Evaluation of Acidic Paper Deterioration in Library Materials by Pyrolysis-Gas Chromatography

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Evaluation of Acidic Paper Deterioration in Library Materials by Pyrolysis-Gas Chromatography

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Pyrolysis-gas chromatography (Py-GC) was used to evaluate deteriorated acidic paper in old books. A tiny piece (ca. 0.25 mg) of deteriorated paper from each book was subjected to Py-GC measurement at a 300°C pyrolysis temperature. Levoglucosan and its dehydrated form levoglucosenone were typical degradation products, whereas primarily only levoglucosan was observed in control samples of undamaged new paper. The relative intensity of levoglucosenone was much higher in samples taken at the heavily deteriorated marginal edge than in those taken from the center of the same page of an old book. Accordingly, levoglucosenone observed in the pyrogram can be used as a marker to evaluate the degree of deterioration of acidic paper. The formation of levoglucosenone can be attributed to the slow deterioration process of paper, in which the dehydration reaction plays an important role, accompanied by the chain scission of cellulose. The Py-GC method for paper evaluation was also applied to clarify the effect of storage conditions on the deterioration of paper materials and to evaluate the long-term deterioration of the British Parliamentary Papers (1801–1986) collected at the Kyoto University Library.

1. Introduction

A severe problem worldwide is the gradual and inevitable deterioration of paper in old books and documents stored in libraries. This problem is mostly caused by the acidic nature of the rosin-alum additive used for sizing since the late nineteenth century. Sulfate ions accompanied by protons liberated from the sizing agent attack paper materials. The pages of severely deteriorated books are very brittle and cannot be turned safely in an ordinary manner. To preserve and restore such degraded materials appropriately, the degree of deterioration must be evaluated.

Various mechanical tests are available for this purpose, but they usually destroy or damage historical library materials. Pyrolysis-gas chromatography (Py-GC) provides a simple but rapid and extremely sensitive analytical tool that requires only minute sample amounts, generally on the sub-mg order. The procedure has been demonstrated to be successful for the characterization of various synthetic polymers and natural organic products (Tsuge et al. 2011) as well as photo-yellowing trigger compounds (Seino et al. 2004) and various additives, applied in trace amounts, in paper (Yano et al. 1991, 1992; Ishida et al. 1994a, 1994b).

In this study, Py-GC was performed to evaluate the possibility of characterization of deteriorated paper in old books. The mechanism of deterioration of acidic paper is discussed, including the effect of storage conditions on the paper materials. Finally, the deterioration of the British Parliamentary Papers (1801–1986) was systematically evaluated.

2. Experimental

2.1 Paper samples

A selected page of an old book (*Censo de Poblacion*, published in 1932 in Mexico) was used as a deteriorated paper sample. Figure 1 shows a photograph of the cover page of the book, which was deeply colored, and the mechanical strength of the sampled paper was quite weak, with a folding endurance (number of double folds until breakage) of 20.

In addition, the same page near the cover of two copies of the booklet *Shiryoukan Shozoushiryo Mokuroku* (published in 1952 in Japan) stored under different conditions in the National Institute of Japanese Literature located near Tokyo was also tested (Fig. 2). The booklet on the left in Figure 2 was stored wrapped in paper in a stock room without air-conditioning and was in much better condition than the one on the right, which was placed on the open bookshelf for daily use. It was referenced routinely in an air-conditioned room during working hours and was subject to abrupt fluctuations of temperature and relative humidity.

In addition, randomly chosen pages in selected 140 volumes of the British Parliamentary Papers (1801–1986) were also subjected to analysis by Py-GC and the results compared with double-fold test measures of deterioration.

2.2 Conditions for Py-GC measurements

A temperature programmable microfurnace pyrolyzer (Frontier Lab, PY-2020D, Koriyama, Japan) was attached to the injector (at 300°C) of a GC (HP 5890, Palo Alto, CA, USA)

