Çankaya University Journal of Science and Engineering
Volume 8 (2011), No. 1, 15–25

Comparison of Sample Preparation Techniques Used in Luminescence Dating Methods

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Özet. Lüminesans ile tarihlemede, içerisinde kuvars vb. mineralleri içeren örneklerdeki lüminesans sayımı temeldir. Optik Uyarmalı Lüminesans (OSL) ve Termolüminesans (TL) yöntemleriyle gerçekleştirilen tarihlendirme çalışmalarında çeşitli teknikler kullanılarak örnek hazırlanmaktadır. Bu örneklerin hazırlanması kullanılan tekniğe bağlı olarak farklı aşamalar içermektedir. Bu aşamaları belirlemek, birbiriyle karşılaştırmak ve en uygun teknikleri saptamak amacıyla gerçekleştirilen bu araştırmada kimyasal uygulaması, ezme ve eleme işlemleri ele alınmıştır. Kimyasal uygulaması, ezme ve eleme işlemleri kullanılarak hazırlanan farklı 9 grup örneğin OSL ve TL sinyal şiddetleri elde edilmiş, tekniğe bağlı olarak sinyal şiddet değişimlerinin incelenmesi ve karşılaştırılması yapılmıştır. Elde edilen sonuçlara dayalı olarak, lüminesans yöntemlerle gerçekleştirilecek tarihlendirme çalışmalarında kullanmak üzere en uygun örnek hazırlama teknikleri belirlenmiştir.

Anahtar Kelimeler. Lüminesans tarihlendirme, örnek hazırlama tekniği, ezme, eleme.

Abstract. Age determination by the luminescence dating method is based on measuring the luminescence of samples that contain quartz or similar minerals. Accurate determination of the luminescence signal is essential and closely related to the sample preparation. Many kinds of techniques are used for sample preparation in Optically Stimulated Luminescence and Thermoluminescence dating. In this study, different sample preparation techniques, including crushing by hand or mortar, sieving by hand or sieve shaker and chemical application were compared. Different groups of samples were prepared and then the OSL and TL luminescence signals were examined. According to results, the best sample preparation techniques were determined.

Keywords. Luminescence dating, sample preparation technique, crushing, sieving.

1. Introduction

Luminescence dating is a method that is used to determine the time that has elapsed since sediment was last exposed to sunlight or a piece of pottery was last heated. It is based on the emission of light, when the material is heated or illuminated and can be applied to the materials that contain quartz or feldspar. Therefore, this method

Received June 28, 2010; accepted January 25, 2011.

ISSN 1309 - 6788

is a widely used for environmental dosimetry and dating archeological and geological materials [1-4].

Geological and archaeological materials, such as bricks, tiles, pottery, or porcelain are routinely used in the dating. In addition luminescence methods provide the possibility for dating earthquakes and different kinds of materials such as anthropological bones and teeth [5-7]. Recently, Yüce *et al.* [8] applied hydrazine reagent to human tooth enamel to determine beta dose response and OSL signal stability characteristics. Even if the techniques are different, the sample preparation procedures of luminescence methods contain certain common processes. To get the accurate age of the sample these processes should apply in such a way as to avoid causing additional luminescence, or loss of luminescence.

Luminescence dating method is based on the constituent mineral grains of the sediment such as quartz, or feldspars. Because the method is specific, the signals should be collected very carefully for an accurate age calculation. Determining the most suitable procedure and applying it correctly to the samples provides reliable results.

Therefore, the sample preparation procedure is very important. A good sample preparation process is based on appropriate laboratory facilities, the sample and its mineral content. So in this study, we aim to find the best sample preparation procedure for luminescence dating methods. By investigating the sample preparation methods presented in national and international luminescence articles, we determined the common processes, such as crushing, sieving and chemical processes. By changing the order of the processes in application, nine different sample preparation techniques were generated. Then these techniques were applied to a common sample that was a pottery sherd and the change of the luminescence signal was examined according to the applied technique. The crushing process was applied by hand or mortar and the sieving process was applied by hand or sieve shaker. Then the luminescence signals were obtained and their relation to the applied technique was explained. Based on these results, we propose specific sample preparation techniques both for OSL and TL dating.

2. Experimental Section

2.1. Sample preparation. Sample preparation techniques are summarized in Figure 1. A part of an ancient pottery sherd was used for the study that was taken from an ancient region of Mardin in Turkey.

