LABORATORY KOTALLA

SINCE 1979

WORLDWIDE OLDEST PRIVATE LABORATORY SPECIALIZED FOR TL-ANALYSIS

TL - Authenticity test on porcelain

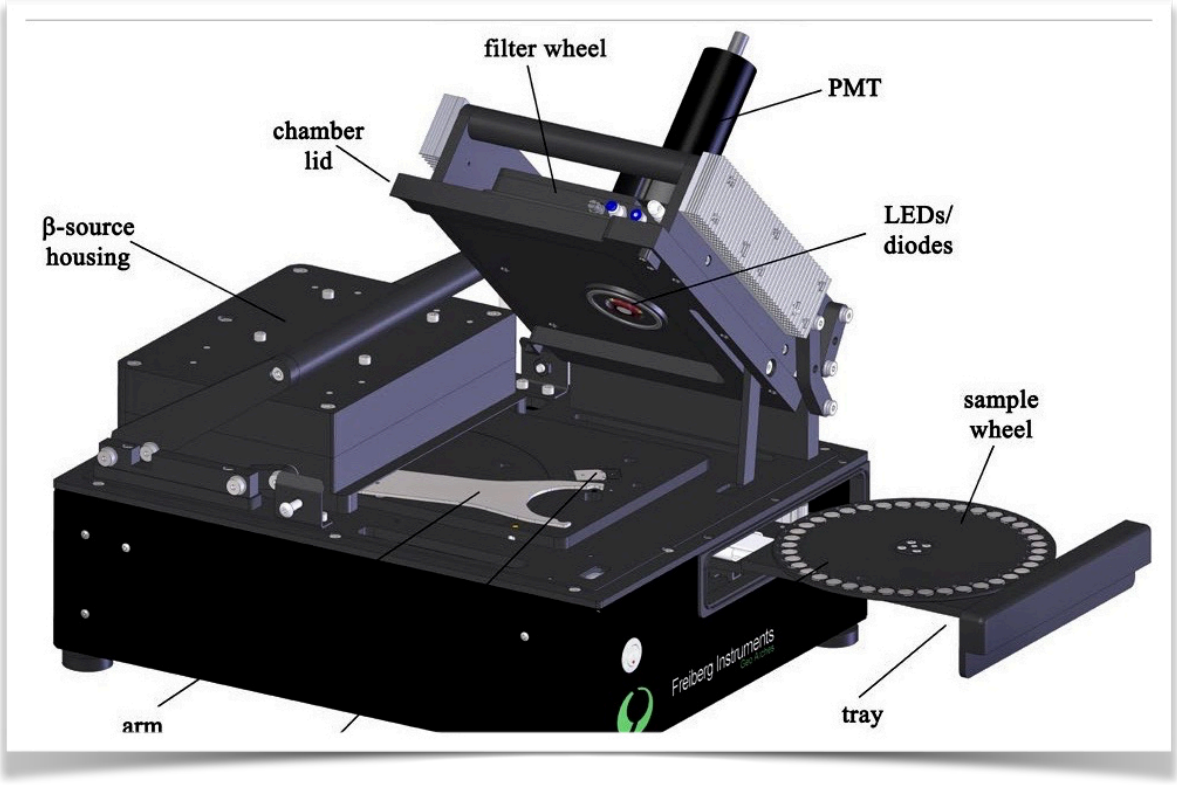
Using various thermoluminescence methods and sampling techniques.

