ASG

APPLICAZIONI SCIENTIFICHE GENERALI

application note

DOSIMETRIC CHARACTERISTICS OF LIF: Mg, Cu, P (GR-200 A)

E. MARTELLA

DOSIMETRIC CHARACTERISTICS OF LiF:Mg,Cu,P (GR-200A)

E. MARTELLA

INTRODUCTION

Lithium fluoride doped with magnesium, cupper and phosphorus (LiF:Mg,Cu,P) was first produced by Nakajima et al. (1) in 1978 in powder form. This material had some drawbacks such as a relatively high zero signal, an inconvenience in handling and a poor reproducibility (2). Only ten years later a Chinese laboratory began to manufacture on a commercial scale sinthered chips 4.5 mm diameter and 0.8 mm thickness, available on the international market as GR-200 A.

The present paper deals with the most recent results obtained on batches of GR-200 A chips.

LIGHT EMISSION SPECTRA

The light emitted by LiF:Mg,Cu,P is similar to that of LiF:Mg,Ti, with a peak emission at a wavelength of approximately 380 nm (3).

GLOW CURVE

Glow curves of LiF:Mg,Cu,P (GR-200A) and LiF:Mg,Ti (TLD-100) are compared in fig. 1, for a heating rate of 8 °C/s (4).

The position of the main dosimetric peak is similar, but the lower-temperature peaks, responsible for short- and medium-term fading, are situated at rather different temperatures. In GR-200A peak n.1 lies at 125 °C and has a half-life of the order of one day. Peak n.2 lies at 160-170 °C: its approximate half-life should be 3-4 months.

The higher temperature peaks (n. 4 and 5), found also by other Authors (5, 6, 7), are not completely emptied by the normal heating regime, restricted to a maximum temperature of 240 °C. They therefore account for the residual background signal present when previously dosed material is re-read without subsequent annealing (6, 7, 8); for further details see Zero signal.

Deconvolution data of the glow-curve of GR-200A has been published by Bacci et al (5).

ANNEAL AND PREHEAT

The commonly suggested cycle is 10 min at (240 ± 2-5) °C (2, 6, 8, 9, 10). Basing on the fact that in an ordinary ceramic crucible the TLDs take about 5 min to reach the prescribed temperature of 240°C (fig. 2), Scarpa (11) recommends an annealing cycle of 15 min. For doses higher than 100 mGy even longer cycles, up to 40 min, are suggested (3, 12).

According to the Manufacturer a careful control of the annealing temperature is very important for achieving a good reproducibility: temperature inaccuracies of the order of 2-5 °C could affect re-usability, glow-curve and sensitivity of the dosemeter. Driscoll et al. (6) claim that 300 °C for 1h reduce the sensitivity to 25% of the original one; 235 °C and 245 °C for 10 min produce a sensitivity decrease of 5% and 30%, respectively, over 5 cycles.

This criticality of annealing temperature implies that careful checks of the actual temperature present inside the furnace used for heat treatments are frequently carried out. (13).

According to Piters and Bos (14) the cooling rate in the annealing procedure is an important parameter, influencing glow-curve, sensitivity and repeatability. However, for cooling rates of 30-50 °C/min, normally found in laboratory use (as for natural cooling in a light ceramic container), the experiments showed a decrease of sensitivity of only 3% over the first eight re-use cycles, and no appreciable change afterwords. Therefore, These Authors (14) conclude that a constant sensitivity can be obtained by an initialisation oven annealing procedure, consisting of 10 min at 240 °C, followed by a fast cooling (150 °C/min), repeated at least 8 times.

The preheat (or pre-readout anneal) cycle prescribed by the Manufacturer is 5-15 s at 135 °C, in the reader. Higher temperatures are recommended by some Authors: 150 °C for 5 s (2, 10), 160 °C for 10 s (9) and 160 °C for 16 s (6). Recent experimental studies (15) show that a good cancellation of peak n. 2 (see fig.1), responsible for medium-term fading, implies an in-reader preheat cycle of 30 s at 160 °C or, as an alternative, an in-oven preheat cycle of 10 min at 130 °C.

READOUT CYCLE

The maximum temperature to be reached during the reading cycle is (240±5) °C (1, 2, 10). On the basis of some experimental data (8) an even more critical restriction to (240±2)°C might be necessary. Other experimental data (1, 15, 16) show that this limitation strictly applies only when a "plateau" heating regime is used: in this case the suggested cycles are 240°C for 10 s (4, 10, 15, 16), or 240°C for 12 s (6) or 230°C for 20 s (15, 16).

According to Scarpa et al. (15, 16), for linear heating mode on a manual reader the best reproducibility is achieved by using a maximum temperature of

270 °C, provided the end of the heating ramp coincides with the end of the acquisition time; in hot-gas automatic readers with non-linear heating the optimum gas temperature would be between 240 and 270°C.

For dose levels of 10 mGy or more there is no advantage of using nitrogen flow during readout (8).