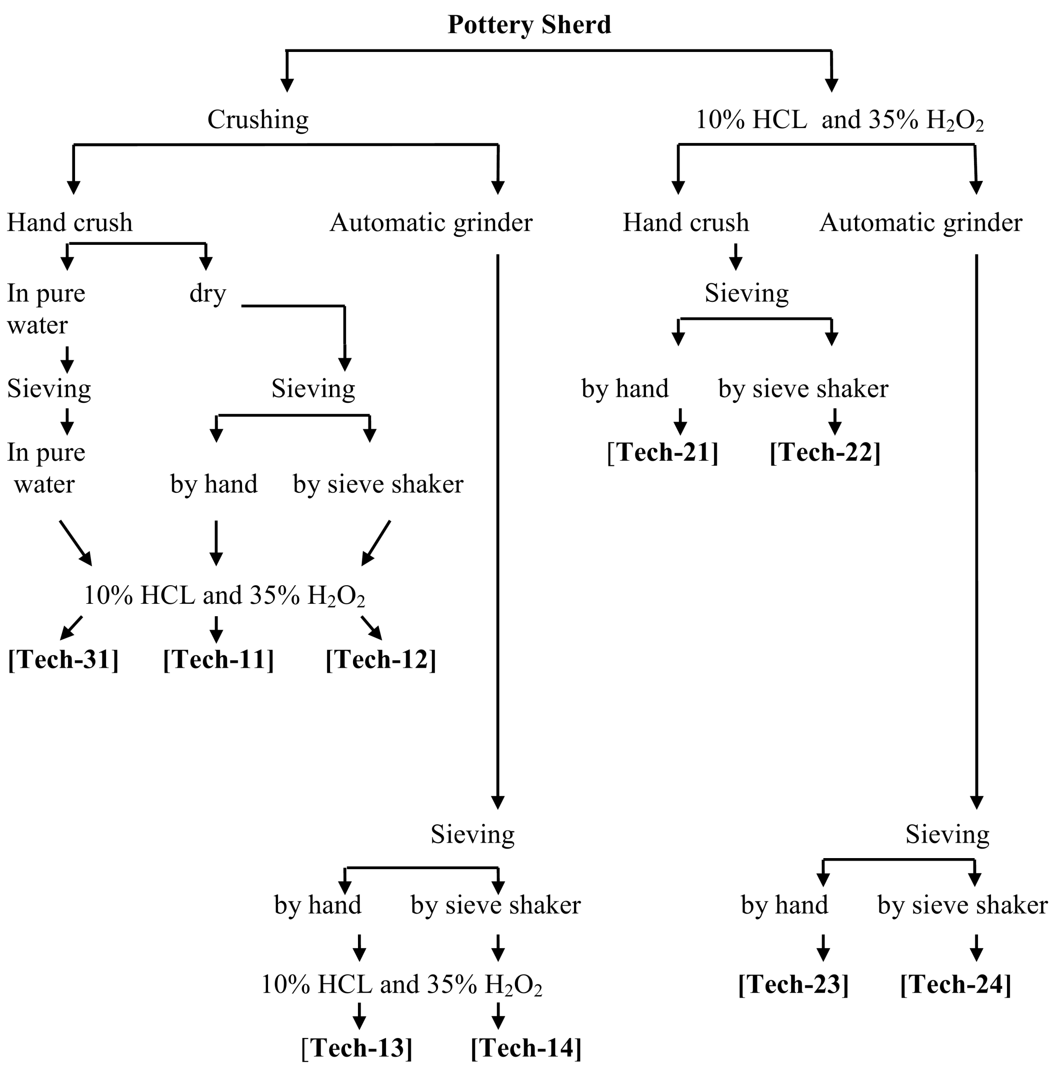
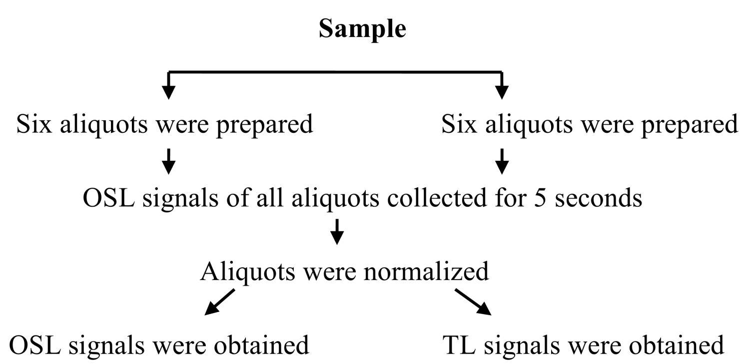


FIGURE 1. Flow chart of applied techniques.

