h$.

During the pulse: \[ \Delta T(t) = \frac{P\tau}{C} \{1 - \exp(-t/\tau)\}, \]
with $\tau = C/k$, $C$ the heat capacity, and $k$ the heat link with the frame.

After the pulse: \[ \Delta T(t) = \Delta T(t_h) \exp (-(t - t_h)/\tau), \]
with $\Delta T(t_h)$ following from the formula above.

Without heat relaxation, the temperature after the heat pulse should have been \[ \Delta T = \frac{P t_h}{C}. \]
The extrapolated after-curve should have this value, and we look for the $t$ where this happens.

Combining all this leads to:\[ P \frac{t_h}{C} = \left(\frac{P\tau}{C}\right) \{1 - \exp(-t_h/\tau)\} \exp \left(-\frac{t_{\text{extrapol}} - t_h}{\tau}\right). \]

Or: \[ \frac{t_{\text{extrapol}}}{t_h} = -\left(\frac{t_h}{\tau}\right) \ln \left[ \left(\frac{t_h}{\tau}\right) \cdot \exp(-t_h/\tau) / \{1 - \exp(-t_h/\tau)\} \right]. \]

This gives the extrapolation time in “units” $t_h$ as a function of $t_h/\tau$. 
Extrapolation time

We had the formula:

\[ \frac{t_{\text{extrapol}}}{t_h} = -(\frac{\tau}{t_h}) \ln \left( \frac{(t_h/\tau) \cdot \exp(-(t_h/\tau))}{1 - \exp(-(t_h/\tau))} \right). \]

It is remarkable that, for \( t_h/\tau \) not too large, the results for the extrapolation time all show to be close by half way the heat pulse. More remarkable is that the deviations from halfway the pulse showed to be nearly linear in \( 1/\tau \) !!

The formula yields:

\[ t_{\text{extrapol}} - \frac{t_h}{2} = \text{const} \cdot \frac{t_h^2}{\tau}. \]

The const varies from 0.0417 for very long relaxation times (\( t_h/\tau \) nearly zero*) to 0.0415 for \( t_h/\tau = 0.7 \), in perfect agreement with the simulation results…

NB: for larger values of \( t_h/\tau \), the hybrid method is inappropriate.

NB*: for these small values of \( t_h/\tau \) the constant can be calculated exactly: 1/24.
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Near transitions

Measuring correct C-values near transitions is very difficult.

A sharply peaked C, as in a first order process, can even not be determined directly. The observed value will depend on the chosen $\Delta T$. Problems will even be larger if the step starts or ends within the peak region.

The observed C-value for step $\Delta T_1$ is larger than for step $\Delta T_2$.

Both values have an only poor relation with the real peak dimensions.
Near transitions

- If, in case of a first order transition, the added heat in the pulse is smaller than the latent heat, the transition is only covered by several successive steps.
- It will be, then, very difficult to prevent the transition from taking place partly during temperature drift outside the heat pulses, with unknown direction.
- Hysteresis of the transition may enhance the difficulties.

=> For determining the latent heat, small steps are inappropriate.
Near transitions

Best strategy seems to be:

- Determine with small steps the position of the peak.
- Make one big step, covering the whole transition, like $\Delta T_2$ in the figure.
- The difference between the observed $\Delta Q$ and the extrapolated background value gives the latent heat according to:

$$L = \Delta Q - \int_{\Delta T_2} C_{extr} \cdot dT$$

The step $\Delta T_2$ is sufficiently large to cover the whole transition.
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Equipment

For measuring specific heat by the hybrid method we have the following equipment available:

- A cryostat (Oxford Instruments with 9T superconducting magnet and VTI).
- A sampleholder with heater and thermometer.
- A frame heater and frame thermometer.
- A dedicated low-T thermometer bridge.
- A computer-controlled current supply for the pulses.

- A precision multimeter (multichannel) for reading pulse characteristics, frame temperature, and T-bridge output.
- A computer-controlled current supply for the frame.
- A clockpulse supply for synchronisation (the “pacemaker”).
- A computer with specific-heat program, and GPIB and RS232 connections.
Equipment

- The Oxford Instruments cryostat with VTI (flow-type cryostat) and 9T magnet.
- The VTI is not used for controlling the frame temperature (too slow).
- The controller keeps $T(\text{VTI})$ in the direct environment of $T(\text{frame})$.
- The VTI controller can be controlled by the specific-heat program (GPIB).
Equipment

The Oxford Instruments Controller.