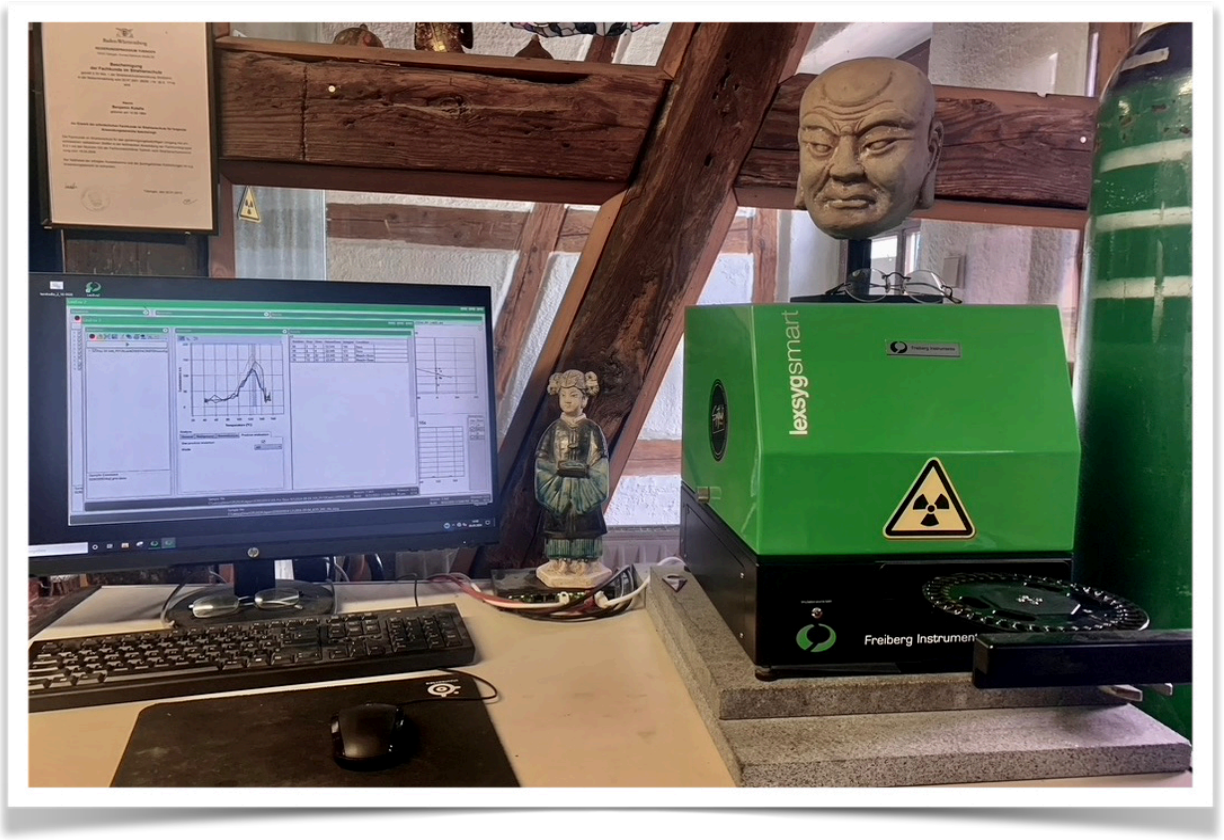
Pre-Dose MA, Pre-Dose AM , TAC

Fine grain TL additive and TL regenerative

LIPS Element Material Analysis

In our tests, all five techniques are used and presented in an expert report with an overall result.




lexsygsmart
Freiberg Instruments


KEYENCE
Laserbasierte
Materialanalyse-Einheit
NEU Modellreihe EA-300
26 Fe
28 Ni
29 Cu
Mikroskopie und Materialanalyse
Einfach. Schnell. Präparationsfrei.

Pre-dose technique MA

The following protocol “multiple activation pre-dose” follows Aitken (1985).

According to Stoneham (1991) at least 3 slices are necessary for this, in Aitken (1985), Wang (2009) and others it is not stated that several slices are necessary for multiple ß-doses.
Consequently, a single dose seems to be sufficient and only a single dose of ß is described.
Note : However, it is questionable whether a single slice with a dose of ß is sufficient, since it does not allow for quality control. In this respect, the approach of Stoneham (1991) seems comprehensible and at the same time low measurement and material expenditure, especially for authenticity tests.
This absolutely excludes the possibility that the pre-dose effect dating can be manipulated by any artificial irradiation in order to arrive at an artificially desired created age value measurement!

‘Multiple-activation’ (MA) measurement protocol pre-dose according to Aitken

(1985): Test dose (e. g. 0. 01 Gy) TD ß
2) TL measurement @5°C/s to 150°C immediately after irradiation: S0 (integral around 110°CPeak) as ‘dose‘ with indication of the test dose
3) Heating to activation temperature @2°C/s and cooling (e. g. 25°C)
4) Test dose (e. g. 0. 01 Gy)
5) TL measurement @5°C/s to 150°C immediately after irradiation: SN (integral around 110°CPeak) and cooling (e. g. 25°C) as a ‘can’ with indication of the test dose
6) ß-irradiation
7) Heating to 150°C with @2°C/s and cooling (e. g. 25°C)
8) Test dose (e. g. 0. 01 Gy) TD ß
9) TL measurement @5°C/s to 150°C immediately after irradiation: S‘N (integral around 110°C peak) as ‘bleach+dose‘ with indication of ß-irradiation of 6)
10) Heating to the activation temperature @2°C/s and cooling (eg 25°C)
11) Test dose e. g. 0. 01 Gy) TD ß
12 TL measurement @5°C/s to 150°C immediately after irradiation: SN+ß (integral around 110°C peak) and cooling (e. g. 25°C) as a ‘bleach+dose‘ with an indication of ß-irradiation of 6)

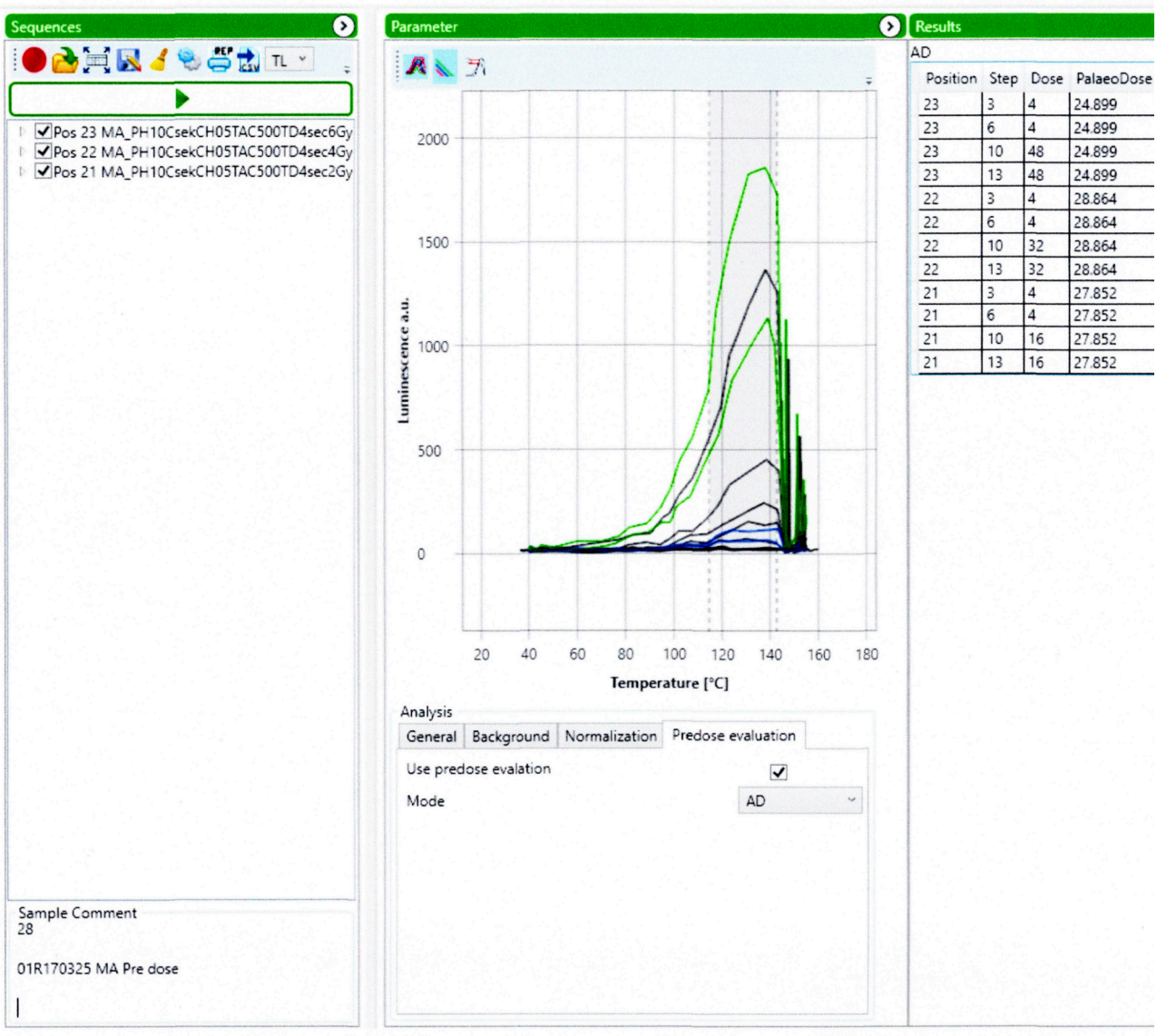
The use of ‘natural+dose’ is used for identification for an automatic analysis of the data. Here, either in the measurement sequence or before the analysis, the status and the applied additive dose (zero for un irradiate) must be entered manually.
Note: highest additive signal should be at least twice the natural signals).
An apparent paleodose is calculated for each slice (or additive dose group) according to the MA protocol and the paleodose is calculated by Regression analysis of these results against the previously applied additive dose (Bailiff, 1991):Regression analysis of the results of the MA results (here evaluated dose) against the additive dose (from Bailiff, 1991) to determine the paleodose