SENSITIVITY. ZERO SIGNAL AND DETECTION THRESHOLD

The sensitivity of GR-200A is far higher than that of LiF:Mg,Ti (TLD-100), generally accepted as a standard TL material. In fact, the glow curves shown in fig. 1 were obtained using a dose of 10 mGy for GR-200A and 400 mGy for TLD-100. Referring to ^{60}Co gamma radiation and in terms of peak area, the ratio GR-200A/TLD-100 is evaluated between 25 (12) and 40 (6,9). This sensitivity is therefore twice that of $CaSO_4$:Dy and CaF_2:Dy, which are not tissue-equivalent TL phosphors.

The zero-dose (or background) signal immediately after annealing is equivalent to a dose of approximately 0.3 μGy and is the sum of four major components: NRI light emission of chips, effect of environmental radiation acting after annealing, planchet infrared emission and dark current of the photomultiplier (10). The situation is quite different for previously dosed, and not oven-annealed, dosemeters: in this case a rather high residual signal is observed, depending on the presence of the already mentioned high-temperature glow peak, not completely emptied during the readout cycle. This residue corresponds to a fraction of around 2% of the previous dose (2,8)

The minimum detectable dose (detection threshold) is reported to be between 0.1 and 1.5 μGy (2, 4, 6, 9).

REPRODUCIBILITY

Only one Author (17) reports a slow irreversible decrease of response after repeated use. No appreciable decrease of response after 27 successive cycles of annealing, irradiation, preheat and readout is mentioned in recent experiments carried out using a linear heating mode (15, 16), as shown in fig. 3. Similar results are reported for a plateau heating regime (fig. 4).

The investigations undertaken up to now give a dispersion index of repeated readouts of 0.6% - 2.8%, in terms of standard deviation (4, 9, 15, 16). There is statistical evidence (18) that for commonly used TL systems based on LiF and BeO these fluctuations are mainly due to the long-term instability of the readers, even when constancy checks based on a reference light source are performed.

Horowitz and Horowitz (8) propose a formula for correcting for residual signal when no annealing is carried out after each use: the application of this formula allows to keep the S.D. of repeated readouts within 2.2% even in these adverse experimental conditions.

ENERGY DEPENDENCE

A summary of the results of the main studies carried out on the energy dependence of response of GR-200A (9, 16, 19, 20) is shown in fig. 5. Data published by other Authors (2, 6) confirm this behaviour. It is evident that, in contradiction to all other TL materials, the response of LiF:Mg,Cu,P, relative to ^{60}Co gamma radiation, is below unity in the medium energy range, with a minimum of 0.7-0.8 at about 100 keV. For lower energies the response increases to reach a maximum around unity at about 40 keV, and then decreases again.

Anyway, fig. 5 shows that, for practical purposes, the energy response of GR-200 A is within ± 15% over the whole range 15 keV - 1.2 MeV.

FADING

Wang et al. (2) found no fading after 1 and 2 months storage at room temperature, nor when the relative humidity was as high as 90%.; at 50°C they report a 3% monthly fading. These results are confirmed by Driscoll et al. (6) for a 2-month storage at 20-25°C and 95% R.H. Other experiments (16) show that no fading can be detected even within a period of 6 months, provided that an appropriate preheat treatment (see paragraph 2) is done before the readout, in order to get rid of peaks n. 1 and 2.

LINEARITY

There is a general agreement that the light output of GR-200A is linear to dose in the range from 1 μGy up to about 10 Gy (8, 9, 10). Some recent results (16) are plotted in fig. 6 in a log-log graph.

If the 10 Gy point is not included (beeing affected by the saturation of the photomultiplier), the coefficient of determination r^2 is 0.9997, showing a very good linear fit.

RESPONSE TO NEUTRONS

The response of GR-200A to fast neutrons, relative to that to ^{60}Co gamma rays, has been evaluated (21) as (0.01±0.01), which is certainly the lowest of the tissue-equivalent TL materials descovered to date. This suggests that LiF:Mg,Cu,P could serve as an excellent discriminator for gamma ray dose measurements in mixed field dosimetry.

GR-200A is relatively insensitive to thermal neutrons as well: a response of 0.45 Gy ^{60}Co gamma radiation for a flux of 10^{10} n cm^{-2} is reported (22), corresponding to 18% of the response of TLD-100. Even better results are published (23) for ^{6}Li- depleted ^{7}Li:Mg,Cu,P dosemeters, commercialized as GR-700 A, which were found to have a relative response of 0.2%, normalized to gamma rays.

PRACTICAL APPLICATIONS OF GR-200A DOSEMETER

Wang et al. (2) and Zha et al. (10) emphasize the fact that, due to its very high sensitivity, the use of LiF:Mg,Cu,P GR-200A in environmental dosimetry can reduce the monitoring period to a day or even less: the monitoring efficiency is enhanced, minimizing the influence of changes in environmental conditions, and so minimizing the additionally introduced systematic errors.

Extensive investigations on the practical use of GR-200A have been carried out by Scarpa et al. (24), especially in the field of environmental gamma dosimetry, using a Reuter-Stokes high-pressure ionization chamber (mod. RS 111) as a reference dosemeter. The measurements were performed in several indoor environments in the Casaccia Energy Research Centre (Roma, Italy). Table 1 summarizes the results of some experiments, in terms of dose and dose rate evaluated by TL chips and by RS chamber, and the ratio, R_{exp}, of the two dose rates.