First, after removing its 1cm outer layer, the pottery sherd was gently crushed to suitable sizes. Then it was separated into certain main parts in order to apply the determined techniques. The first part of the pottery sherd was crushed by hand and the second part with an automatic mortar. By hand, using a mortar and a pestle a gentle crushing process was done, until the grains had been reduced to $< 90\mu$m dimension. The same treatment was applied to the third part when it was in pure water. Crushing with an automatic mortar and pestle was carried out by rotating it for 10 min. After that all the crushed samples were sieved with a $< 90\mu$m grain size fraction by hand or sieve shaker according to the applied technique. By hand, using the sieve, the crushed samples were sieved for 10 min. The other parts were sieved in sieve shaker for 10 min. Finally all these samples were washed in 10% HCl until the reaction finished, and in 35% H_2O_2 for 12 hours to remove carbonates and organic materials.

After washing in pure water they were left to dry. These prepared samples were called Tech-11, Tech-12, Tech-13, Tech-14, and Tech-31. The fourth part of the sample was first washed in 10% HCl until the reaction finished and in 35%H_2O_2 for 12 hours to remove carbonates and organic materials. Then it was crushed by hand or automatic mortar and sieved by hand or sieve shaker. Finally, these samples were called Tech-21, Tech-22, Tech-23, and Tech-24. For the TL and OSL measurements, grains were pasted using silicon spray on aluminum discs of 10mm diameter and 0.5mm thickness and then the natural luminescence signals were collected. All these preparation procedures were done in a dark room under the subdued red lamp.

In this study all the luminescence signals were collected from coarse polymineral grains, meaning that quartz and feldspar minerals were not separated. The normalization of the aliquots were done by collecting all the aliquots' OSL signals during an interval of 5 seconds.



2.2. Measurements. The apparatus used in this study is the Optical Dating System 9010 Reader, developed by Spooner *et al.* [9], and the Harshaw 3500 Thermoluminescence Dosimeter Reader System. The Optical Dating System was used to observe the OSL of the samples by stimulation with 880 ± 80 nm wavelengths. All data were collected using an IRSL add-on unit for the 9010 automated reader, using TEMT 484 IR diodes that run at 40mA giving a power of about 30 mW/cm^2. Luminescence was detected using a Thorn EMI 9235 QA photomultiplier tube. The thermoluminescence of the samples was measured using the luminescence reader with a heating rate of 5°C/s up to 500°C. The samples was irradiated with a ^{90}Sr β-source with a dose rate of 0,0292 Gy/s on an aluminum disc.

2.3. Equivalent dose measurements. When measuring the equivalent dose of the sample it is important to eliminate the unstable components. Therefore, the preheating procedure for OSL measurements and the plateau test for TL measurements were performed in this study. The plateau region is determined as the stable region of the ratio of the natural and natural+artificial glow curves [1]. The preheating procedure was performed by holding the time constant and increasing the temperature and then vice versa [2]. The experiments showed that a preheat temperature of 200°C for 3 min and the plateau region of 325-400°C was found to be suitable for the polymineral grains.

As mentioned, in the sample preparation, after applying nine different techniques, their natural luminescence signals were read and tabulated in Table 2. To see the effect of the sample preparation procedure on the luminescence signals, age determination was carried out. In order to determine the equivalent doses of the groups, a multiple aliquots procedure (MAAD) was applied [10].

The steps applied in MAAD:

Twenty one aliquots were prepared from each group

▼

The aliquots were normalized by collecting OSL signals for 5 seconds

▼

Irradiation of aliquots (N),(N+4),(N+8),(N+12),(N+16),(N+20),(N+24)Gy

▼

Left for 24 hours

▼

Preheating (200°C, 3 min)

▼

OSL-TL Measurements

2.4. Determination of dose rate. In this study, for the dose rate (annual dose) calculation, a high-purity germanium detector was used to measure the concentration of U, Th and K (Coaxial p-type HPGe Detector with Relative Efficiency: 33%, Ortec). In addition, the water content of the sample was measured, and the cosmic ray contribution and water uptake during burial were also taken into account [1]. Measurements and calculations are tabulated in Table 1.