Regression analysis of the results of the MA results (here evaluated dose) against the additive dose (from Bailiff, 1991) to determine the paleodose

Literature

Stoneham, D. (1991). Authenticity testing. In "Scientific dating methods. " (H. Y. Göksu, Ed.),pp. 175-192.
Bailiff, I. K. (1991). Pre-dose dating. In "Scientific dating methods. " (H. Y. Göksu, Ed.), pp. 155-173.

Aitken, M. J. (1985). "Thermoluminescence Dating. " Academic Press, London.
Wang, W. D. (2009). Study and progress of the thermoluminescence dating of the ancient pottery and porcelain. Science in China Series E-Technoleogical Sciences 52, 1613-
1640. Daniel Richter 2022. Freiberg Instruments Manual



Pre-dose technique AM

Nach Aitken (1985) wird bei der additiven Methode Änderungen der Prä Dosis Charakteristika und eventueller Einfluss durch thermales ‘quenching‘ vermieden. Die thermische Aktivierung erfolgt nur einmal.Die additive pre-dose Methode wurde von Bailiff weiterentwickelt (“modified additive pre-dose“ bzw. ähnlich spike -Methode) und scheint nun die am häufigsten verwendet Methode auch für Keramik und Porzellan zu sein. Da der Messaufwand nur wenig höher ist, bei gleichzeitigen klaren Vorteilen für erfolgreiche Ergebnisse wird nur dieses im Folgenden beschrieben. Hierbei wird im Prinzip eine MA für Scheibchen mit unterschiedlichen additiven Dosen angewendet.
Temperaturempfehlung folgen hier Stoneham (1991), abweichend bei anderen Autoren.
Scheibchen erhalten unterschiedlich sich erhöhenden additive ß-Bestrahlung (N, N+ß, N+2ß,N+3ß, N+4ß) wobei für natürliche Scheibchen (N=natural) Dosis = 0. Alle Scheibchen erhalten einen preheat (PH) @5°C/s bis 150°C und werden folgendermaßen gemessen, wobei sowohl die jeweilige Testdosis als auch die Betabestrahlung bei allen Scheibchen jeweils konstant sein müssen:

Messprotokoll “modified additive pre-dose”:

1) Additive ß-Bestrahlung (Null für natürliche ‘natural‘: N, N+ß, N+2ß, N+3ß, N+4ß)
2) Preheat auf 150°C mit @2°C/s und Kühlung (e.g. 25°C)
3) Testdosis (e.g. 0.01 Gy) TDß
4) TL-Messung @5°C/s bis 150°C sofort nach der Bestrahlung: $\rightarrow S_0$ (Integral um 110°CPeak) als ‘dose‘ unter Angabe der Testdosis
5) Erhitzung auf die Aktivierungstemperatur (siehe Kapitel 2) @2°C/s und Kühlung (e.g. 25°C)
6) Testdosis (e.g. 0.01 Gy) TD
7) TL-Messung @5°C/s bis 150°C sofort nach der Bestrahlung: $\rightarrow S_N$ (Integral um 110°CPeak) und Kühlung (e.g. 25°C) als ‘natural+dose‘ unter Angabe der additiven Dosis
8) Fixe ß-Bestrahlung (e.g. 1.0 Gy)
9) Erhitzung auf 150°C mit @2°C/s und Kühlung (e.g. 25°C)
10) Testdosis (e.g. 0.01 Gy) TDß
11) TL-Messung @5°C/s bis 150°C sofort nach der Bestrahlung: $\rightarrow S'_N$ (Integral um 110°C Peak) als ‘bleach+dose‘ unter Angabe der ß-Bestrahlung von 6)
12) Erhitzung auf die Aktivierungstemperatur @2°C/s und Kühlung (e.g. page 7 of 9
Daniel Richter 25°C)
13) Testdosis (e.g. 0.01 Gy) TDß
14) TL-Messung @5°C/s bis 150°C sofort nach der Bestrahlung: $\rightarrow S_{N+ß}$ (Integral um 110°C-Peak) und Kühlung (e.g. 25°C) als ‘bleach+dose‘ unter Angabe der ß-Bestrahlung von 6)