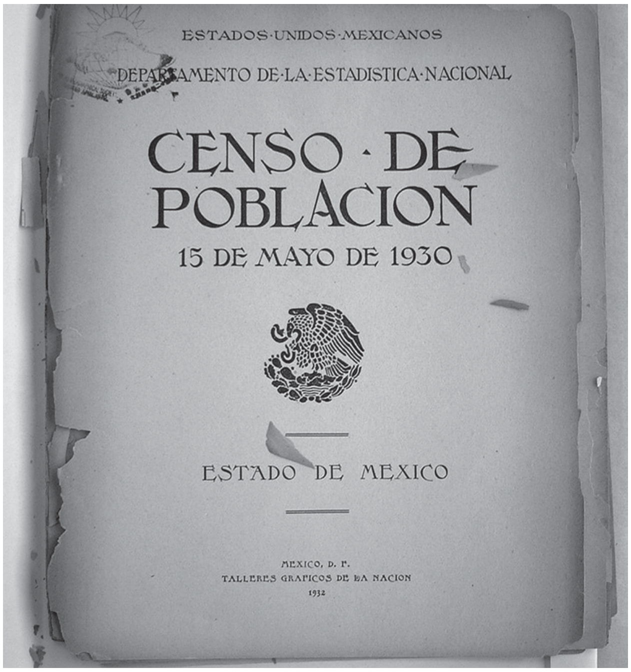

Fig. 1 Photograph of the cover page of *Censo de Poblacion,* published in 1932 in Mexico

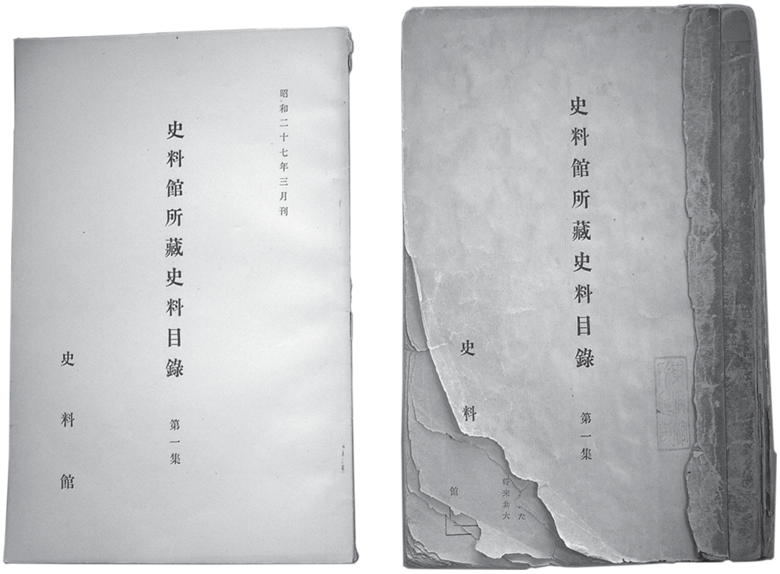

Fig. 2 Photograph of two copies of an old booklet (*Shiryokan Shozoushiryo Mokuroku*, 1952, Japan) preserved under different conditions: left, stored wrapped in paper in a stock room; right, placed on an open shelf for daily use (Ohtani et al. 2009)

equipped with a flame ionization detector. A few small pieces of the paper sample (total weight, ca. 0.1 mg) punched by the middle size of a Harris micropuncher (Frontier Lab, HMP-0.75D, Koriyama, Japan) from a prescribed area of the test sheet (page) were placed into a platinum sample cup. The sample in the cup was dropped into the center of the pyrolyzer heated at 300°C under a helium carrier gas flow (50 mL min^{-1}). A part of the flow (1 mL min^{-1}) reduced by a splitter was introduced into a metal capillary separation column (Frontier Lab, Ultra ALLOY^{+}-5; 30 m long × 0.25 mm i.d., Koriyama, Japan) coated with immobilized 5% diphenyl-95% dimethylpolysiloxane (0.25 μm film thickness) together with pyrolysis products. The column temperature was initially held at 40°C for 5 min and then programmed to 280°C at a rate of 10°C min^{-1}. For peak identification, the pyrolyzer was also attached to a gas chromatography-mass spectrometry (GC-MS) system (JEOL, AM-II 150, Tokyo, Japan) with electron ionization at 70 eV (Ohtani et al. 2009).

3. Results and discussion

3.1 Key product for acidic paper deterioration

Figure 3 shows a typical pyrogram of deteriorated paper, sampled from a highly deteriorated edge of a page in the damaged book (1932, Mexico) and an undeteriorated reference sample.