Table 1. Annual dose data.

U (ppm)	Th (ppm)	K (%)	W	ACD (mGy/a)	Annual Dose (mGy/a)
4.48 ± 0.18	9.19 ± 1.40	1.33 ± 0.05	0.44 ± 0.006	0.1370	2.47 ± 0.12

ACD: annual cosmic dose, W: saturation water content.

3. Results and Discussion

Natural OSL and TL results of the samples are listed in Table 2.

Table 2. Natural luminescence counts of the samples.

Sample	OSL(counts)	15% Interval of OSL	TL (counts/s)	20%Interval of TL
Tech-11	1520±76	<u>1520±76</u>	12531±626	12531±626
Tech-12	2373±118	2373±118	8366±418	<u>8366±418</u>
Tech-13	2282±114	2282±114	7823±391	7823±391
Tech-14	1756±87	<u>1756±87</u>	11926±596	<u>11926±596</u>
Tech-21	1134±56	<u>1134±56</u>	48058±2402	48058±2402
Tech-22	1634±81	1634±81	65064±3253	65064±3253
Tech-23	1656±82	<u>1656±82</u>	64069±3203	64069±3203
Tech-24	1139±56	1139±56	60058±3002	60058±3002
Tech-31	1417±70	<u>1417±70</u>	9449±472	<u>9449±472</u>

OSL results were obtained by reading each aliquot for 200s and TL results were collected by reading each aliquot's TL plateau region tested before as 325-400°C. As tabulated in Table 2, there is a distribution of the data obtained by applying the different techniques to the same sample and the distribution displayed a wider range in TL than OSL. The samples consist of both feldspar and quartz, whereby the OSL results are based on the feldspar, and TL results on the quartz in the same sample. These results indicate that the OSL and the TL intensity variations seem to be closely related with the sample preparation technique. This led us to focus on the importance of choosing and applying the right technique to increase the reliability of the ages. Our approach relied on calculating the systematic and experimental errors. We obtained the average of the luminescence counts of all TL results. Then according to systematic and experimental error results, the error limits were computed at 20% for the TL method. Using this knowledge, the results, produced by the different techniques were restricted to a ±20% range for the TL interval from the average and this determined the applicable sample preparation techniques. The same procedure was applied to the OSL results and, according to systematic and experimental error results, the error limits were computed at 15% for the OSL method according to [1]. The results restricted to the ± 15% range for OSL and the ±20% range for the TL are underlined in Table 2.

In this way, five different types of technique (Tech-11, Tech-14, Tech-21, Tech-23, Tech-31) for the OSL dating method and three types of technique (Tech-12, Tech-14, Tech-31) for the TL dating method appear within the error limits.

3.1. Crushing. Analysts frequently need to crush geological or archaeological samples for OSL or TL dating. In this study, the crushing process was applied by hand or automatic grinder. The comparison of these two different processes is done by comparing the obtained luminescence signals of Tech-11, Tech-13 and Tech-21, Tech-23. As is shown by the sample preparation flow chart (Figure 1) the crushing mechanism was the variable factor in four samples only. There was also a notable increase in the counts of Tech-13 and Tech-23 with respect to Tech-11 and Tech-21. It seems that crushing with the automatic grinder increases the OSL signals. Therefore we thought that the crushing process has an influence on the luminescence signal of the sample. However, the TL intensity of the same size grains decreased by crushing with an automatic grinder. Toyoda *et al.* [11] also observed similar results in TL when (106-150) μm quartz grains were crushed by an automatic grinder. Hiraga *et al.* [12] declared that TL intensities increase with increasing stress. In addition, Takeuchi *et al.* [13-15] proposed models of TL resetting in the near-surface layers of quartz grains during milling. This means that during the crushing process, friction, mechanical stress and pressure are the very important factors. Therefore, these results should be considered while preparing the sample.