TAB 1 - ENVIRONMENTAL GAMMA RADIATION AS MEASURED BY GR-200A DOSEMETERS AND REUTER-STOKES IONIZATION CHAMBER

EXP. n.	LOCATION OF MEASURING INSTRUMENT	EXPOS. TIME (h)	GR-200 A		REUTER-STOKES		Rexp
			dose (mGy)	rate (nGy/h)	dose (mGy)	rate (nGy/h)	
1	Radioact. measurements lab.	191	15.49 ± 0.36	81.09	18.70	97.89	0.83 + 0.02
2	Radiotoxicology lab.	194	19.93 ± 0.20	102.9	25.73	132.8	0.77 ± 0.01
3	Chemisty lab.	140	15.58 ± 0.18	111.3	20.05	143.2	0.78 + 0.01
4	Gammabeam control room	166	14.61 ± 0.16	88.00	17.61	106.1	0.83 ± 0.01
5	Gammabeam irradiation room with six ^{90} Sr shielded sources	94.7	20.76 ± 0.56	219.2	27.81	293.7	0.75 + 0.02

In most experiments R_{exp} is around 0.8, which means that GR-200A measures 20% less than RS chamber. This result can be explained by the quite different energy response curve of the two dosimetric systems (fig. 7): the R_{exp} of 0.8 indicates that in the environmental gamma radiation present inside the building the medium energy component (70 to 500 keV) is predominant. The theoretical value of the above mentioned ratio (R_{th}) calculated in room 1, based on the results of a gamma spectrometry, was in very close agreement with R_{exp} (24).

CONCLUSIONS

The main advantages of LiF:Mg,Cu,P GR-200A TL dosemeters are:

- very high sensitivity, up to 40 times that of LiF:Mg,Ti TLD-100;
- very low detection threshold, of a fraction of µGy;
- quick pre-use anneal cycle, lasting only 10 or 15 min;
- satisfactory reproducibility of readouts;
- no appreciable fading within 6 months;
- good linearity up to 10 Gy;
- nearly flat energy response in the range 15 keV-1.2 MeV;
- low response to neutrons in mixed fields.

A drawback is certainly the criticality of the annealing temperature of 240°C, which requires frequent controls of the actual temperature inside the furnace used for thermal treatments.

REFERENCES

1 - T. Nakajima, Y. Murayama, T. Matsuzawa, A. Koyano - Development of a new highly sensitive LiF thermoluminescence dosimeter and its applications, Nuclear Instr. Meth., 157, 155-162, 1978

2 - S. Wang, G. Chen, F. Wu, Y. Li, Z. Zha, J. Zhu - Newly developed highly sensitive LiF(Mg,Cu,P) TL chips with high signal-to-noise ratio, Rad. Prot. Dosim. 14, 223-227,1986

3 - L.A. DeWerd, J.R. Cameron, Wu Da-Ke, T. Papini, I.J. Das - Characteristics of a new dosemeter material: LiF(Mg,Cu,P), Rad. Prot. Dosim. 6, 350-352, 1984

4 - G. Scarpa, M. Moscati - Caratteristiche dosimetriche del nuovo LiF:Mg,Cu,P, Proc. XXVI Congr. Naz. AIRP (Italian Association for Radiation Protection), Verona (Italy), 13-15 Sept. 1989, p. 337-342

5 - C. Bacci, R. Darnilano, C. Furetta, B. Rispoli, J. Zhu, G.G. Cai, A. Delgado, J.M. Gomez Ros - Study of the kinetics paramaters of LiF:Mg,Cu,P, CEMAT 658 Sp ISSN 614-087-X, Madrid, 1990

6 - C.M.H. Driscoll, A.F. McWhan, J.B. O'Hagan, J. Dodson, S.J. Mundy, C.D.T. Todd - The characteristics of new LiF preparations and sensitised LiF, Rad. Prot. Dosim. 17, 367-371, 1986

7 - Y.S. Horowitz (Ed.) - Thermoluminescence and thermoluminescent dosimetry, Boca Raton, Fl, CRC Press, 1984

8 - Y.S. Horowitz and A. Horowitz - Characterisation of LiF:Cu,Mg,P (GR-200) for personnel thermoluminescence dosimetry, Rad. Prot. Dosim. 33, 279-282,1990

9 - L. Lembo, M. Pimpinella, F. Monteventi, U. De Maio, R. Poli, I. Sermenghi - Un'analisi comparativa delle caratteristiche dosimetriche di alcuni materiali termoluminescenti, Proc. XXVI Congr. Naz. AIRP (Italian Association for Radiation Protection), Verona (Italy), 13-15 Sept. 1989, p. 435-446

10 - Z. Zha, S. Wang, F. Wu, G. Chen, Y. Li, J. Zhu - Measurement of extremely low level dose with LiF(Mg,Cu,P) TL chips, Rad. Prot. Dosim., 17, 415-418, 1986

11 - G. Scarpa - Heating curve of a ceramic capsule introduced in a commercial furnace set at 240°C, Private communication, 1991

12 - B.C. Bhatt, S.S. Shinde, R.C. Bhatt - Comparative dosimetric studies of three LiF TL phosphors, Rad. Prot. Dosim. 27, 21-27, 1989

