

# Using natural luminescent materials and highly sensitive sintered dosimeters MCP-N (LiF:Mg,Cu,P) in radiation dosimetry.

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The main trend in radiation dosimetry nowadays is the use of solid state detectors. Luminescent dosimetric techniques are part of this field. This paper aims to present the application of thermoluminescence as a tool in measuring natural nuclear radiation, namely the application of highly sensitive sintered dosimeters MCP-N (LiF:Mg,Cu,P) in environmental monitoring and the possibility of using natural crystals with luminescent properties in retrospective dosimetry. Thermoluminescent MCP-N detectors based on LiF:Mg,Cu,P can be used in environmental monitoring for periods as short as two weeks. A set of detectors was placed conform standard procedures for 6 weeks in a location with presumed normal gamma background. The annual gamma dose rate determined was 0.695mGy. The influence of building materials radioactivity was also observed over the same period of exposure proving the sensitivity of the method. Also the accumulated dose in quartz grains from ancient pottery was determined and this enabled us to date those artifacts, the ages obtained being in agreement with the ones presumed by the archaeologists.

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## 1. Introduction

Thermoluminescence requires the perturbation of a system from the state of thermodynamic equilibrium, via the absorption of external energy into a metastable state. This is then followed by the thermally stimulated relaxation of the system back to its equilibrium condition.

So, thermoluminescence is the emission of light during heating of a solid sample (insulator or semiconductor), previously excited by radiation. The TL material absorbs energy during exposure to radiation and stores this energy until heated. The intensity of emitted light as function of the temperature is the thermoluminescence glow curve.

Although the first theoretical elaboration of thermoluminescence was submitted in the middle of the last century there is no general theoretical model up to now. The theoretical explanations are based on electron band theory. Simple models can explain basic features like the shape of the glow curve, but the more complex models involve sets of coupled, non-linear, first order, differential equations.

For dosimetry applications the integrated area under the glow curve or the peak high has to be proportional to the radiation dose. Thus we are having a relative method, based on accurate calibration.

Thermoluminescence was suggested to be used as a research tool in the fifties and now has two main applications. The first one is related to the use of sintered solid state luminescent detectors in dosimetry, namely environmental monitoring, accidental dosimetry or

monitoring nuclear facilities. The other main application is the use of natural crystals such as quartz, feldspars or zircon for retrospective dosimetry and this lead to the development of dating techniques.

Since its occurrence every living being is exposed to natural ionizing radiation. This radiation comes from the earth itself (gamma background) or comes from cosmos (cosmic radiation) and causes that all goods, food, and the air that we breathe to be partially radioactive. In addition to natural radiation, the contribution from man-made ionizing radiation sources should not be neglected.

The average radiation burden for the population is estimated to be around 3.6 mSv/y of which 2.6 mSv/y comes from natural sources. Soil and buildings on average contribute to 0.4 mSv/y and the cosmic radiation 0.3 mSv/y. These factors were monitored. The rest is mainly due to radon.

The objective of environmental monitoring is to provide data on natural background radiation. In this way areas where the contribution of the man-made radioactive sources is high can be determined and measures for protection can be undertaken. A permanently country-wide background monitoring with passive dosimeters could serve as a basis for the calculation of the contribution to dose in unfortunate cases of accidental situations.

Thermoluminescent dosimetry systems are permanently developed and improved. The main TLD used in environmental monitoring at the present are: LiF:Mg,Cu,P; CaSO<sub>4</sub>:Dy; CaF<sub>2</sub>:Dy; Al<sub>2</sub>O<sub>3</sub>:C; LiF:Mg,Cu,Na,Si.

LiF:Mg,Cu,P TL pellets are the most popular dosimeters used in environmental monitoring due to their high sensitivity that permits usage over a broad range of environmental surveys: in short-term measurements lasting from a few hours to a few days and in long term monitoring which lasts for months or years. In 1987, MCP-N (LiF:Mg,Cu,P) sintered pellets, of 4.5mm diameter and 0.9mm thickness were first developed by Niewiadomski in Krakow, Poland. Over the following years the properties of this detectors such as fading, light sensitivity, lowest detectable dose, self-dose, zero-dose, energy response, and the influence of annealing and readout conditions on detector stability have been systematically studied and optimized. MCP-N type detectors are now commercially available at TLD Poland and are used by hundreds of laboratories around the world. This is the kind of detectors we also used.