3.2. Sieving. Sample preparation techniques also include sieving before dating with luminescence methods. This stage is important to specify the size of the grains and the sample can be sieved many times during preparation. Therefore, to investigate the effect of sieving on the TL and OSL signal, the process was carried out on the same sample at different times at room temperature then irradiated at 10 Gy and counts were obtained after a preheating procedure.

Table 3. Effect of sieving on the TL and OSL counts.

Sample	**OSL Counts (for 200s)**	**TL Counts** ($\times 10^3$)
Sieving one time by hand	36701	998
Sieving forty times by hand	79703	1260

Samples gave more counts both in TL and in OSL when they were sieved 40 times in a running process. The results are listed in Table 3 and the signals are in Figure 2. There was also a notable increase in the counts of Tech-22 with respect to Tech-21, both in TL and OSL, when sieving was applied by sieve shaker.

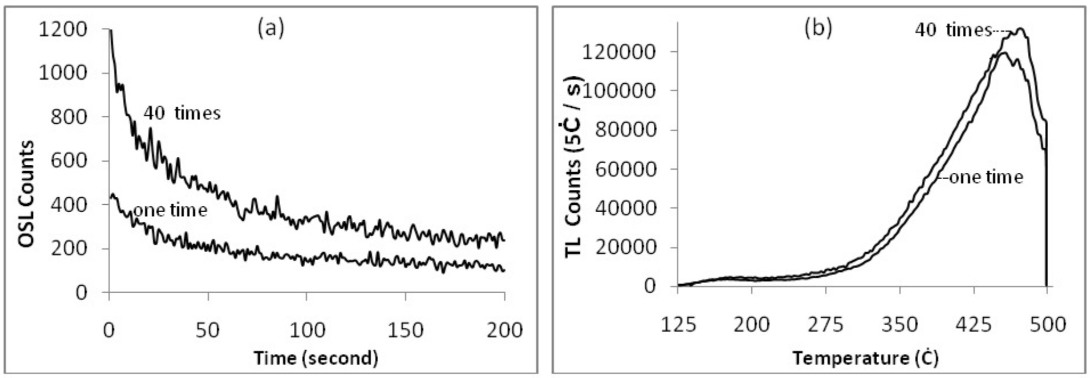


FIGURE 2. Increasing of (a) OSL signal and (b) TL glow curves after sieving forty times.

3.3. Chemical treatment. Chemical treatment was applied to the samples to remove carbonates and organic materials. In the sample preparation procedure, this process was performed for some groups at the beginning and for the other groups at the end. However, the treatment duration was the same for all the samples. At this stage, following the progress of the reactions is essential to avoid any harm to the quartz or similar minerals. Therefore all the processes should be applied carefully.

3.4. Age. In this study, OSL equivalent dose determination was done using polymineral grains by the MAAD procedure [10]. All aliquots were subjected to preheating before normalization and measurements. Normalization is done by collecting luminescence counts from all the discs during an interval of 5 second at first, while avoiding any harm to the natural signals. Irradiation was done for 4, 8, 12, 16, 20, 24Gy doses. The behavior of the sample against to the dose is drawn in Figure 3. OSL and TL curves were drawn, and the equivalent dose was calculated by extrapolation to the dose axis as in Figure 4. Table 4 shows the results of the equivalent dose behaviors of the samples. Although all of the groups were prepared from one pottery sherd, equivalent doses and ages were different from each other but in an agreement. For this pottery sherd the age was found only using the OSL and TL methods and the age which was found was the expected age.

Samples in Table 4 were chosen intentionally because their natural luminescence counts were restricted to the error limits. So the results are in agreement and provide a good match with each other.