13 - G. Scarpa, C. Caporali, M. Moscati - Survey of the characteristics of furnaces used in Italy for TLD thermal treatments, Rad. Prot. Dosim. 33, 343-346, 1990

14 - T.M. Piters and A.J.J. Bos - Influence of the cooling rate on repeatability of LiF:Mg,Cu,P thermoluminescent chips, Rad. Prot. Dosim. 33, 91-94, 1990

15 - G. Scarpa, M. Moscati, A. Soriani - Studio sulla tecnica di azzeramento e di lettura del LiF:Mg,Cu,P, Proc. XXVII Congr. Naz. AIRP (Italian Association for Radiation Protection), Ferrara (Italy), 16-18 Sept. 1991 (in press)

16 - G. Scarpa, M. Moscati, A. Soriani - Ulteriori studi sulle caratteristiche dosimetriche del LiF:Mg,Cu,P (GR-200A), Proc. IV Symp. sulle metodologie radiometriche e radiochimiche nella radioprotezione, Alghero (Italy), 10-13 April, 1991

17 - A.J.J. Bos and J.D. Dielhof - Does the most sensitive thermoluminescent material come from China? Some characteristics of LiF:Mg,Cu,P (GR-200) TL chips, Proc. Symp. on thermoluminescent dosimetry, Bilthoven, The Netherlands, 1989, p. 43-48

18 - G. Scarpa, A. Alberici, S. Ledda, V. Klamert - An experimental evaluation of the reproducibility of TLD systems using LiF and BeO, Rad. Prot. Dosim. 33, 323-326, 1990

19 - F. Wu, Z. Zha, J. Li, Z. Zhu - LiF(Mg,Cu,P) thin dosemeter for skin dose measurement, Rad. Prot. Dosim. 33, 331-334, 1990

20 - B. Chandra, A.R. Lakshmanan, R.C. Bhatt, K.G. Vohra - Annealing and re-usability characteristics of LiF(Mg,Cu,P) TLD phosphor, Rad. Prot. Dosim. 3, 161-167, 1982

21 - Y.S. Horowitz and B. Ben Shachar - Thermoluminescent LiF:Cu,Mg,P for gamma ray dosimetry in mixed fast neutron-gamma radiation fields, Rad. Prot. Dosim. 23, 337-342, 1988

22 - A.S. Pradhan and R.C. Bhatt - Thermoluminescence response of LiF(Mg,Cu,P) and LiF TLD-100 to thermal neutrons, ^{24l}Am alphas and gamma rays, Rad. Prot. Dosim. 27, 185-188, 1989

23 - S.S. Wang, G.G. Cai, K.O. Zhou, R.X. Zhou - Thermoluminescent response of ^{6}LiF(Mg,Cu,P3 and ^{7}LiF(Mg,Cu,P) TL chips in neutron and gamma ray mixed radiation fields, Rad. Prot. Dosim. 33, 247-250,1990

24 - G. Scarpa, M. Moscati, A. Soriani - Use of LiF:Mg,Cu,P in environmental gamma dosimetry. Proc. 5th Int. Symp. Nat. Rad. Environment, Salzburg, 22-28 Sept. 1991 (in press)

25 - A. Horowitz and Y.S. Horowitz - Optimisation of LiF:Cu,Mg,P for radiation protection dosimetry, Rad. Prot. Dosim. 33, 267-270,1990

26 - Y.S. Horowitz and N. Stern - Relative thermoluminescent efficiency of LiF:Cu,Mg,P to alpha particles: theory and experiment, Rad. Prot. Dosim. 33, 287-290, 1990

27 - J. Azorin, A. Gutierrez, T. Niewiadomski, P. Gonzalez - Dosimetric characteristics of LiF:Mg,Cu,P TL phosphor prepared at ININ, Mexico, Rad. Prot. Dosim. 33, 283-286, 1990