Literatur

Stoneham, D. (1991). Authenticity testing. In "Scientific dating methods." (H. Y. Göksu, Ed.), pp. 175-192.
Bailiff, I. K. (1991). Pre-dose dating. In "Scientific dating methods." (H. Y. Göksu, Ed.), pp. 155-173.
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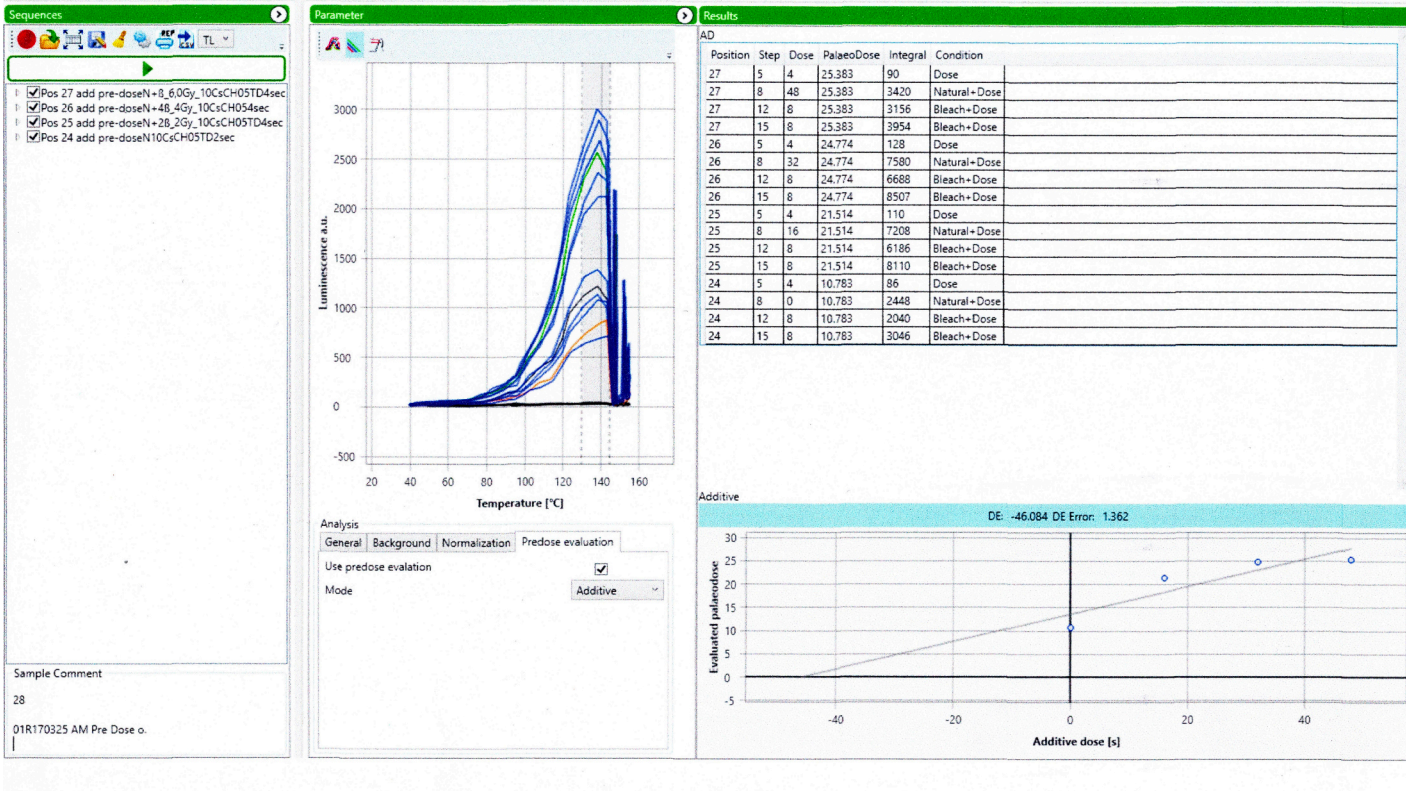


TAC Determination of the activation temperature

Proof that there is no deactivation in the respective sample material of the pre-Dose peak in the course of the pre-dose measurements.

The first pre-dose test we performed was the thermal Activation characteristic (TAC), a profile of the sensitivity increase of the 110° C. TL peak as a function of the temperature to which the sample is heated. The TAC is useful for determining the temperature required for maximum sensitization of the 110°C peak. It also provides an initial estimate of the accumulated dose (the total dose including that from the natural background). The TAC is also useful for identifying samples that may have been caused by the

Environmental conditions were partially sensitized. This is achieved by comparing the shape of the TAC curve, obtained by gradual thermal sensitization of the accrued dose, with the TAC curve obtained by sensitization of a subsequently applied laboratory dose of a magnitude comparable to the accumulated dose. The same method was also proposed for checking possible changes in the properties of the quartz, which are caused solely by heating.

(Bailiff, 1983).