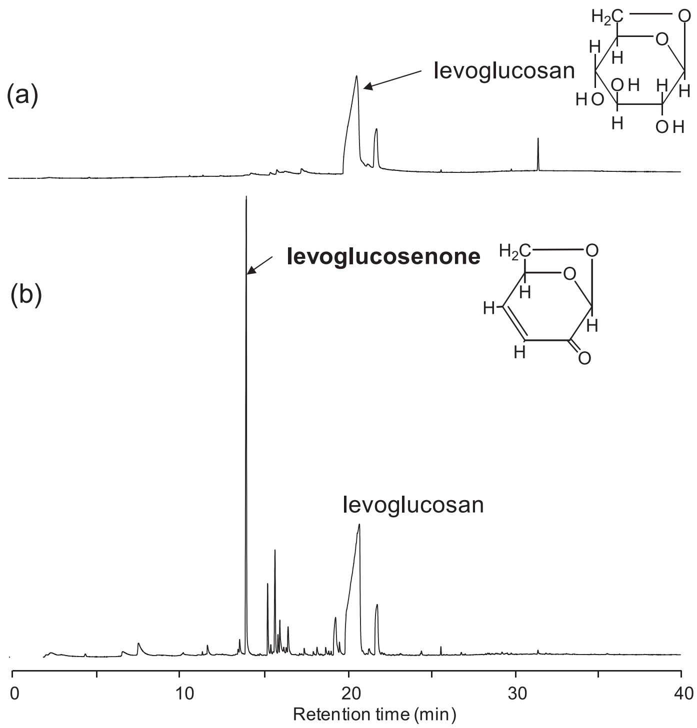

Fig. 3 Pyrograms of paper samples at 300°C: (a) an undeteriorated reference sample; (b) a highly deteriorated sample (1 cm from the edge of a page in *Censo de Poblacion*, 1932, Mexico) (Ohtani et al. 2009)

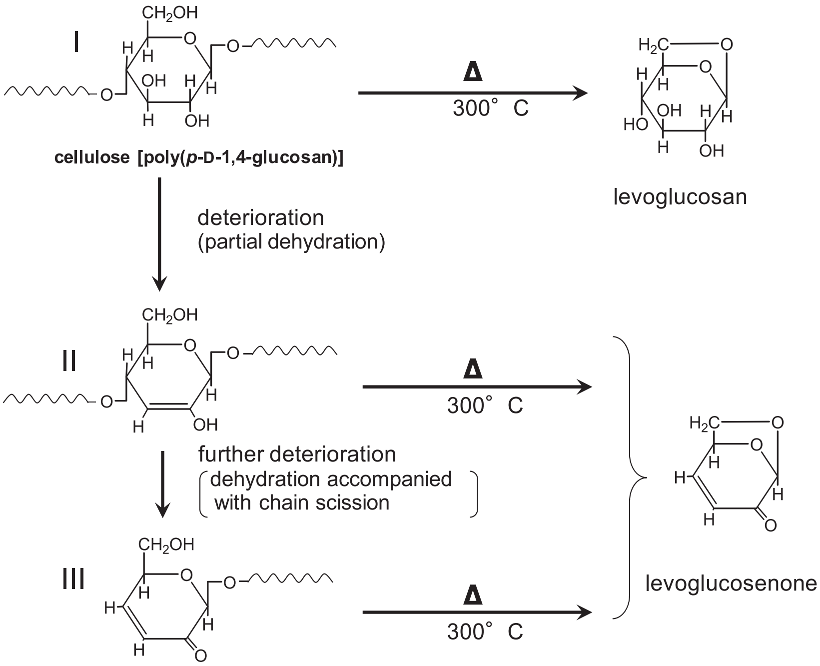

Fig. 4 Possible deterioration mechanisms of acidic paper along with related pyrolysis products (Ohtani et al. 2009)

The undeteriorated paper (commercially available filter paper) showed a peak of 1,6-anhydro-*p*-D-glucopyranose (levoglucosan), which is a typical pyrolysis product of cellulose (Tsuge et al. 2011). Some additional products were observed in the highly deteriorated paper. Among these products, the most intense peak was identified from the observed mass spectrum as 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone).

Figure 4 shows a possible deterioration mechanism of acidic paper based on the observed pyrograms along with the related pyrolysis products. In the case of undeteriorated paper (I), levoglucosan is typically formed from cellulose through pyrolysis (Ohtani et al. 2009). The levoglucosenone observed specifically in the deteriorated paper sample corresponds to a dehydrated product of levoglucosan through the elimination of two water molecules, and the deterioration under an acidic condition is closely related to the dehydration reaction in the glucose unit of cellulose. A dehydrated anhydroglucose unit (II) of the chain may easily form levoglucosenenone. Further dehydration leads to a chain scission in the chain (III), which is the cause of the loss of strength of the paper. Also the type III unit is prone to levoglucosenone formation. Therefore, the levoglucosenone formed from the dehydrated parts of cellulose through pyrolysis reflects the degree of chemical changes in the paper.