Left from above:
- the VTI controller,
- the central unit,
- the level indicators and
- the magnet current supply.

The right part contains the VTI-pump and computer.
Equipment

The frame heater is because of practical reasons attached to the connector at the low end of the vertical stainless steel tube. It consists of 18 (270 $\Omega$, 0.5 W) metal film resistors (3 series of 6 parallel).

The frame thermometer is a simple Rhutenium-oxide resistor (16 k$\Omega$ at 300K) with an only limited accuracy, positioned under the teflon tape.
The sampleholder as delivered by Oxford Instruments is a sapphire plate with heater and thermometer.

It was attached to the frame with the thin electrical wires only.

This showed to be too vulnerable.

We attached 4 extra composite wires to the sapphire plate and fixed these to the frame.
Equipment

- The sample thermometer is a Lake Shore Cernox resistance thermometer (300 Ω at 77K and 40 Ω at 300K, no field dependence in this region).
- The Oxford Instruments calibration was found not to be sufficiently accurate. The thermometer is “in situ” recalibrated against a dedicated Lake Shore standard sensor.
- The sample heater is a thin film resistor (765 Ω at 300K) on the back side of the sapphire plate (no thermal-conduction problems).
Equipment

Electronic components scheme for measuring specific heat in the MagLab system. The Keithley multimeter also measures the voltage of the heat pulse (not drawn). The “pacemaker” is the heart-beat of the system governing accurate timing of actions.
Equipment

The electronics in reality.

From above:

the low-T resistance bridge,
the Keithley sampleholder current supply and multimeter,
the current supply for the frame heater,
the “pacemaker”,
the monitor,
and the computer.
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• The set-up works (worked..) quite well.

• **Typical sample data**: 3*2*1 mm, m=50 mg. The 3*2 surface has to be polished for good heat contact with the sapphire plate.

• After upgrading the sampleholder with extra composite support wires, we found values for the relaxation time, $\tau$, ranging from about 10s (the empty holder at 20K) up to more than 5 minutes for (holder+sample) at higher T.

• The values for $\tau$ increase with T from 20 to 100K, go thereupon through a broad maximum at about 150 K and decrease subsequently to about half the maximum at 300 K. These values are well fitting the range for the hybrid method to work well.
Some results

• The sampleholder contribution amounts from 0.2 mJ/K at 20 K up to 12 mJ/K at 330 K, which are about the values found for 30 mg copper, and therefore of the same order of magnitude (or smaller) than our typical sample contributions.

• The samples are attached to the holder with some heat-conducting grease. The contribution of the grease amounts to only a few percent of the empty holder contribution.

• This grease-contribution is difficult to determine exactly, because the exact amount of grease is not well known, so correction for it is a deliberate guess.
Some results

• We performed a **test measurement** on a sample of about 70 mg spec-pure copper. This test is done in the old sampleholder without extra support wires. However, we don’t believe this to be of significant influence.

• The results were all somewhat higher than the literature values. Up from 100 K the difference was about 1%, between 20 and 100 K the difference amounted up to about 2% at 80K. These are satisfying numbers. A plot follows on the next slide.

• Part of the observed difference may be caused by the grease contribution, for which was not corrected, but was guessed to be of the same order of magnitude than the observed difference, or somewhat smaller. This makes the agreement of the copper test results with observed literature values even better.
Some results

Results on Cu sample (open symbol) compared with NBS data on Cu (closed symbol). The difference may be attributed to grease which was not corrected for.
Some results

Specific-heat results on a 60 mg MnFeP$_{0.45}$As$_{0.55}$ sample. The shift of the peak with field is clearly visible, as well as a small impurity peak (MnO ?) at about 120 K.
Mn$_{1.94}$Cr$_{0.06}$Sb

(measured summer 2007)

$T_C = 220$ K.

In a B-field of 2 T

$T_C$ shifts 8 K to the left.

NB: the transition is not a normal Curie point.
Acknowledgements

- Staff and coworkers:
  - E. Brück
  - F. R. de Boer
  - K. H. J. Buschow
  - Lian Zhang
  - O. Tegus
  - L. Caron
  - .. many others..
Acknowledgements

For electronics and programming:
- Gerrit Hardeman
- Hans Gerritsen

For upgrading the sampleholder:
- Wim Koops

For all recent repairs:
- Hugo Schlatter
Thank you for your attention