Working condition- “TL Authentication“

TL-systems:

2 x Lexsysmart Freiberg Instruments ; Daybreak Tl 1150; Tl 1100;
Alpha and Beta Multiple Sample Irradiator 2 Daybreak
1 x Keyence EA-300 LIBS chemical elements analyses

Filter: Schott BG 39-BG29 KG 3 ; Daybreak Corning 7-59 / 5-60; Schott BG-39

PMT Hamamatsu H7360-02 Lexsmart ; EMI 9235QA Daybreak

ß-Source: Lex Sr 90 0,131 Gy/sec. 01.04.2017 Daybreak 0,068 Gy/sec 01.04 2017

a-Source: CM-244 Curium 0,5 mCi

Working method:
Fine grain sedimentation following treatment in diluted hydrochloric acid.
2 Grain size fraction following repeated double sedimentation 4- 11 and 15-50 micro m
ultrasonication in the beginning to get all the fine grains into suspension to get rid oft he
sub-micron particles.Measurements are carried out in an ultra- pure nitrogen atmosphere of
at least 5,0 N2.

Regeneration and Addition (MAR-MAAD) method (Second glow -
Normalization) Pre-dose TL. TAC

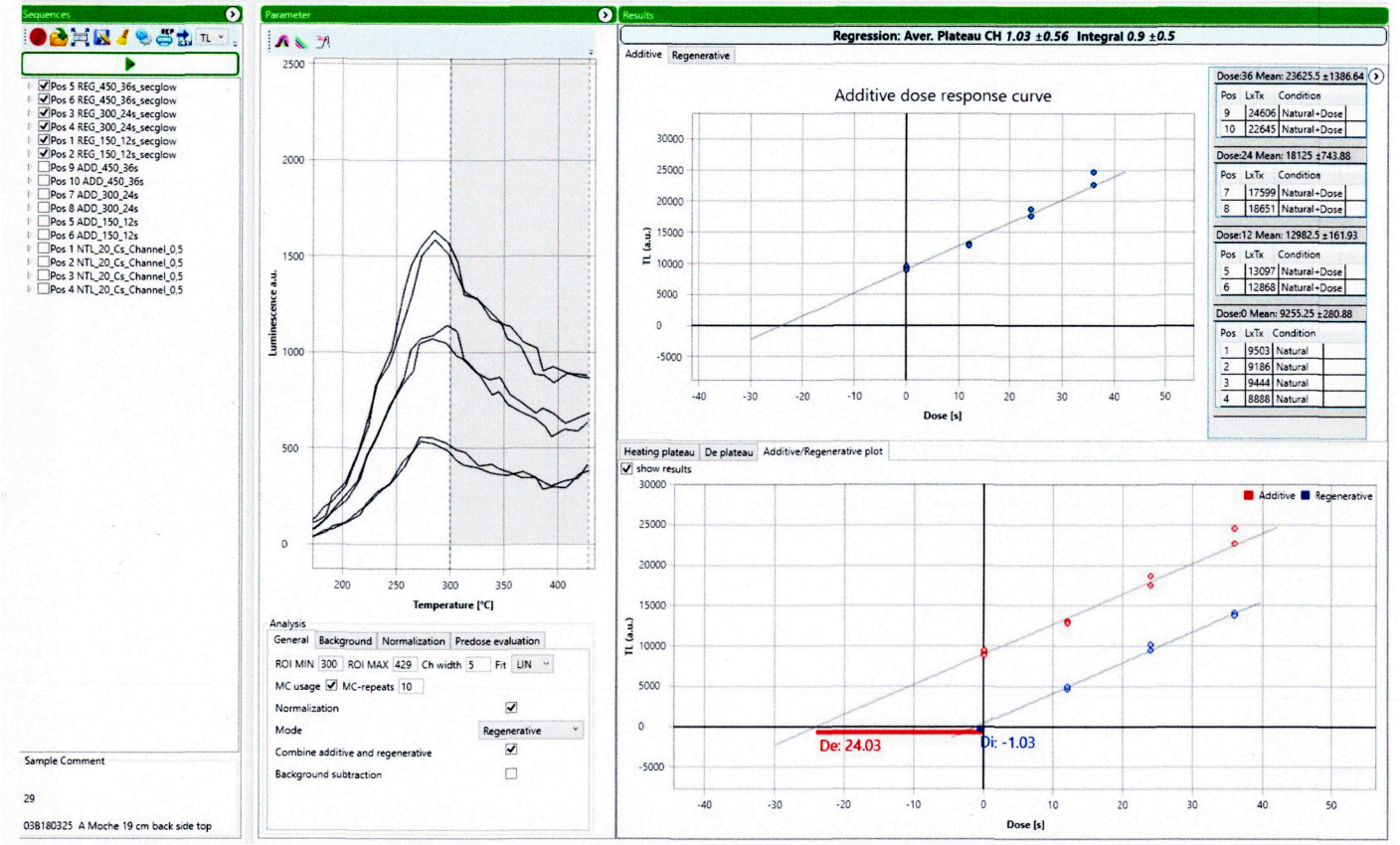
Result provides a statement on the last time of firing-melting process- .
The age specification contained in the TL expertise refers to the so-called "firing age"
of the sample(s) (minerals), i.e. to the time at which they were last heated to a temperature
of over 500 degrees C and mentions the place on the object from which the sample (s)
was / were taken.TL measurements to specify age can be falsified if objects have been subjected extrem high X and Y radiation doses or neutron bombardment.X - (not by Pre-dose Tl dating !!) radiation, for example during the course of baggage -medical controls, is no significance.(Error factor under 0,1 %)

The TL-Report do not provide on the investigation of polymers (synthetic and natural resins)
of all kinds.If an sample has been remodeled, the date of the sample will the last firing and
not the date of remodeling . Th and U value with ICP/MS K value with AMS/AES can be order separate .

Sampling:

Samples are taken using a carbide drill (diameter 1,5 -2mm) or Dental Tools .Samples must be taken not under a strong incidence of light. As a rule, two samples are taken from each test specimen, which are subjected to two separate TL analyses , in each case specifying the drilling position.The sample quantities are minimal (50-200 mg).If binders in the samples are discovered in one of the samples to be tested, the TL expertise carries the appropriate reference.Condition and restoration on the objects can be proofed by separate methods!!