3.2 Evaluation of degree of paper deterioration by Py-GC

Figure 5 shows the differences in the observed pyrograms for the deteriorated paper sample

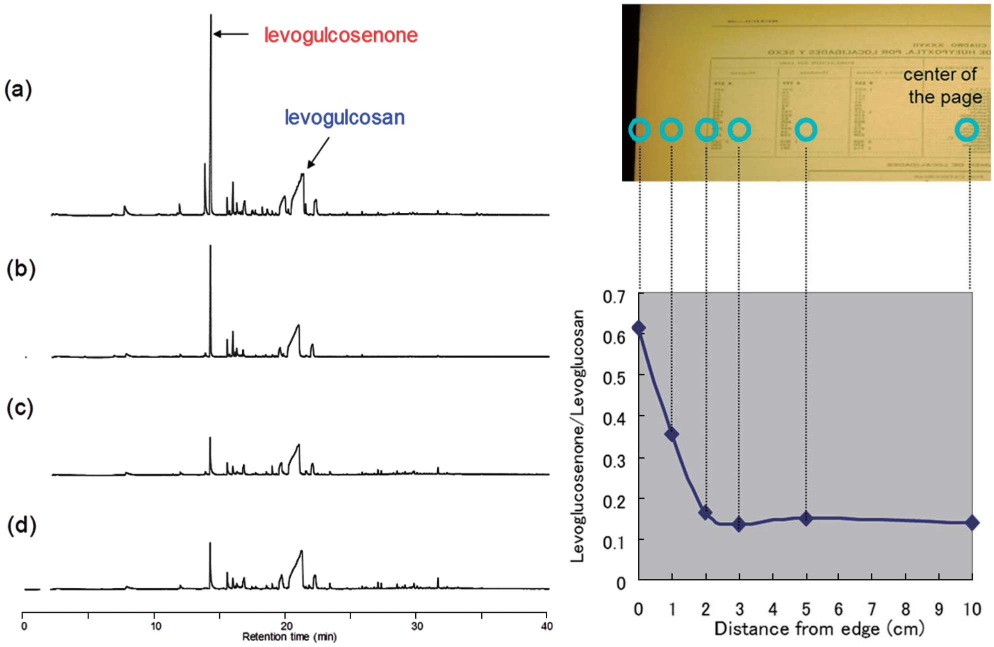

Fig. 5 Pyrograms of deteriorated paper sampled at various positions in a page of an old book (*Censo de Poblacion*, 1932, Mexico): (a) edge; (b) 1 cm from the edge; (c) 2 cm from the edge; and (d) 10 cm from the edge (center), with the relationship between the relative peak intensity of levoglucosenone and sampling distance from the edge is also shown

(1932, Mexico) taken at various locations on the same page, along with the relationship between the relative peak intensities of levoglucosenone to levoglucosan and the distance of the sampling position from the edge of the given page.

Generally, paper deterioration was much more severe at the marginal part of page than at the center. Correspondingly, the levoglucosenone peak was the most intense at the edge (Fig. 5a), and its relative intensity gradually decreased toward the center of the page. The fact that levoglucosenone was still observed in the central part of the page (Fig. 5d) indicates that the paper sample was markedly damaged even in the center. Interestingly, the change in the peak intensities of levoglucosenone was quite consistent with the variation in coloration observed in the deteriorated paper sheet (Fig. 5 photo). This demonstrates that the relative peak intensity of levoglucosenone observed in the pyrogram is a good measure of the degree of deterioration for acidic paper.

3.3 Effect of storage conditions on acidic paper deterioration

The archival materials that were published more than 50 years ago but kept under different conditions (Fig. 2) were characterized by Py-GC to clarify the effect of the storage conditions on acidic paper deterioration.

