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The thermal device of the Guinier image foil camera in the Geological Institute, BAS: calibration and usage experience

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Along with its normal (flat sample) mode, the unique for Bulgaria Guinier image foil camera in the Geological Institute (Bulgarian Academy of Sciences) can also be used in capillary mode. In this mode a dedicated ceramic heater can be attached, so that the whole setup is turned into a powerful thermal device. The possible uses of this device are numerous, most important of which are: determination of the thermal expansion coefficient(s) of the studied sample in each crystallographic direction; detect anomalous or negative thermal expansion trends; register phase transitions (reversible or non-reversible), witness purely temperature driven solid state reactions (formation or dissolution of ISS) etc. The successful use of the device, however, requires some preliminary experience and prompt calibration. For this type of thermal device calibration is crucial, since the sample in the glass capillary and the detecting thermo-couple react differently to the received infrared radiation and respectively experience different resultant temperature. Finding a function, well describing this difference for each given temperature in the technically applicable temperature range (ambient – 900 °C) is the aim of the calibration. Although the most important, calibration is not the only issue in using this thermal device. There are a whole lot of possible mistakes that a novice can do. Our experience in calibrating and first usage of the device is shared in the following paper.

Key words: X-ray diffraction, Guinier camera, capillary tube, thermal device, calibration.

INTRODUCTION

The Guinier image foil camera G-670 (Huber Diffraktiontechnik GmbH & Co. KG), available in the Geological Institute, Bulgarian Academy of Sciences, can be used with either swinging flat or rotating capillary specimen holders (Fig. 1 and 2).

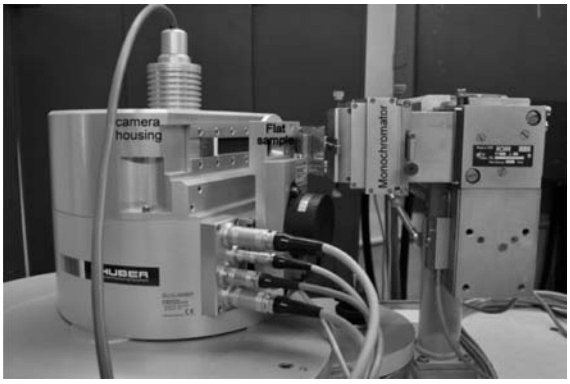

Fig. 1. Swinging flat sample setup

Fig. 2. Rotating capillary setup

In both cases the sample is radiated by monochromatic (pure Kα_1) beam, transmitted through the sample and diffracted beams in the range 3–100° 2θ are simultaneously registered on the reusable image foil, lying at the back wall of the cylindrical camera housing. The foil is then read by a laser reader and data recorded to file. Finally, the foil is erased and ready for the next data collection.

The capillaries used are 0.5 mm thick with 0.01 mm wall thickness. Commercially available capillary tubes of this size can be made of special

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Fig. 3. Capillary adjustment

Fig. 4. Heater device

glass, boron-rich glass, or quartz glass. The linear absorption coefficients of CuK_α in these materials vary from 110 (in special glass) to 76 cm^{-1} (in quartz glass). Respective values for MoK_α are approximately 10 times lower. Both boron- and quartz- glasses have comparable and acceptable for most purposes absorption coefficients, however, softening temperature of boron glass is about 820 °C, while for the quartz glass it is 1730 °C. Keeping in mind, that technically achievable temperature limit of the device is 900 °C, the use of quartz glass is economically reasonable only for studies in the higher-most end of the temperature range. In most other cases far cheaper boron-glass is the better choice.

Filling of the powdered sample in the capillary tube is facilitated by the funnel that it usually has on one end. However, some source of vibration should be applied on it too, in order to move all powder particles down to the capillary bottom. A dedicated vibrating device named “capillary boy” is offered by Huber Diffraktiontechnik GmbH & Co. KG.

Once filled, the capillary is to be glued in its holder. This is made using wax, if normal ambient temperature studies are to be done, and special, heat resistant, bi-component glue in case of high temperature studies. The holder is then adjusted in a special goniometric head, so that it is rotated strictly along its own axis, exposing all the sample particles simultaneously to the direct X-ray beam (Fig. 3).

High temperature setup is achieved by attaching a ceramic fork with built-in heating coil. The heater is adjusted over the capillary tube, containing the powdered sample (Fig. 4).

Adjustment is a rather tricky point. Following are some practical advices, from our experience:

- The length of the capillary must be chosen properly, so that the entire sample is placed fully inside the heater and its top is as close to the thermocouple (the ball in the upper-most part of the heater, Fig. 5) as possible. The latter is achieved also by proper adjustment of the heater height. If longer, part of the sample (outside the heater) will remain less heated and will produce inconclusive results. If shorter, the sample will either remain far from the thermocouple and its temperature will differ too much from that registered by it, or the heater has to be lowered too much and may be hit by the rotating capillary holder.
- Positioning the heater over the capillary should start with rotating the ceramic fork around its own axis, so that the line connecting its two legs passes through the axis, holding the heater shoulder (i.e. it is made strictly radial to the arc, drawn by moving the heater shoulder). Otherwise, adjustment will almost surely end up with broken capillary.

