

## NORMALIZATION OF THERMOLUMINESCENCE DATA

W. L. MEDLIN, *Socony Mobil Oil Company, Inc., Field  
Research Laboratory Dallas, Texas.*

### ABSTRACT

In measuring the intensity of thermoluminescence in rock samples, variations in self-absorption within the sample must be accounted for. This paper describes two methods for doing this. One consists of mixing a thermoluminescent internal standard with the sample. The other involves measuring the diffuse reflectance of the sample in powder form and computing an appropriate normalization factor. A method is also described which corrects for transparency changes in a single sample due to heating.

### INTRODUCTION

Thermoluminescence has been applied with some success to problems of stratigraphic correlation and age determination of limestones. Both applications make use of glow curve data involving measurements of absolute emission intensities. But such measurements are subject to large errors because of self absorption effects within the sample. In many specimens variations in transparency give bigger effects than actual changes in emission intensity. So there is a serious need for methods of normalizing glow curve emission data for differences in opacity of the materials.

This paper describes three methods which should be applicable to nearly all limestone samples. One method uses an internal thermoluminescent standard. Another consists of measuring changes in diffuse reflectance from which the differences in absorption can be inferred. A third method, applicable to changes in a single sample, involves measurement of variations in luminescent emission intensity.

### INTERNAL STANDARD METHOD

The use of an internal thermoluminescent standard is analogous to techniques used in *x*-ray diffraction and spectrographic analysis. In this case the standard is a thermoluminescent material added in dilute proportions so that its emission is appreciably absorbed by the sample. The change in emission from the standard is taken as a measure of self absorption of its own thermoluminescence by the sample.

If the glow curve of the standard has an isolated peak of high intensity, it is convenient to normalize the data by taking the intensity ratio of each sample glow peak to the standard peak. This means that there are several, rather special requirements for the standard. It must have a glow curve whose peaks do not interfere with any of those due to the sample. Its glow curve should be simple, preferably with a single peak and the prominent part of its emission must occur in a temperature range where the sample glow is relatively low and unimportant. Also the intensity of

emission in this region must be great enough so that dilute mixtures (5–10 per cent) can be used. Finally, the spectral distribution of the standard emission should be similar to that of the sample.

The prominent part of nearly all limestone glow curves is restricted to temperatures above 300° K. For samples excited at low temperature the glow curve below 300° K. consists of a featureless region of low emission. This is illustrated in Fig. 1 which shows glow curves for samples of calcite and dolomite excited by  $\alpha$ -rays at liquid nitrogen temperature. These

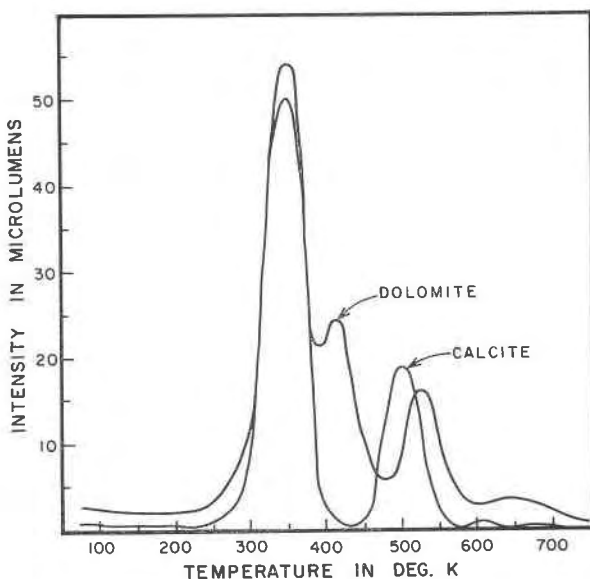


FIG. 1. Glow curves of representative samples of natural calcite and dolomite.

glow curves, and mixtures of the two, are representative of the thermoluminescence of nearly all limestone samples. Therefore a suitable standard would be one with a prominent glow peak below 300° K. and very little emission above this.

One of the well known commercial phosphors,  $\text{ZnF}_2$  with  $\text{Mn}^{2+}$  activator, has a glow curve of this type. When prepared under the proper conditions it has a single high intensity glow peak at 205° K. and no important emission above 300° K. (Johnson and Hughes, 1957). Since  $\text{Mn}^{2+}$  is also the impurity activator for most of the prominent glow peaks in calcite (Medlin, 1959) and dolomite (Medlin, 1961), the emission spectra are quite similar (Medlin, 1963b). So this material fits all of the requirements described above.

The  $\text{ZnF}_2$  standard has a serious disadvantage, however, in that it cannot be mixed homogeneously with calcite or dolomite. Apparently this

is due to differences in density. None of the usual mixing procedures give results with better than 30–40 per cent reproducibility.