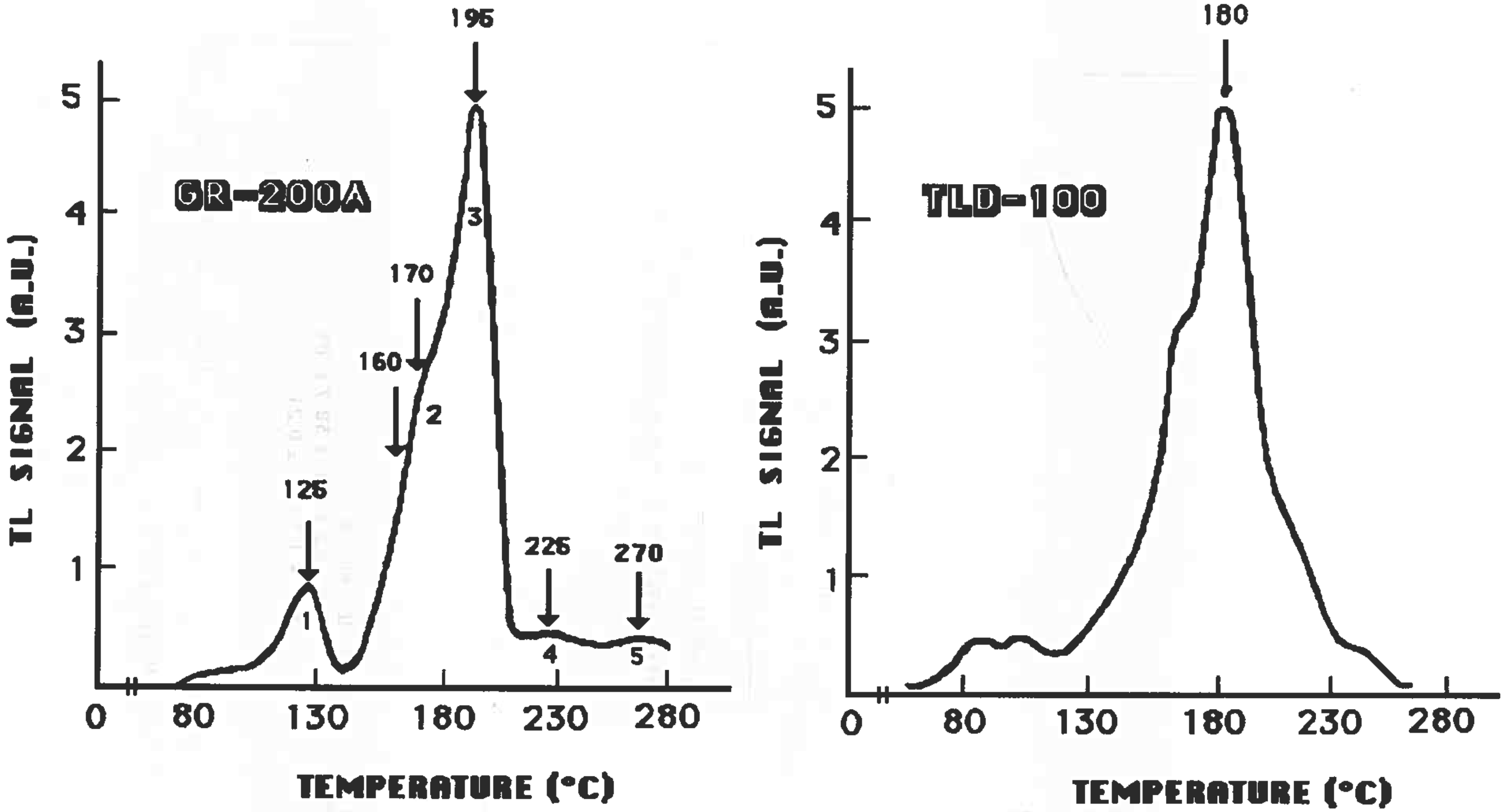

FIG. 1

Glow curves of LiF:Mg,Cu,P (GR-200A)
irradiated to a dose of 10 mGy
Heating rate: 8 °C/s

Glow curves of LiF:Mg,Ti (TLD-100)
irradiated to a dose of 400 mGy
Heating rate: 8 °C/s

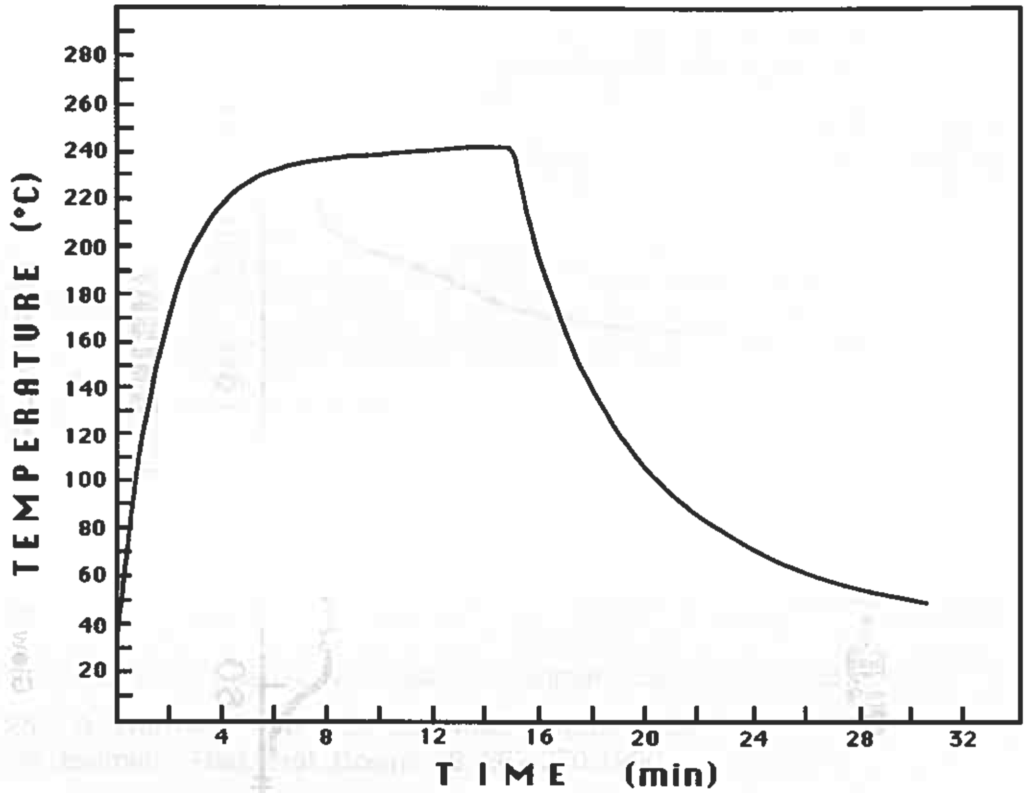

FIG. 2 - Heating and cooling down curve of a ceramic capsule introduced in a commercial furnace set at 240°C