Fig. 5. Ceramic heater fork with the detecting thermocouple ball in the uppermost part of the opening

- Once in right position, the heater should be rotated around its own axis again, so that the opening between the legs of the fork is oriented towards the 2θ range of interest. One should keep in mind, that the heating device narrows the range of outgoing reflections to some 30 degrees 2θ. This is why the range of interest should be chosen in advance and targeted by proper rotation of the heater.
- In any case one should make sure, that the capillary is equally distant from both legs of the fork. This guarantees that the primary beam will not touch any of them. This rule should be followed also for the heat-keeping cover (Fig. 6). Otherwise, "alien" reflections will be detected.
- The overall setup of the device does not allow the operator to place his eye wherever necessary for all the adjustments. We found it very useful to place a handy mirror on the receiving window of the camera (just don't forget it there ☺).

Heating is controlled by a special heat controller, responsible for gaining and keeping the required sample temperature unchanged for the required period of time. This is achieved by periodically turning the heating coil current on and off. The duration and periodicity of the heating impulses are dynamically adjusted, depending on the values fed back by the thermocouple. Although the controller can be operated manually from its grip, it is normally communicated through the main system software. This software allows the user to plan his experiment, by creating a temperature profile, based on start, stop and step temperature values, using also desired durations for each step, with respective dwell time and diffraction pattern collecting time.

PID values are another important parameter of the experiment. Since PID is not anything specific to this device, but a parameter set, lying in the base of the general process control theory, it will not be described here. However, it is worth to mention, that correct choice of PID values is very important for the good operation of the heating device. If improper PID values are chosen, the sample temperature in the beginning can vary too widely around the chosen value, and many materials can be destroyed before required diffraction pattern is collected. Even few seconds of overheating can cause a loss of some phase transition pattern (a permanent loss if the transition is irreversible), or even complete melting or evaporation of the sample. Good sources of initial information on the topic are [12, 15].

Fig. 6. The heat-keeping cover, preventing too much air convection and respectively fast cooling of the sample

Calibration. Both the sample and the thermocouple in this device receive the main part of their heat by direct infrared radiation from the ceramic mounted heating coil. Because of the open design of the device, the importance of the air flow as heat transferring agent is rather low. Even the role of the heat keeping cover, which slows down the air convection around the sample and thermocouple, is mostly to avoid pretty fast cooling of the sample, rather than helping to heat the device volume. Receiving equal amounts of heat, however, the sample and the thermocouple reach different resulting temperatures, because of their rather different heat capacities (45.3 J/mol.K for the quartz glass, opposed to 25.9 J/mol.K for the Pt/Rh thermocouple). Soundly, this difference is almost negligible at lower temperatures, but becomes rather significant with temperature rise.

Since the device operating software only receives the thermocouple temperature, finding an equation, well modeling the sample temperature for any given thermocouple temperature, is crucial for obtaining conclusive study results. This is the aim of the calibration procedure.

All *calibration approaches* are based on comparison of the thermocouple temperature with some independent evidence for the real sample temperature. Three kinds of physical phenomena can be employed as independent temperature evidences: known thermal expansion coefficients; known melting temperatures; known phase transition temperatures. The advantage of the first approach is that it can give a continuous series of d-values (and respective temperatures, calculated from the known expansion coefficient) to plot against the respective thermocouple temperatures, this way providing a smooth calibration curve in the whole temperature range of interest. Its disadvantage, however, is that the whole calibration curve depends on measurements of just one substance. If there is something wrong with the substance (chemical purity or physical conditions) or with the experiment (zero shift, sample displacement

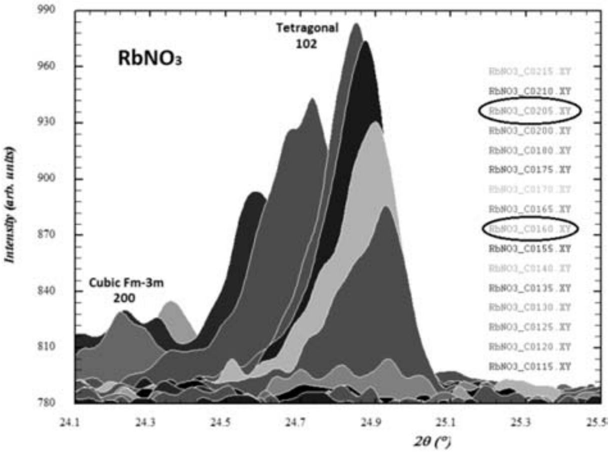


Fig. 7. Example of RbNO3. Tetragonal phase appears on flat background at 160 °C. So does the cubic phase at 205 °C