Much better results have been obtained using synthetic quartz with Ti added as an activator. The Ti impurity produces a prominent glow peak at 165° K. (Medlin, 1963a) and there are several other closely spaced peaks in the 250–600° K. range. But under suitable conditions of preparation the 165° K. peak can be made three to four orders of magnitude more

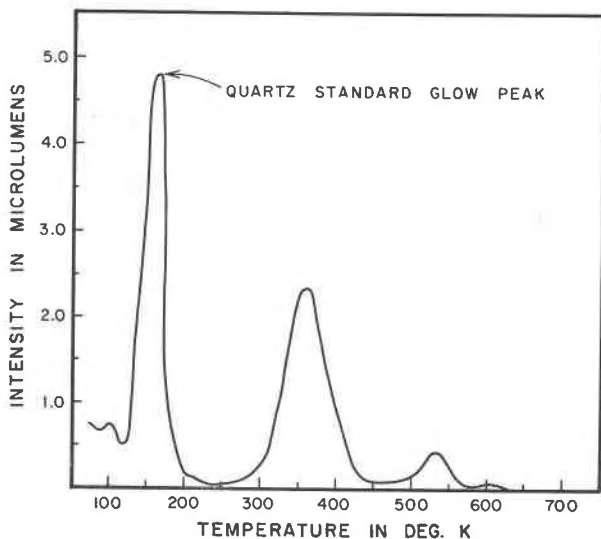


Fig. 2. Glow curve of a representative limestone sample containing 5 per cent Ti-activated quartz as a thermoluminescent standard.

intense than any of the others. In dilute mixtures, where the 165° K. peak has about the same intensity as the limestone glow peaks, there is no interference from quartz emission above 300° K.

Figure 2 shows the glow curve of a representative limestone sample mixed with 5 per cent of the quartz standard. The 165° K. glow peak is intense enough to use an even more dilute mixture with most limestones. But for concentrations below 5 per cent, weighing errors and mixing problems are troublesome. When both the standard and the sample are passed through a 325-mesh sieve and thoroughly mixed the results for the 5 per cent mixture are reproducible to within 10 per cent.

The disadvantage of the quartz standard is that its emission spectrum is unlike the one for the limestone glow peaks. The spectrum for the 165° K. quartz glow peak consists of a series of bands which cover most of the visible range (Medlin, 1963a), whereas the limestone glow peaks are

an orange emission corresponding to a single band in the 6700 Å region (Medlin, 1963b).

This is probably not a serious problem in most limestones, however, as shown by the reflectance spectra of Fig. 3. These curves were measured in the usual way by comparing the diffuse reflectance from several powdered limestone samples with a MgO standard. A Beckman Model DU spectrophotometer with reflectance attachment was used for this purpose. The results, for samples covering a wide range of transparencies, show

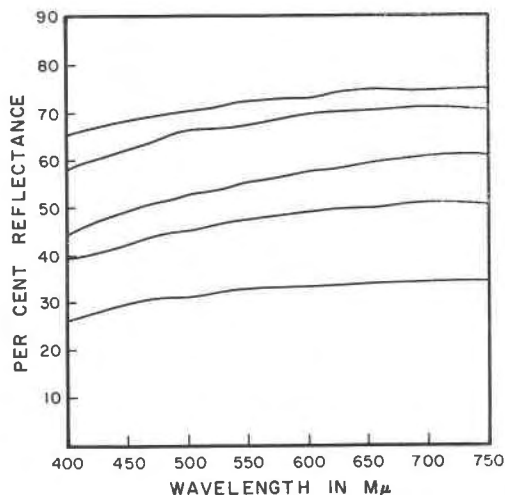


FIG. 3. Diffuse reflectance spectra of some powdered limestone samples.

that the absorption does not change much with wavelength. Furthermore, the variations which do occur are reproduced to good degree in all samples.

Synthetic preparation of the quartz standard involves hydrothermal crystallization of powdered samples from solutions containing the proper amount of Ti (Medlin, 1963a). This procedure is difficult and time consuming. It can be avoided in many cases by using natural samples which contain large concentrations ( $> 50$  ppm) of Ti. A general requirement is that the 165° K. Ti glow peak be at least two orders of magnitude greater than the other glow peaks. This seems to be adequate for all but a few limestone samples where the low temperature thermoluminescence is unusually high.

A disadvantage of the internal standard technique is that the emission from the standard is not absorbed in exactly the same way as the glow from the sample. In fact there are some surface grains whose emission is not absorbed at all. Because of this, the correction factor indicated by a

reduction in standard emission will always be too small. This effect is minimized by adding only dilute amounts of the standard and having both it and the sample finely divided.