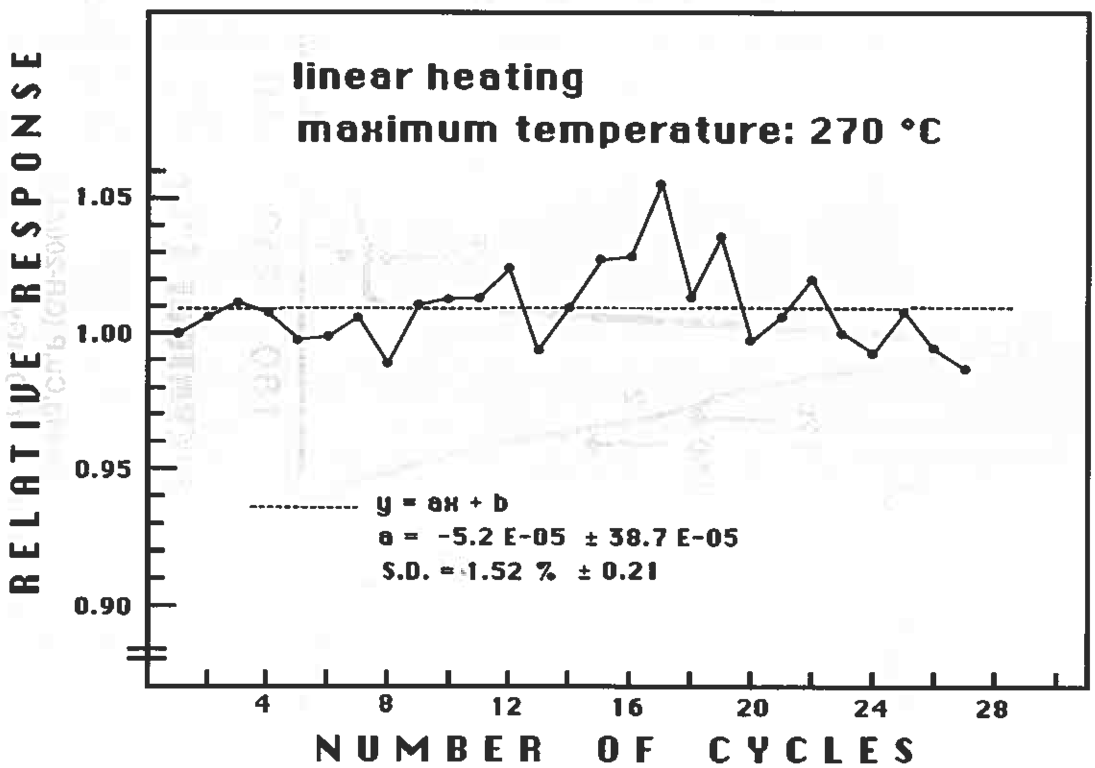

FIG. 3 - Reproducibility of response of GR-200A during 27 successive re-use cycles. The readouts were carried out using a linear heating regime, with a maximum temperature of 270°C. Heating rate 9 °C/s