The second part of our work concerned the determination of the accumulated dose inside the quartz coarse grains that we extracted from some pottery shreds. The dating of pottery by means of thermoluminescence has been investigated in the last thirty years in different laboratories all over the world. The principles of TL dating were widely discussed by Aitken (Aitken et al 1968; Aitken 1985) and Mejdahl (1970). Fleming (1970, 1971) has developed two techniques of TL dating. A comprehensive study concerning the laboratory procedures and protocols has been done by Ann Wintle (Wintle 1998). Unfortunately no laboratory in Romania uses thermoluminescence as a standard procedure for dating. As far as we are aware the only attempt of applying the TL method in dating was made in 1996 by a team from Bucharest and the study concerned speleothems dating (Labau et al., 1996). In the present work TL datings of ancient ceramics found on different archaeological sites from Romania are given. Five types of Eneolithic pottery were extracted from two different archaeological sites namely Alba-Iulia and Zau de Campie. Archaeologists believe that all of this samples are artifacts produced by Petresti Culture (3000-4000 BC). Also two types of Roman ceramics were investigated.

## 2. Experimental method

### A) Environmental dosimetry

Highly sensitive LiF:Mg, Cu, P

The environmental gamma background was measured using a batch of LiF:Mg, Cu, P dosimeters. The dosimeters went through the regeneration treatment consisting in a 10 minute preheat at 240°C. Then the background was measured. Of the existent batch a subset was used for construction the calibration curve. For this sets of dosimeters were irradiated with known gamma doses. A calibrated gamma source with a known dose rate  $D=6.9889 \text{ Gy/h}=0.001941361 \text{ Gy/s}$  was used..

The dosimeters were placed in an area with assumed normal radioactive background in conformity with the standard procedure namely placing them at 1m above ground level and cover them in aluminum foil to get rid of the beta contribution. They were left there for six weeks, a relative short period for passive measurements.

For reading a Harshaw TL 2000 reader was used. A constant heating rate of 5°C/s was employed, and integrating recordings were performed in the temperature range: 120-240°C for avoiding the unwanted unstable peak at 110°C and getting the most of the rest of the glow curve, namely the main dosimetric peak.

To test the sensitivity of the method a batch of dosimeters were placed inside a bulding to see if the influence of the radioactivity of the building materials can be observed.

### B) Retrospective dosimetry

Natural crystals with dosimetric properties (quartz)

Sample extraction

The pottery shreds were collected from a uniform soil, relatively free of rocks and building materials. The depth from which the shreds were collected ranged between 0.5m (Roman 1) and 3.2m (Zau 1). A sufficient amount of soil surrounding the buried pottery was taken to estimate the dose rate from the radioactive elements to which the ceramics was exposed.

Sample preparation

The quartz inclusion technique was used. 2mm of the outer surface of the pottery were removed to eliminate the beta radioactive contribution of the soil, followed by a gentle crushing. The grains larger than 200µm were removed by sieving. Then the samples were treated with 4N HCl for carbonate removal and repeatedly washed with dionized water and H<sub>2</sub>O<sub>2</sub>. The fine grains in suspension were removed. For eliminating fine grains also sieving and acid attack were performed. For etching the outer surface of the grains and eliminating the feldspars a treatment with 40% HF for 30 minutes was made.

Accumulated dose determination (paleeosose or equivalent dose)

For the TL measurements a Harshaw 2000 reader system was used. The quartz grains were placed on a controlled heated tray (50C/s). Integrated measurements were performed in the temperature interval 250-400oC as quartz exhibits its main dosimetric peak at 375oC. Background corrections for the TL signals were performed. The natural TL signal was determined as an average of six measurements (six sample discs) for each ceramic type.