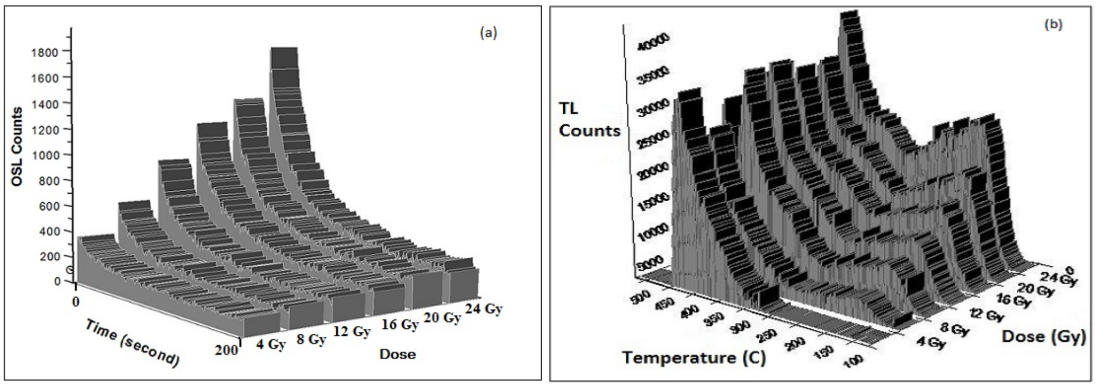


FIGURE 3. Three dimensional plot of the OSL (a) and TL (b) signals for MAAD protocol.

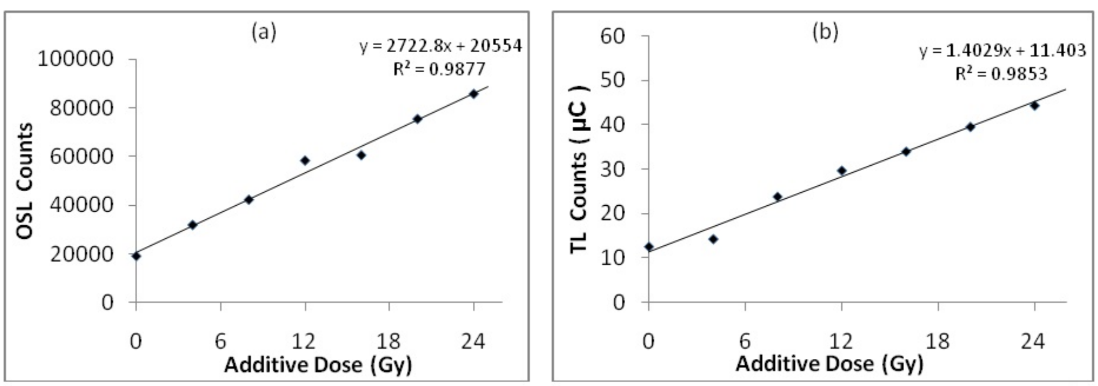


FIGURE 4. Equivalent dose determination for OSL(a) and TL(b) methods by MAAD protocol.

TABLE 4. Obtained equivalent doses and ages for the applied techniques.

Method	**Sample**	**Equivalent Dose(Gy)**	**Annual Dose(mGy/a)**	**Age (yrs)**
OSL	Tech-11	7.58±0.37	2.47±0.12	3060±280
TL	Tech-12	8.16±0.40	2.47±0.12	3300±300

4. Conclusions

According to the results, the luminescence signals are closely related to the sample preparation technique. Applying the right technique is essential for an accurate age calculation.

In this study different sample preparation techniques were applied to the same sample and the OSL and TL luminescence results of these techniques were examined. Their intensity variations and the possible reasons of these variations have been explained. After the applicable techniques for OSL and TL were determined according to those procedures, ages were calculated both in OSL and for a one sample in TL. The calculated equivalent doses in OSL displayed a good agreement within the limits of error. Through these results, we can say that the approach to determine the right techniques for the OSL and TL methods is acceptable and the determined techniques are applicable.

It was also observed that crushing is a very important factor. When it was applied in a very hard way, for example with an automatic grinder, it increased the surface area of a sample and caused a decrease of TL counts. But OSL counts did not decrease by crushing with an automatic grinder. Conversely, OSL counts were increased in general. It seems that mechanical stress and pressure are important factors in this study.

As mentioned in Section 3.2, more frequently sieved samples gave higher luminescence counts. This may be attributed to electrification by friction. However, more definite proof is needed about the effects of sieving. Nevertheless, it is clear that too frequent repetition of the sieving process can change luminescence counts and thus the age of the sample can be uncertain.

In addition we researched the effect of chemical treatment on OSL/TL signals when it was applied to the sample at the beginning or at the end of the process of preparing. However we did not find any evidence that application at the beginning or at the end changed the signals. This can be further studied by changing the treatment durations.

In conclusion, we propose specific sample preparation techniques for OSL and TL dating methods. But these techniques can change depending on the sample and its mineral content. We hope that the results obtained in this study will be helpful for the development of luminescence methods.

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