



**FIGURE 21** Thermoluminescence of fresh and freeze-dried  $\text{SiO}_2$  gels (microbeads) after  $\gamma$ -irradiation at  $-196^\circ\text{C}$  (30 kGy).

freeze-dried gels, the  $-120^\circ\text{C}/-100^\circ\text{C}$  emission is first almost completely erased and then disappears (for 2% residual moisture). At the same time the low-temperature peak increases and sharpens.

We think that low-temperature thermoluminescence applied to freeze-dried solids is susceptible to give us new information on the water “traps” within the solid material, and that with a better knowledge of the temperature, magnitude, and shape of the emission peaks we might be able to beam some light on the role of residual moisture in freeze-dried products and on the mechanisms binding water molecules to their supporting matrix.

## UNCONVENTIONAL DEVELOPMENTS: NEW PROSPECTS

### Water Is Not the Only Available Solvent

Until now, almost all lyophilization operations have been carried with aqueous solutions, but we know since a long time that water is not the only solvent that can sublimate from the frozen state.

*Mineral solvents:* We did show, decennia ago, that ammonia and carbon dioxide, which are most interesting solvents, might distill away from the frozen state. The case of carbon dioxide is even a rather remarkable one since it sublimates at high speed, at atmospheric pressure, and at a low temperature of  $-78.8^\circ\text{C}$ . Moreover, it is a nontoxic chemical and leaves no analytically measurable traces in the final dry product. Knowing its exceptional solvent properties in the super-critic state it might become a very valuable extraction and supporting medium for many unstable chemicals and biologicals that need to be stabilized as dry forms.

$\text{NH}_3$  is more difficult to handle but it might offer equally interesting openings for the preparation of transient compounds manufactured in