For determining the equivalent dose the additive dose procedure was used assuming that the sensitivity to the laboratory irradiation is the same as it had been for radiation during burial (Wintle 1998). The radioactive source used was a Co-60 gamma source with a dose rate of 6.9272 Gy/h. A growth curve was constructed on the basis of three additive  $\gamma$  doses using six samples for each dose. For estimating the supraliniarity correction the samples were annealed for two hours at 500oC and then a  $\gamma$  regeneration growth curve was constructed on basis of the TL signals measured after the irradiation with four different known doses.

To be able to date these ceramics the annual dose was also determined.

The annual dose from the burial soil was estimated by means of gamma spectrometry using a NaI(Tl)

scintillation crystal and a NP-424 four channel analyzer (Gamma – Hungary). Because uranium and thorium ores should be in series equilibrium with their daughter products the main peaks used were 1764.5 keV (Bi-214 in U-238 series) and 2614.5 keV (Tl-208 in Th-232 series). For potassium the 1460 keV peak was used (Hossain et al. 2002). The concentrations in ppm and % for potassium were calculated and the dose was estimated using the conversion factors given by Bell 1977.

The internal annual dose coming from the shred matrix itself was determined using instrumental neutron activation. The samples were irradiated for 15 minutes in channel K11 of reactor TRIGA, Pitesti Romania. The thermal neutron flux was  $6.91 \cdot 10^{12} \text{ n/cm}^2/\text{s}$  and the ratio thermal per epithermal neutron flux was 43.13. After a decay time of 180h K0 method was used for determining

the concentrations of U and Th. The nuclear data used were G. Erdtmann-Neutron activation table and F. De Corte-Atomic Data and nuclear data tables 85 (2003).

The cosmic dose rate in the soil was accepted to amount to 0.150 mGy/ year (Van Den Haute 1999).

### 3. Experimental results

A) The background of the dosimeters used is very low as it can be seen in table 1. This shows the fact that the low limit of detection is very good and these dosimeters can be use for short term measurements:

The results obtained for the exposure time are presented in tables 1 and 2

Table 1. Background signal of LiF:Mg, Cu, P TLDs.

TLD no	1:2	3:4	5:6	7:8	9:10	11:12	13:14	15:16	17	Mean back-ground (nC)	Standard dev (nC)
Background signal (nC)	2.43 2.41	2.7 2.38	2.37 2.64	2.6 2.5	2.5 2.35	2.66 2.02	2.57 2.46	2.65 2.66	2.72	2.49	0.218

Table 2. Environmental gamma doses for six weeks of exposure in an environment with assumed normal radioactivity.

TL signal (outside (nC)	Mean TL signal (outside) (nC)	Standard deviation (nC)	Accumulated dose in 6 weeks (mGy)
32.71 38.25 26.51	32.49	6.4	0.0803

Table 3. Environmental gamma background for six weeks of exposure inside a building made of bricks.

TL signal (inside building) (nC)	Mean TL signal (inside building) (nC)	Standard deviation (nC)	Accumulated dose (mGy)
36.71 42.51 31.91	37.04	5.3	0.0916

The annual dose rate was calculated and  $D_\gamma = 0.695 \text{ mGy/y}$  was obtained.

Inside the monitored building the annual gamma dose rate was  $D_\gamma = 0.793 \text{ mGy/an}$

The results show a normal radioactive background. This gamma background contain both the contribution on the terrestrial gamma radiation and cosmic radiation. At one meter above ground the terrestrial gamma dose rate can vary in normal conditions between 0.2 mGy/y and 1mGy/y depending on the types of rocks in the soil. Considering the cosmic radiation to be 0.26-0.28mGy/y we can see that we are placing in normal limits.