The importance of this feature has been estimated by artificially darkening a high transparency calcite sample with carbon dust. A 5 per cent quartz mixture was used for the standard. Both the sample and the standard were sieved through a 325-mesh screen; and the results were judged by changes in the ratio of the 350° K. calcite glow peak to the 165° K. quartz peak. The data showed that this ratio increased by about 15 per cent for each tenfold decrease in 165° K. glow peak intensity.

In most cases this would not give errors much larger than the variations in reproducibility. But for samples covering a wide range of transparencies, appropriate corrections would be required. These can easily be made on the basis of results for an artificially darkened sample.

#### REFLECTANCE MEASUREMENTS

When the optical absorption coefficient is known in the wavelength region of interest, self absorption of thermoluminescence can be readily evaluated. The appropriate relation is derived as follows.

If  $\mu$  is the absorption coefficient and  $i dx$  the intensity of emission due to a layer  $dx$ , then

$$(1) \quad dI = i dx - \mu I dx$$

where  $I$  is the observed intensity. For small absorption of the exciting radiation ( $x$ -rays,  $\gamma$ -rays, etc.),  $i$  can be considered constant and (1) gives,

$$(2) \quad I = \frac{i}{\mu} (1 - e^{-\mu x}).$$

In the absence of absorption the intensity would be simply  $ix$ . So self absorption reduces the intensity of emission by the factor,

$$(3) \quad f = \frac{\mu x}{1 - e^{-\mu x}}.$$

In polycrystalline rock samples direct measurements of the absorption coefficient are unreliable because of light scattering effects. As a substitute, measurements like those in Fig. 2 of the diffuse reflectance of powdered samples can be made with reliability. The absorption coefficient at the appropriate wavelength can then be determined with reasonable accuracy (Kubelka, 1948) from the relation,

$$(4) \quad \mu = \frac{S(1 - R)^2}{2R}$$

where  $S$  is a scattering factor and  $R$  is the reflection coefficient for a sample thick enough to be opaque.

This relation can be substituted into (3) to give the desired normaliza-

tion factor. But the result is not useful without a value for the scattering factor,  $S$ , which depends on particle size, composition, and packing of the sample. All of these factors can be duplicated with suitable accuracy by using finely sieved samples packed in a reproducible manner. An approximate value for  $S$ , applicable to most limestone samples, can be determined by comparing the absorption coefficient of a clear single crystal of calcite with the reflectance data of the same sample after grinding, sieving, and packing in the appropriate manner.

Since most limestone samples are fairly opaque,  $e^{-\mu x} \ll 1$  for thicknesses of a millimeter or more. When this is true the expression for  $f$  can be approximated by the simpler relation,

$$(5) \quad f \approx \mu x = \frac{Sx(1-R)^2}{2R}$$

Therefore for most limestones the self absorption can be roughly accounted for by multiplying the glow peak intensities by the factor,  $(1-R)^2/2R$ , assuming  $S$  and  $x$  remain fixed within suitable limits. The error in this procedure may be fairly large, however, for samples of higher than average transparency.

We have used the reflectance method to normalize the glow peak data for a representative group of limestone samples. The results were compared with data obtained by the internal standard technique. The two methods give good agreement but in general the reproducibility of the internal standard results was better.

#### LUMINESCENCE MEASUREMENTS

For some applications, repeated measurements in a single sample are affected by transparency changes due to heating. An example is the procedure for age determination based on natural thermoluminescence (Zeller *et al.* 1957). The usual procedure is to heat the sample to eliminate all natural glow before irradiating it to measure the artificially induced emission. Darkening induced by the heating seriously affects a comparison of the natural and artificial glow.

In such cases, the degree of darkening can be determined by measuring the changes in intensity of luminescent emission. In limestones the luminescence is due almost entirely to excitation of the same  $Mn^{2+}$  emission which accounts for most of the thermoluminescence. Therefore the same emission centers are involved in both cases and so the absorption effects are identical.

Luminescence in limestones cannot be optically excited because the  $Mn^{2+}$  absorption is too low. So indirect excitation through host lattice absorption of  $x$ -rays or  $\gamma$ -rays is necessary. This means that a method of detecting emission during  $x$ - or  $\gamma$ -ray irradiation is required. The lumines-

cent intensity is then measured before and after heating and the glow curve data are normalized to account for the observed changes.

It is also possible that luminescence measurements could be used for glow peak normalization in place of the diffuse reflectance or internal standard techniques. This would require, of course, that the unabsorbed luminescence of all limestones be essentially constant in intensity.