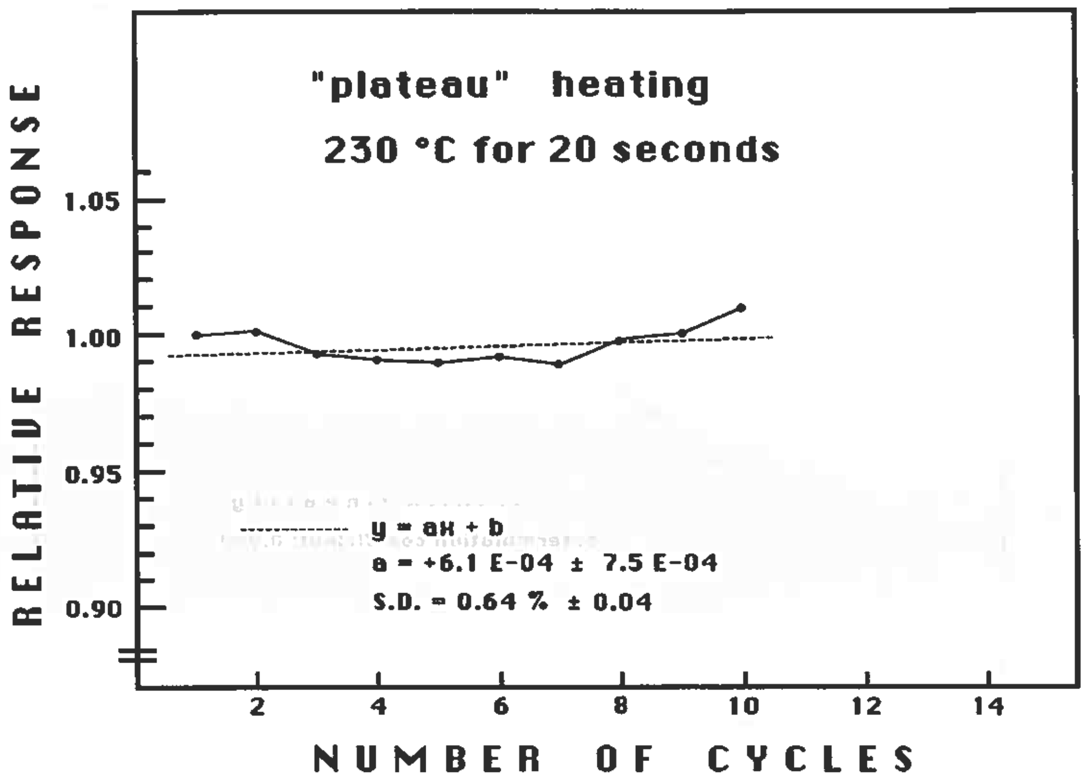

FIG. 4 - Reproducibility of response of GR-200A during 10 succesive re-use cycles. The readouts were undertaken by a "plateau" heating regime at 230°C for 20 s