Photos:
The laboratory requires one photo for the compilation of a Tl expertise.
The laboratory guarantees strict confidentiality in the processing of TL-analyses and the compilation of TL expertise’s.Expertise's are printed out without specifying the name of the commissioning party.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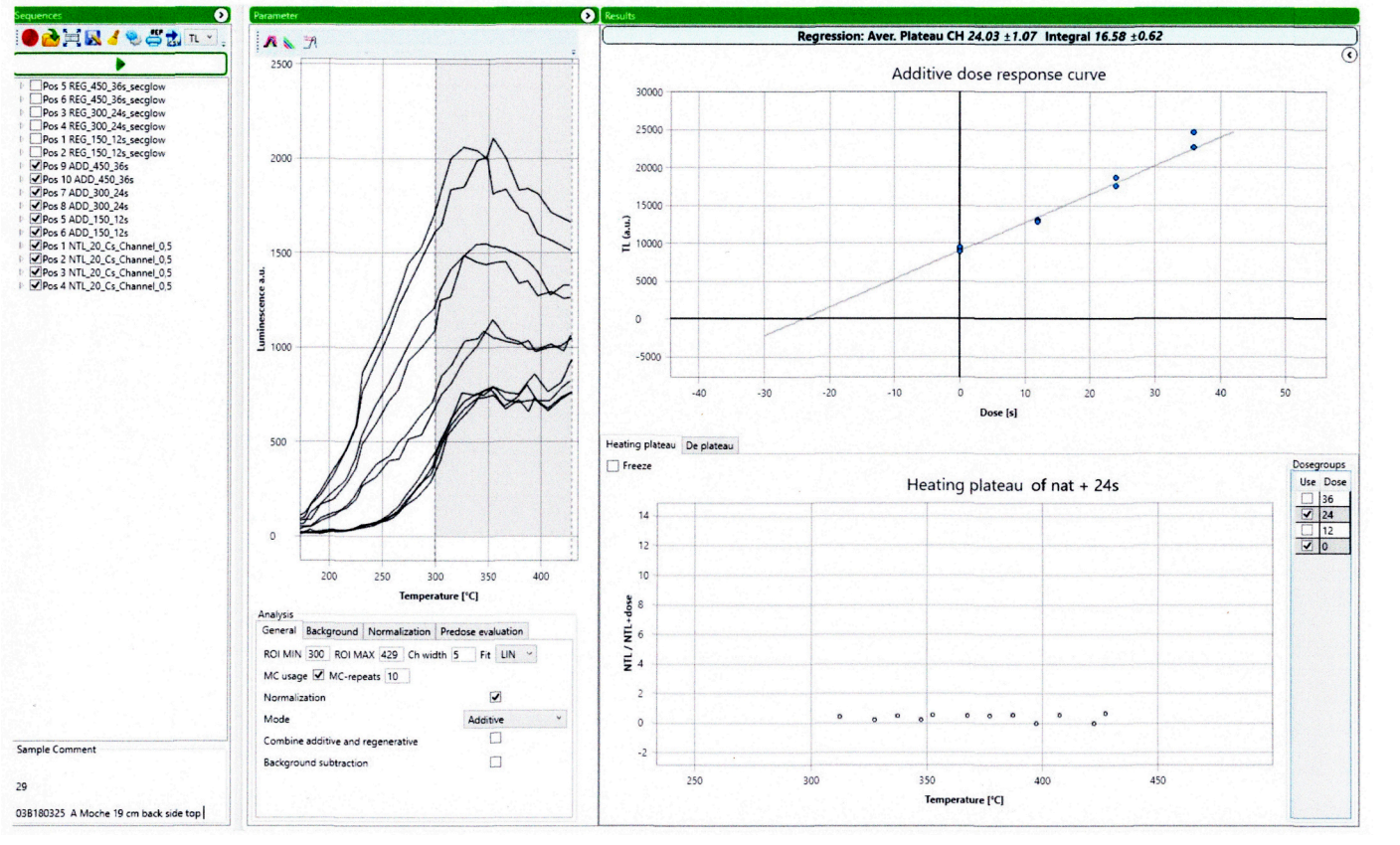
Pos 3 REG_300_24s_secglow
Pos 4 REG_300_24s_secglow
Pos 1 REG_150_12s_secglow
Pos 2 REG_150_12s_secglow
Pos 9 ADD_450_36s
Pos 10 ADD_450_36s
Pos 7 ADD_300_24s
Pos 8 ADD_300_24s
Pos 5 ADD_150_12s
Pos 6 ADD_150_12s
Pos 1 NTL_20_Cs_Channel_0.5
Pos 2 NTL_20_Cs_Channel_0.5
Pos 3 NTL_20_Cs_Channel_0.5
Pos 4 NTL_20_Cs_Channel_0.5
Sample Comment
29
03B180325 A Moche 19 cm back side top
Parameter
Luminescence a.u.
Temperature [°C]
Analysis
General Background Normalization Predose evaluation
ROI MIN 300 ROI MAX 429 Ch width 5 Fit LIN
MC usage MC-repeats 10
Normalization
Mode Regenerative
Combine additive and regenerative
Background subtraction
Results
Regression: Aver. Plateau CH 1.03 ±0.56 Integral 0.9 ±0.5
Additive Regenerative
Additive dose response curve
TL (a.u.)
Dose [s]
Dose:36 Mean: 23625.5 ±1386.64
Pos LxTx Condition
9 24606 Natural+Dose
10 22645 Natural+Dose
Dose:24 Mean: 18125 ±743.88
7 17599 Natural+Dose
8 18651 Natural+Dose
Dose:12 Mean: 12982.5 ±161.93
5 13097 Natural+Dose
6 12868 Natural+Dose
Dose:0 Mean: 9255.25 ±280.88
1 9503 Natural
2 9186 Natural
3 9444 Natural
4 8888 Natural
Heating plateau De plateau Additive/Regenerative plot
show results
Additive Regenerative
De: 24.03
Di: -1.03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Pos 3 REG_300_24s_secglow
Pos 4 REG_300_24s_secglow
Pos 1 REG_150_12s_secglow
Pos 2 REG_150_12s_secglow
Pos 9 ADD_450_36s
Pos 10 ADD_450_36s
Pos 7 ADD_300_24s
Pos 8 ADD_300_24s
Pos 5 ADD_150_12s
Pos 6 ADD_150_12s
Pos 1 NTL_20_Cs_Channel_0.5
Pos 2 NTL_20_Cs_Channel_0.5
Pos 3 NTL_20_Cs_Channel_0.5
Pos 4 NTL_20_Cs_Channel_0.5
Sample Comment
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03B180325 A Moche 19 cm back side top
Parameter
Luminescence a.u.
Temperature [°C]
Analysis
General Background Normalization Predose evaluation
ROI MIN 300 ROI MAX 429 Ch width 5 Fit LIN
MC usage MC-repeats 10
Normalization
Mode Additive
Combine additive and regenerative
Background subtraction
Results
Regression: Aver. Plateau CH 24.03 ±1.07 Integral 16.58 ±0.62
Additive dose response curve
TL (a.u.)
Dose [s]
Heating plateau De plateau
Freeze
Heating plateau of nat + 24s
NTL / NTL-dose
Temperature [°C]
Dosegroups
Use Dose
36
24
12
0