Figure 4 shows that this may well be the case for most limestones. The data shown here give the intensity of luminescence vs  $Mn^{2+}$  content for

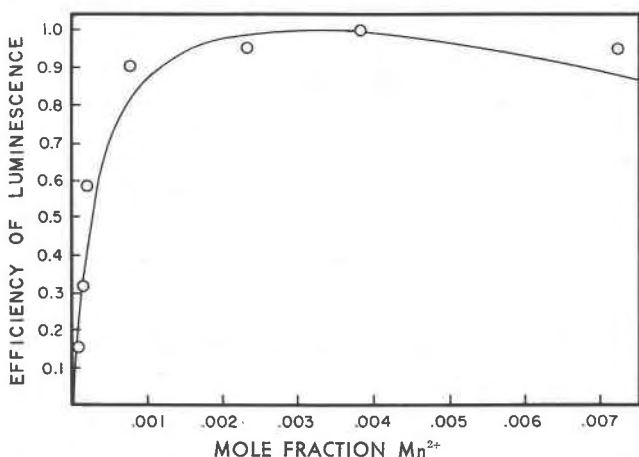


FIG. 4. Efficiency of luminescence as a function of  $Mn^{2+}$  content for some synthetic calcite samples.

some synthetic calcite samples prepared from high purity reagents. The results are representative of the behavior of activator impurities whose luminescence is quenched when other activator ions are located within a certain number of lattice distances. The curve drawn through the data points was computed for the case where this distance is 2 lattice spacings (Johnson and Williams, 1950).

Between 700 and 7000 ppm the luminescent efficiency, plotted in Fig. 4, does not change by more than 10 per cent. This range includes the  $Mn^{2+}$  content of most limestone samples. So if the results for the synthetic samples are applicable to natural specimens the luminescent intensity would be a suitable normalization index for glow curves. There are, however, two factors which might prevent this: (1) the quenching effect of other impurities, and (2) the quenching effects of lattice imperfections such as dislocations, vacancies, edges, etc.

The only common impurities which are expected to quench the  $Mn^{2+}$  emission are Fe, Co and Ni. All of these inhibit the thermoluminescent emission but have little effect on the luminescence (Medlin, 1963c). The importance of lattice defects has not been thoroughly investigated. But it

was found that the luminescence of some uncolored chalky limestones was only 10–15 per cent lower than that of single crystals with 1000–2000 ppm  $Mn^{2+}$ . These samples were representative of the maximum variation in crystallinity of most limestones. So, differences in the number of lattice defects does not appear to be an important factor.

On the basis of these results Fig. 4 seems applicable to most limestones; and normalization of glow curve data by this method appears feasible. However a more extensive evaluation will be necessary before the technique can be used with confidence.

#### CONCLUSIONS

Variations in transparency of limestone samples has an important effect on the measured intensity of thermoluminescence. These effects can be accounted for by either of two methods: (1) an internal thermoluminescent standard such as Ti-activated quartz can be mixed with the sample and changes in its thermoluminescent intensity used as a normalizing index; (2) the diffuse reflectance of the powdered sample can be measured and substituted in an appropriate normalization expression.

Changes in transparency of a single sample, such as those induced by heating, can be evaluated by measuring the differences in luminescence emission intensity. This requires a method for measuring emission during excitation by  $x$ -rays or  $\gamma$ -rays.

#### ACKNOWLEDGMENTS

The author wishes to thank J. M. Waite, W. H. Shelton, and R. D. Roland for their assistance and Socony Mobil Oil Company, Inc. for permission to publish this paper.

#### REFERENCES

- JOHNSON, P. D. AND F. L. HUGHES (1957) Energy states and luminescent processes in the  $ZnF_2:Mn$  phosphor. *Jour. Chem. Phys.* **26**, 612–617.
- , AND F. E. WILLIAMS (1950) The interpretation of the dependence of luminescent efficiency on activator concentration. *Jour. Chem. Phys.* **18**, 1477–1483.
- KUBELKA, P. (1948) New contributions to the optics of intensely light-scattering materials. *Jour. Opt. Soc. Am.* **38**, 448–457.
- MEDLIN, W. L. (1959) Thermoluminescent properties of calcite. *Jour. Chem. Phys.* **30**, 451–458.
- , (1961) Thermoluminescence in dolomite. *Jour. Chem. Phys.* **34**, 672–677.
- , (1963a) Thermoluminescence in quartz. *Jour. Chem. Phys.* **38**, 1132–1143.
- , (1963b) Emission centers in thermoluminescent calcite, dolomite, magnesite, aragonite and anhydrite. *Jour. Opt. Soc. Am.* **53**, 1276–1285.
- , (1963c) Trapping centers in thermoluminescent calcite. *Phys. Rev.* (in press).
- ZELLER, E. J., J. L. WRAY AND J. F. DANIELS (1957) Factors in age determination of carbonate sediments by thermoluminescence. *Bull. Am. Assoc. Pet. Geol.* **41**, 121–129.

*Manuscript received, June 7, 1963; accepted for publication, August 22, 1963.*