Figure 6 shows the pyrograms of the paper pieces sampled from corresponding positions in the same page from each booklet (Ohtani el al. 2009). The levoglucosenone peak is high

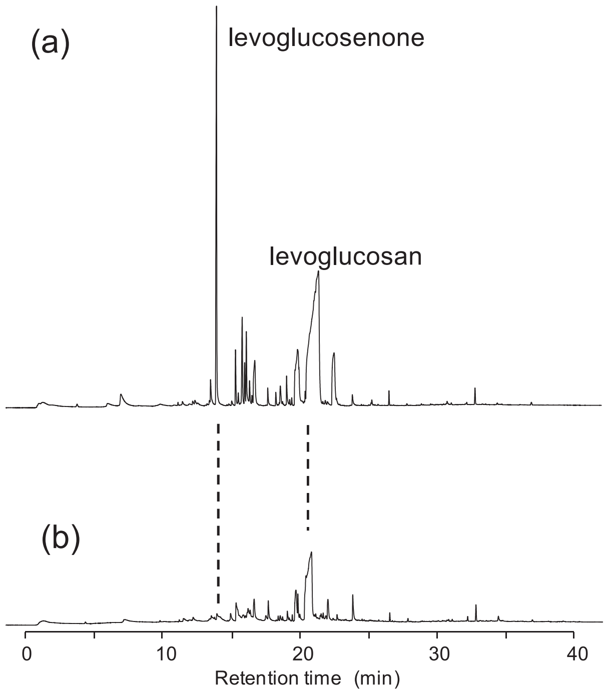

Fig. 6 Pyrograms of paper samples from identical books stored under different conditions as shown in Fig. 2: (a) open shelf and (b) stored and wrapped. The books were sampled at equivalent positions of the same page (Ohtani el al. 2009)

in the case of the highly damaged (open-shelf) book and is negligibly low for the stored copy. This result clearly indicates that the damage in the open-shelf book was brought about not only by the mechanical stress of daily use but also through chemical deterioration produced by light exposure. The fluctuation in environmental temperature and humidity also probably contributed to the degradation.

3.4 Systematic evaluation of deterioration in the British Parliamentary Papers

Deteriorations in the British Parliamentary Papers, which are collected at the Kyoto University Library, were also systematically evaluated by Py-GC.

Figure 7 shows the relationships between the relative peak intensities of levoglucosenone to levoglucosan observed in the pyrograms of the sample pages and the evaluation values obtained through the double-fold test for the corresponding pages. Larger values for the double fold test (maximum of 4) indicate a lower mechanical strength of the test sheet. Although the values were roughly correlated with each other, some paper samples showed low mechanical strength despite a low levoglucosenone intensity. This result suggests that, in addition to dehydration, other processes such as oxidation, hydrolysis and depolymerization might contribute to the long-term deterioration of acidic paper.

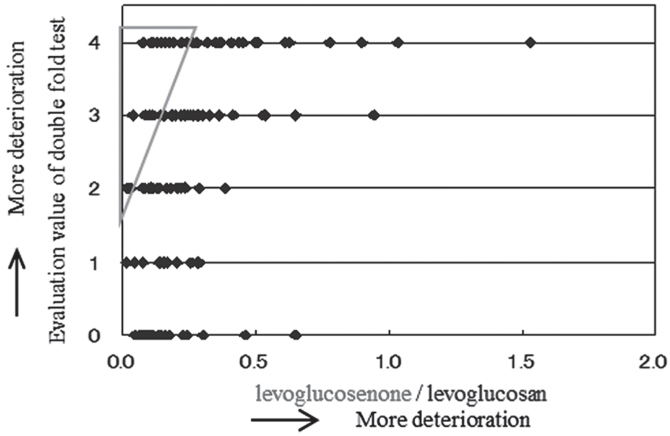

Fig. 7 Relationship between the results of the double-fold test and relative intensity of levoglucosenone in the observed pyrograms for about 140 selected volumes of the British Parliamentary Papers. The points within the triangle indicate samples that showed low mechanical strength and low levoglucosenone intensity

4. Conclusion

Levoglucosenone and levoglucosan were present in pyrograms of deteriorated acidic paper, whereas only levoglucosan was observed in undeteriorated samples. The relative intensity of levoglucosenone corresponds to the damage level of the old paper samples. Accordingly, levoglucosenone observed in the pyrogram can be used as a marker to evaluate the degree of deterioration of acidic paper. The formation of levoglucosenone from deteriorated paper through pyrolysis suggests that dehydration reactions play an important role, accompanied by the chain scission of the cellulose main chain during acidic paper deterioration. The Py-GC evaluations of the booklets in relatively good and deteriorated conditions demonstrated that the ageing was strongly affected by storage conditions, but the dehydration reaction may not be the only contributor to deterioration in acidic paper.

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