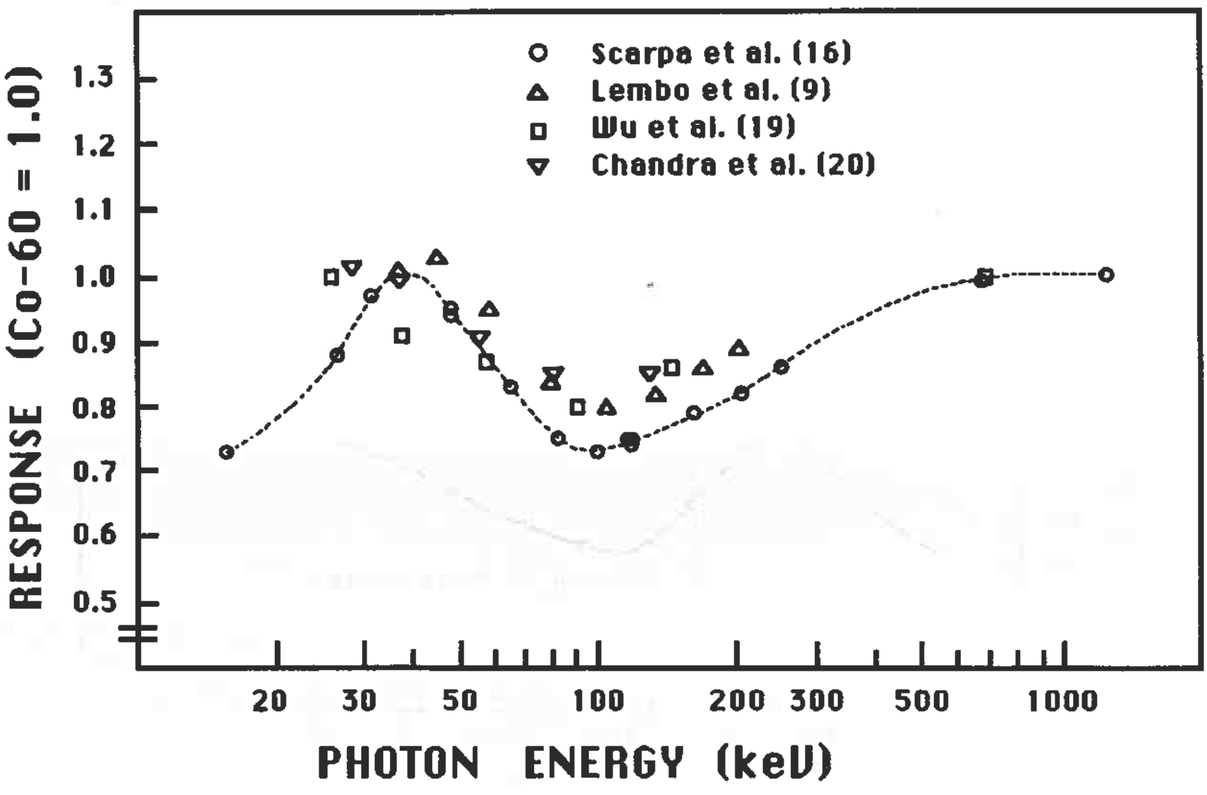

FIG. 5 - Energy dependence of GR-200A according to different Authors

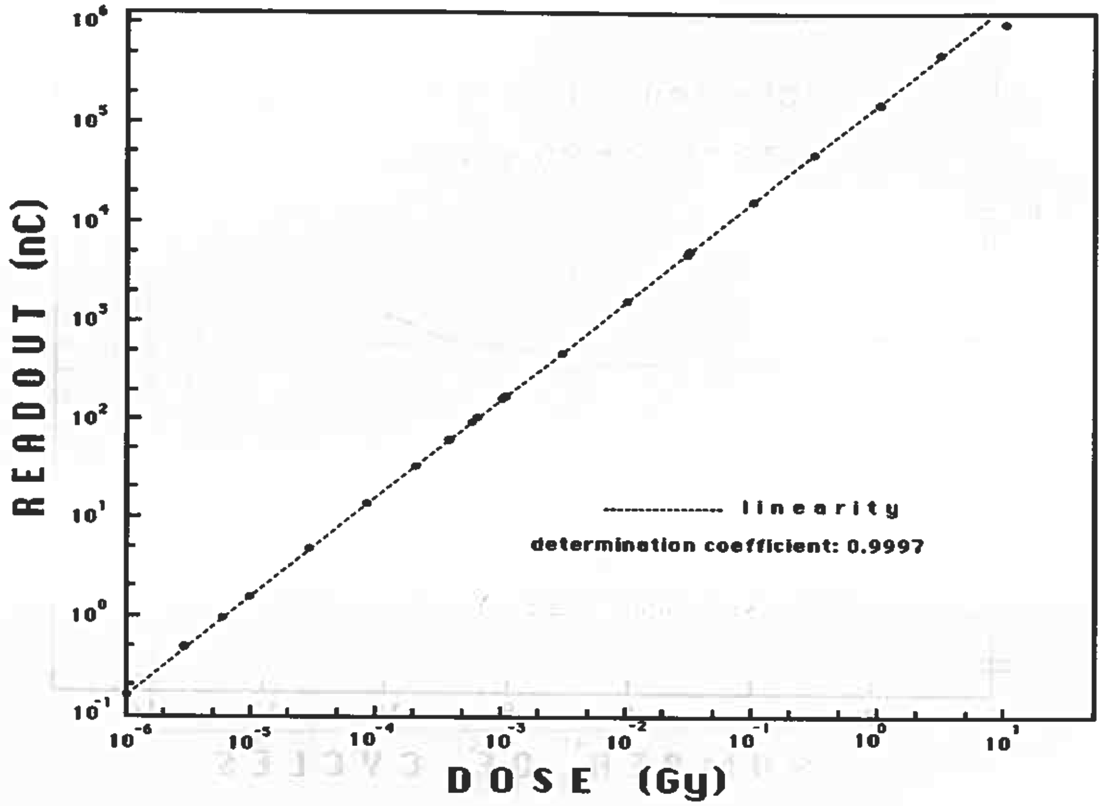

FIG. 6 - Linearity of net readout vs. dose of GR-200A in the range from 1 microgray to 10 gray (the apparent sublinearity of the last point is due to saturation of the photomultiplier)

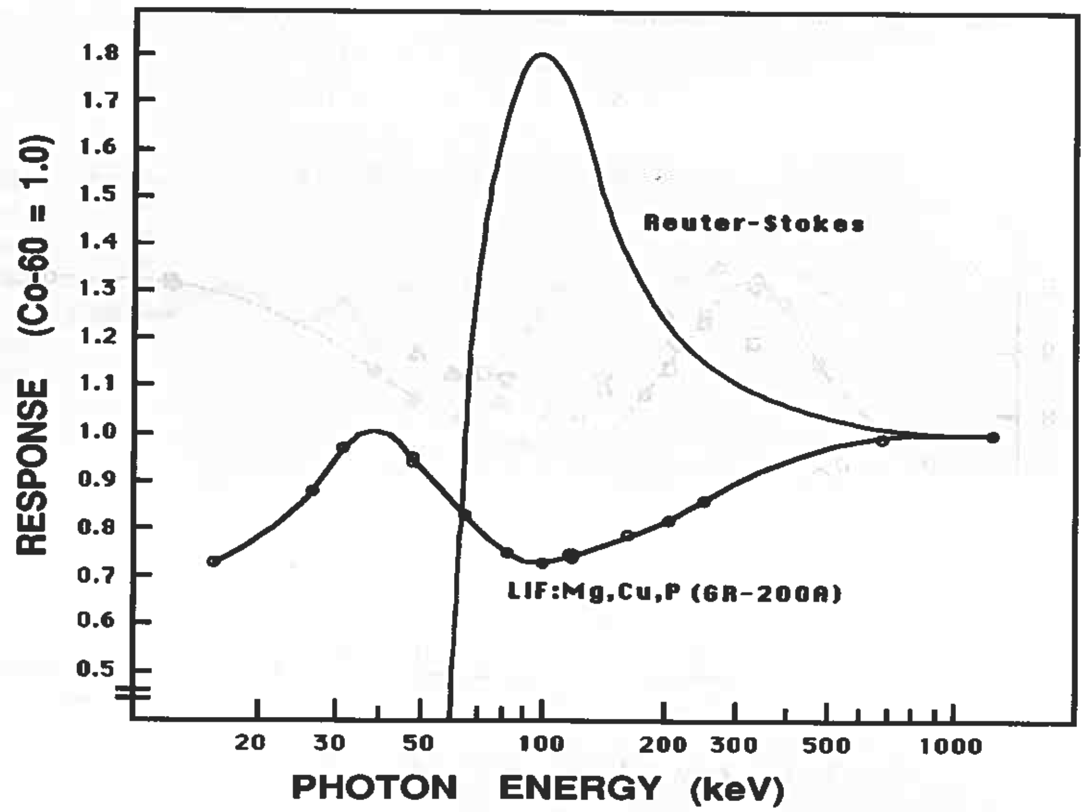

FIG. 7 - Energy response of GR-200A as compared to energy response of a Reuter-Stokes ionisation chamber mod. RS 111