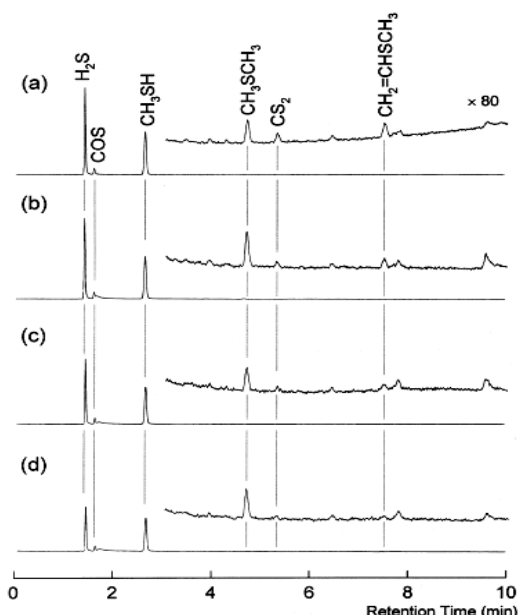


## Photodegradative changes in chemical structures of silk studied by Py-GC with sulfur chemiluminescence detection

**[Background]** Silk is readily damaged and weakened by exposure to light, making its deterioration mechanism of interest. In this work photodegradative changes in the chemical structures of silk were examined by focusing on the changes in the sulfur-containing amino acid residues such as methionine (Met) and Cys and Cys-Cys residues by means of Py-GC with sulfur chemiluminescence detection (Py-GC/SCD).

**[Experimental]** Photodegradation of silk samples was performed by exposure to simulated sunlight in a weather-meter at 46°C and 60 ±5% relative humidity for 5, 27 and 52 days. A vertical microfurnace pyrolyzer (PY-2020D, Frontier Lab), which enables pre-heating free pyrolysis at desired temperatures for thermally labile samples such as proteins, was directly attached to a GC with a fused-silica capillary column. The column effluents were selectively detected by a sulfur chemiluminescence detector (SCD). About 200µg each of silk samples was pyrolyzed at 600°C under a flow of He carrier gas.

**[Results]** To create calibration curves for the determination of sulfur-containing amino acid residues, four standard protein enzymes were measured by Py-GC/SCD. Figure 1 shows the pyrograms of (a) unirradiated silk sample, and silk samples exposed for (b) 5 days, (c) 27 day and (d) 52 days. The intensities of most of the key peaks apparently decrease with increase in irradiation time. The contents of Met, Cys, and Cys-Cys residues in the silk samples were then estimated from the corresponding key peak intensities using the calibration curves. The quantitative results thus obtained for the silk samples are summarized in Table 1. The observed amino acid compositions for both Cys and Met residues of the control sample were about 0.2%, which are in a good agreement with those inferred from DNA sequencing. The RSD for the Cys residue determination was ca. 5% for three repeated runs for the control sample, indicating adequate reproducibility.



**Figure 1.** Pyrograms of photo degraded silk samples at 600°C observed by SCD: (a) not exposed; (b) exposed for 5 days; (c) exposed for 27 days; (d) exposed for 52 days.

**Table 1.** Content of the sulfur-containing amino acid residues contained in exposed silk samples determined by Py-GC with SCD

Amino acid residue	Amount of the amino acid residue (µmol/g) [amino acid composition (wt %)]	Exposed days		
		Control (not exposed)	5	27
Met <sup>a</sup>	14.8±2.9 (0.22)	13.7±2.7 (0.20)	12.4±2.4 (0.18)	10.6±2.0 (0.16)
Cys <sup>b</sup>	14.6±0.8 (0.18)	12.3±0.5 (0.15)	10.3±0.3 (0.13)	7.0±0.2 (0.08)
Cys-Cys <sup>c</sup>	1.48±0.19 (0.036)	0.82±0.22 (0.020)	0.63±0.23 (0.015)	0.54±0.23 (0.013)

<sup>a</sup> From peak intensity of CH<sub>3</sub>SH.

<sup>b</sup> From peak intensities of H<sub>2</sub>S.

<sup>c</sup> From peak intensities of CS<sub>2</sub>.

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