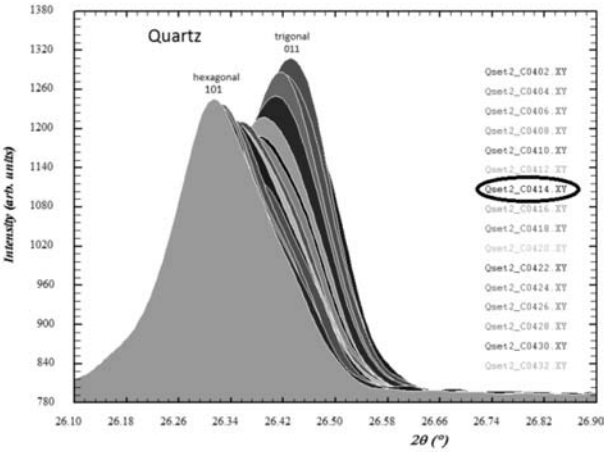


Fig. 8. Typical saddle shape of the stacking diagram for the trigonal/hexagonal transition in quartz

etc.) these errors are cast over the whole range of results as systematic errors.

A big disadvantage of the second approach is that melting is not an abrupt phenomenon. It always takes a temperature range with smooth disappearance of the diffraction lines and hence the accuracy of the calibration curve, created this way, is pretty poor.

For the reasons expressed above, we choose the third approach – using phase transitions in our calibration experiments.

In this approach, each point of the calibration curve is determined by the results of a separate experiment, using proper substance with well known phase transition effect. Before each experiment, available reference data have been carefully investigated, to make sure that there is no discrepancy in the literature, about the character and the temperature at which the targeted phase transition occurs. Another important information to collect before the experiment was to learn at what Bragg angle the most visible transition effect should be expected. This was done in order to adjust the heater and its cover, so that reflections in the respective 2 theta range are to be observed.

Since preliminary reference data showed that the thermocouple systematically shows temperatures lower than the real sample temperature, and at the high end of the range (900 °C) this discrepancy can even reach 250 °C, we used to start stepwise heating far before the expected phase transition. The step was chosen larger at the beginning and was decreased with approaching the expected transition point. The result was a series of diffraction data, which could be plotted in some stacking diagram, to visualize the changes.

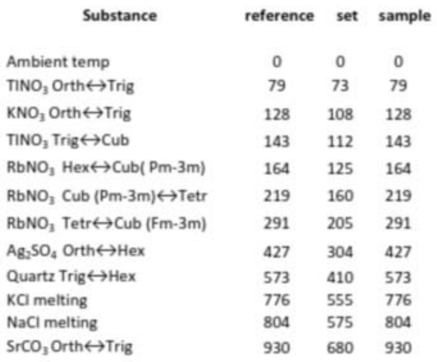
Duration of the heating step. Structural and respective diffraction pattern changes, which appear on heating, require some time to take place. Since the required tempering time is specific for each substance and each phase transition, no general suggestion for the proper step duration can be drawn out. This is why we used to adjust step duration experimentally, by consecutive collection of diffraction patterns at constant temperature, until they remain unchanged.

The character of the change in the diffraction pattern depends on the character of the structural change. Since phase transitions usually refer to slight distortions of the atomic arrangement and respective slight displacements of the diffraction peaks, they are best recognized, when extinction conditions are changed. In this case, a new peak appears right from the flat background (Fig. 7). In most cases, however, the change is expressed by deformation of some peaks, loss of intensity and finally growth of new peak at the foothills of an existing one. Often the new and old peaks coexist over some temperature range, forming a typical saddle shape on the stacking diagram (Fig. 8), but we need certain strict temperature value to assign to the phase transition. We choose to assign it the temperature of first appearance of the new peak, since presumably this should be the point of symmetry change.

The set of substances, used for the creation of the calibration curve, was chosen on the grounds of available reference data, temperature of phase transition and of course – availability in accessible labs. Our choice is given in the following Table 1.