B) The growth curves from Neolithic and Roman samples are shown in the following in Fig.1 and Fig.2

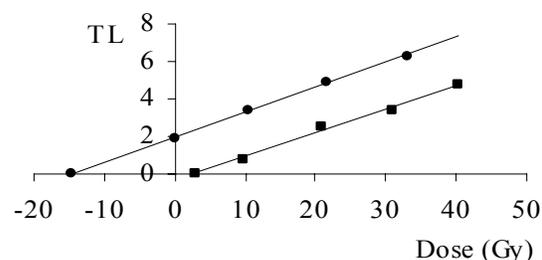


Fig. 1. Growth curve for quartz grain samples extracted from Eneolithic ceramics discovered at Alba-Iulia (Sample Alba 1).

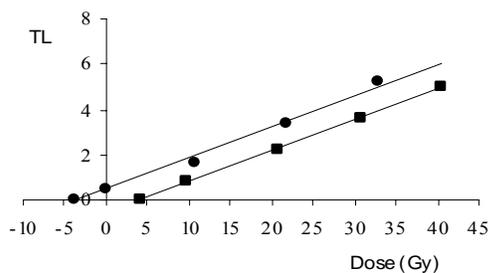


Fig. 2. Growth curve for quartz grain samples extracted from Roman ceramics ( Sample Roman 1).

It can be seen that the paleodose for the Neolithic ceramics is much higher than the Roman case. On the other hand the correction terms for the Roman ceramics are quite high in comparison to the Neolithic pottery especially for the younger sample (Roman 1), 4.17 Gy. These results suggest the differences existent in the composition of the pottery matrix.

The annual doses calculated for the five Eneolithic samples range in a small interval. For the pottery extracted from Alba Iulia site the same value was obtained as expected due to the fact that all these three samples were the same pottery type (3.45 mGy/year). Very close values were obtained for the two samples collected from Zau de Campie respectively 3.53 and 3.36 mGy/year. These data along with the ages obtained are in good agreement to the archaeologists supposition namely that all the artifacts discovered in these two sites are products of the same culture.

Errors involving the determination of the paleodose are less than 5 %. The main problems are related to the estimation of the annual dose, especially the case of external gamma dose. The overall errors for concerning the annual dose are around 6.5 %, resulting as total errors about 8 % for age determination.

The ages obtained are 5028 $\pm$ 400y respectively 5216 $\pm$ 415y in good consistence to the ones estimated by archaeologists (5000-6000y) for the Neolithic samples. For the Roman samples the results are 1798 $\pm$ 140y respectively 1889 $\pm$ 150y.

Table 4. Accumulated doses in quartz grains extracted from pottery and the related ages.

Sample	Equivalent dose(ED) (Gy)	Correction term (I) (Gy)	Archaeological dose (AD) (Gy)	Annual dose (mGy)	TL age (year)	Mean TL age (year)
Alba 1	14.46	2.88	17.35	3.45	5028	5028 $\pm$ 400
Alba 2	14.33	3.05	17.38		5038	
Alba 3	14.40	2.91	17.31		5018	
Zau 1	15.62	2.27	17.89	3.53	5065	5216 $\pm$ 415
Zau 2	14.73	3.32	18.05	3.36	5366	
Roman 1	3.65	4.17	7.82	4.35	1798	1798 $\pm$ 140
Roman 2	5.98	3.35	9.33	4.94	1889	1889 $\pm$ 150

#### 4. Conclusions

Materials that exhibit luminescence properties and also have the specific property of having a proportionality between the amount of light emitted and the dose they were exposed to can be used as solid state dosimeters. These properties of the sintered LiF: Mg, Cu, P and natural quartz crystals extracted from ancient ceramics matrix were investigated and used.

It was shown that LiF: Mg, Cu, P is very sensitive and can be used for environmental monitoring.

The environmental gamma background was monitored in an area with supposed normal radioactivity for 6 weeks. The results obtained are encouraging (0.695mGy/y). Another experiment was to see if the influence of the radioactivity of building materials can be detected for the same short exposure time. The experiment was successful. As an alternative method we use small ionizing chambers. The results are in good agreement with the ones indicated by the TLDs proving the feasibility of the method.

The doses accumulated during the historical time in quartz crystals from ceramics were reconstructed and this also led to age determination of these artifacts.

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