Principles of the TL – Method fine grain Method

There in was given evidence that the measuring of thermoluminescence emitted from objects made of fired clay could be effectively used for the dating and verification of such objects.

Quarz and feldspar as well as a number of other minerals have the ability to store energy generated by radioactive radiation. Under exposure to great heat such minerals release this energy again in form of light impulses. Radioactive radiation is created by the traces of uranium-, thorium-, kalium-, and rubidiumisotope which can be found almost everywhere in the earth's crust.Clay, which is used in the production of every day objects as well as objects of art, generally contains such minerals and radioactive isotopes.

All radioactive energy accumulated and stored by the unfired clay in geological time is destroyed at the point of firing. After a period of cooling the energy storing process starts anew and a certain amount of stored energy is gained annually. At the re-heating of a material sample taken from the fired object impulses of emitted light can be measured in the laboratory which correspond with the time interval between the present observation and the last firing. These findings have provided us with the basic principles of scientific dating methods.

The TL-test concerns itself with 3 variables:

1. The so-called 'archaeological energy ' or N T L - .
the name already indicates that an archaeological, i.e. historical aging has been
registered since the last firing of the object.
2. The 'neutral energy ' - ß or NTL + ß (alpha)
which is the amount of energy emitted by the same material after renewed exposure
to radiation from a gauged radioactive source.
3. The 'annual energy rate ' or JD which represents the annual increase of accumulatively stored energy.

These variables interrelate in the following ways:

$$\frac{\text{archaeological energy}}{\text{neutral energy}} = \text{archae.dose} \qquad \frac{\text{archaeological dose AD/ED}}{\text{annual energy rate D / JD}} = \text{Age}$$

Archaeological / historical and neutral energy rates already provide initial clues to the final test result.

a) In a case where archaeological energy can be established the neutral energycurve, in certain areas, runs proportional to the archaeological curve.b) In the case of a recent copy no proportional run of curves can be observed due to the obvious absence of any archaeological / historical energy.

In order to determine the 'annual energy rate and thereby the exact age of an object,
the object specific energy output of the three basic radiation types; alpha, beta and gamma rays, has to be defined. At this point which touches at the boundaries of nuclear physics, the exact dating of objects of art often becomes problematic.A precise evaluation of the gamma radiation energy is only possible when the exact geological conditions at the location of origin of the examined find are known. Since this is very often no longer possible an insecurity factor of +/- 3 to 20 to 25% of the calculated age has to be taken into account.Alpha and beta rates can be measured in the material samples taken from the object.The exactness of the result, i.e. the calculated age depends on the grade of precision with which these values can be determined. A relative limitation of such insecurities can be archived with the provision of comparative data from secured excavation sites and other safe' sources. Empiric values which can often serve to fill the gaps left in the purely analytical evidence supplying process.The Laboratory Kotalla, as one of the oldest institutes of its kind, is consequently in the fortunate position of being able to take full advantage of their extensive archives.

Lit.: Daniels, C. A. Boyd & D. F. Saunders: Thermoluminescence as a Research Tool. In: Science. 117, 1953, S. 343–349.
F. G. Houtermans & H. Stauffer: Thermolumineszenz als Mittel zur Untersuchung der Temperatur- und Strahlungsgeschichte von Mineralien und Gesteinen. In: Helvetica Physica Acta. 30, 1957, S. 274–277.
N. Grögler, F. G. Houtermans & H. Stauffer: Radiation damage as a research tool for geology and prehistory. In: 5° Rassegna Internazionale Elettronica E Nucleare, Supplemento Agli Atti Del Congresso Scientifico. 1, 1958, S. 5–15.
Chr.Goedicke /Henschel. Datierung-Methoden Baessler Archiv bd 41 Heft
Berlin 1994 Riederer J 1984. Echt und Falsch Berlin,Heidelberg, New York