Table 1. List of used substances and respective reference data

Substance	Reference	Substance	Reference
$TlNO_3$	[3, 4, 5, 6]	Quartz	[3, 13]
KNO_3	[3, 5, 6, 7, 8]	KCl	[3, 15]
$RbNO_3$	[3, 5, 6, 9, 10, 11, 12]	NaCl	[3, 15]
Ag_2SO_4	[3]	$SrCO_3$	[5, 14]



Substance	reference	set	sample
Ambient temp	0	0	0
$TlNO_3$ Orth↔Trig	79	73	79
KNO_3 Orth↔Trig	128	108	128
$TlNO_3$ Trig↔Cub	143	112	143
$RbNO_3$ Hex↔Cub(Pm-3m)	164	125	164
$RbNO_3$ Cub (Pm-3m)↔Tetr	219	160	219
$RbNO_3$ Tetr↔Cub (Fm-3m)	291	205	291
Ag_2SO_4 Orth↔Hex	427	304	427
Quartz Trig↔Hex	573	410	573
KCl melting	776	555	776
NaCl melting	804	575	804
$SrCO_3$ Orth↔Trig	930	680	930

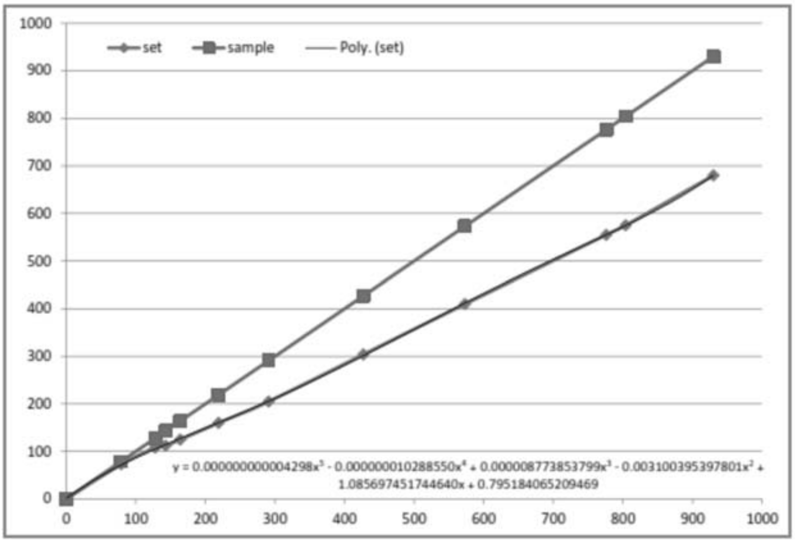


Fig. 9. Constructed calibration curve, with the underlying data base (on the left): list of used substances with known phase transitions; sample (presumably equal to reference) and set (read from the thermocouple) temperatures for each phase transition. Polynomial equation of the approximating curve is given below the set curve

The calibration curve was built on the base of the data, obtained from the above described experiments on the above listed substances. The results are given in Figure 9.

Discussion. The obtained calibration curve confirms the observation of [16], that set temperatures (those sensed by the thermo-couple) are always lower than actual sample ones and at the hot end of the range (900 °C) this difference can reach 250 °C. It is very similar to that in the unpublished study of M. Nippus (2000) from Huber GMBH, who proposes the following approximation function: $T_{set} = T_{sample} - A*(1 - \exp(B*T_{sample}\^{}2))$, where A and B are fitting parameters, specific for each individual heating device. Instead, we found a pretty good fit of the obtained results with a polynomial of order 5. The most satisfying result, however, is that the obtained dependence differs from a simple linear function $T_{set} = 0.7*T_{sample} + 10$ within an accuracy range of ±10 °C, which is acceptable, for many purposes.

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ТЕРМИЧНАТА ПРИСТАВКА НА ЦИФРОВАТА ГИНИЕ КАМЕРА В ГЕОЛОГИЧЕСКИЯ ИНСТИТУТ НА БАН: КАЛИБРИРАНЕ И НАТРУПАН ОПИТ

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(Резюме)

Наред с нормалния (с плосък препарат) режим, уникалната за България цифрова Гиние камера в Геологическия институт (БАН), може да бъде използувана и с препарат в капилярна тръбичка. В този режим е възможно към системата да се добави специален керамичен нагревател, превръщащ установката в мощен инструмент за in-situ термична дифрактометрия. Има множество възможните приложения на тази система, най-важните от които са: определяне на коефициента(ите) на термично разширение на материала по всяко кристалографско направление, установяване на аномални или отрицателни трендове на термично разширение, регистрация на фазови преходи (обратими или необратими), проследяване на термично предизвикани, твърдотелни реакци (образуване на междинни твърди разтвори) и др. Успешната употреба на системата, обаче, изисква някои предварителни знания и внимателно калибриране. За този тип термична приставка калибрирането е от решаващо значение, доколкото препаратът в капилярната тръбичка и отчитащата температурата термодвойка реагират различно на постъпващото инфра-червено облъчване и постигат различна резултатна температура. Целта на калибрирането е да се намери подходяща функция, добре описваща температурното състояние на образеца, за всяка избрана температура на термодвойката в рамките на работния интервал (0–900 °C). Въпреки че калибрирането е основната, то не е единствената трудност при работа с термичната приставка. Има множество възможни грешки, които неопитният изследовател може да допусне. В тази работа авторите споделят резултатите от калибрирането и първоначалния си опит от използуването на системата.