LIPS Analysis

LIBS is one of several analytical techniques that can be deployed in the field as opposed to pure laboratory techniques e.g. spark OES. As of 2015, recent research on LIBS focuses on compact and (man-)portable systems. Some industrial applications of LIBS include the detection of material mix-ups,[8] analysis of inclusions in steel, analysis of slags in secondary metallurgy,[9] analysis of combustion processes,[10] and high-speed identification of scrap pieces for material-specific recycling tasks. Armed with data analysis techniques, this technique is being extended to pharmaceutical samples.[11][12]

LIBS using short laser pulses [edit]

Following multiphoton or tunnel ionization the electron is being accelerated by inverse Bremsstrahlung and can collide with the nearby molecules and generate new electrons through collisions. If the pulse duration is long, the newly ionized electrons can be accelerated and eventually avalanche or cascade ionization follows. Once the density of the electrons reaches a critical value, breakdown occurs and high density plasma is created which has no memory of the laser pulse. So, the criterion for the shortness of a pulse in dense media is as follows: A pulse interacting with a dense matter is considered to be short if during the interaction the threshold for the avalanche ionization is not reached. At the first glance this definition may appear to be too limiting. Fortunately, due to the delicately balanced behavior of the pulses in dense media, the threshold cannot be reached easily.[*citation needed*] The phenomenon responsible for the balance is the intensity clamping[13] through the onset of filamentation process during the propagation of strong laser pulses in dense media.

A potentially important development to LIBS involves the use of a short laser pulse as a spectroscopic source.[14] In this method, a plasma column is created as a result of focusing ultrafast laser pulses in a gas. The self-luminous plasma is far superior in terms of low level of continuum and also smaller line broadening. This is attributed to the lower density of the plasma in the case of short laser pulses due to the defocusing effects which limits the intensity of the pulse in the interaction region and thus prevents further multiphoton/tunnel ionization of the gas.[15][16]

Line intensity [edit]

For an optically thin plasma composed of a single, neutral atomic species in local thermal equilibrium (LTE), the density of photons emitted by a transition from level *i* to level *j* is[17]

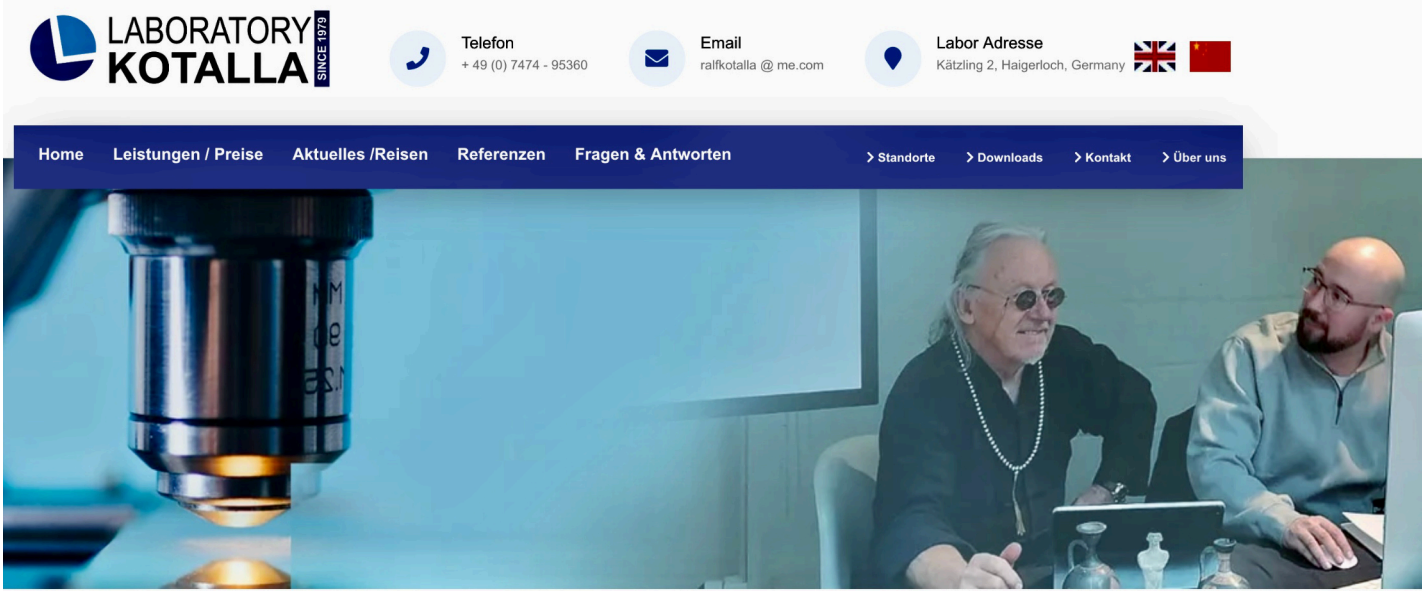
$$I_{ij}(\lambda) = \frac{1}{4\pi} n_0 A_{ij} \frac{g_i \exp^{-E_i/k_B T}}{U(T)} I(\lambda)$$

where :

- I_{ij} is the emission rate density of photons (in $m^{-3}\ sr^{-1}\ s^{-1}$)
- n_0 is the number of neutral atoms in the plasma (in m^{-3})
- A_{ij} is the transition probability between level *i* and level *j* (in s^{-1})
- g_i is the degeneracy of the upper level *i* (2J+1)
- $U(T)$ is the partition function (in s^{-1})
- E_i is the energy level of the upper level *i* (in eV)
- k_B is the Boltzmann constant (in eV/K)
- T is the temperature (in K)
- $I(\lambda)$ is the line profile such that $\int_{-\infty}^{\infty} I(\lambda) d\lambda = 1$
- λ is the wavelength (in nm)

The partition function $U(T)$ is the statistical occupation fraction of every level k of the atomic species :

$$U(T) = \sum_j g_j \exp^{-E_j/k_B T}$$



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