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DETERMINATION OF METOL AND HYDROQUINONE IN A PHOTOGRAPHIC DEVELOPER BY LIQUID CHROMATOGRAPHY

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Metol, hydroquinone and their oxidation products in a photographic developer were satisfactorily analyzed directly by liquid chromatography without any pre-treatment of the developer. The eluent of the liquid chromatography was prepared by eliminating the developing agents from the developer.

Metol[1] and hydroquinone have been used as developing agents in black and white photographic developers. The composition of a developer may vary by not only the processing of photographic film or paper but also aerial oxidation. Change of the developer composition seriously affects the photographic characteristics of processed film or paper. Therefore, it is important in photographic processing laboratories to know the change of developer composition by chemical analysis and to replenish the developer based on the results of analysis.

Many methods of analyzing Metol and hydroquinone in photographic developers have been reported[2]. Most of them need pre-treatment of the sample, take much time, and require a highly skilled technique. The developing agents are easily oxidized by the pre-treatment because they separate from preservatives in the solution. Therefore, another technique is needed to protect the agents from oxidation.

This paper is concerned with an application of high performance liquid chromatography to direct analysis of the developing agents and their oxidation products without any pre-treatment of the developer.

The liquid chromatograph used was constructed as follows: The pump was a Nihon Seimitsu Kagaku reciprocating pump and the detector was a Hitachi 200-10 spectrophotometer with a cylindrical flow cell having a 1 mm i.d. and 10 mm in light path length. The column was Pyrex glass, 3 mm i.d. and 10 mm in length with a water jacket. The column packing material was Hitachi Gel #3011-N. The gel dispersed in eluent, was packed into the column by slurry packing technique. All flow paths were made of Teflon.

The eluent of the liquid chromatography was prepared by eliminating the developing agents from Kodak D-72 developer. The eluent consists of sodium sulfite (anhydrous) 45.0 g, sodium carbonate (anhydrous) 67.5 g, potassium bromide 1.9 g, and water to make 1,000 ml. Therefore, the developing agents were maintained at the same condition as those in the developer. The conditions of analysis used in the experiment were as follows: flow rate 0.43 ml/min., column temperature 60°C. Analyses were performed at a wavelength of 260 nm. Samples were injected into the column with a microsyringe through the septum injector.

Figure 1 shows the chromatograms of Metol and hydroquinone. The retention times of Metol and hydroquinone were about 25 min. and 7 min., respectively.

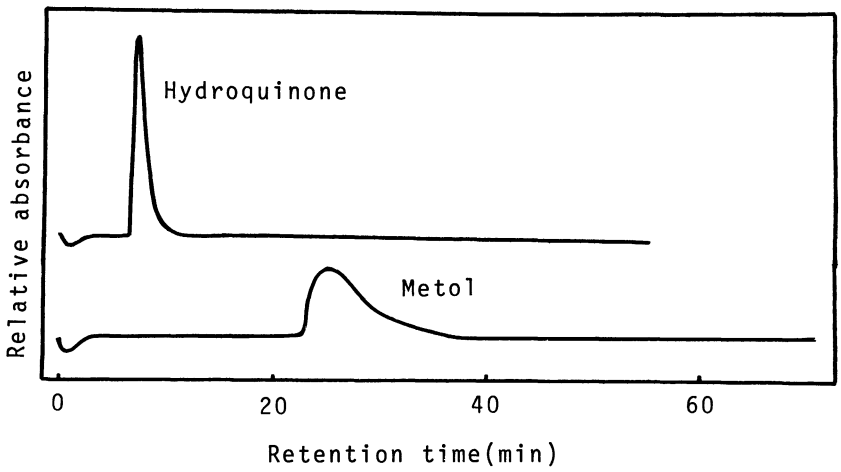

Fig. 1 Chromatograms of hydroquinone and Metol

Figure 2 shows the calibration curves of Metol and hydroquinone. Linear relationships were observed between peak height or peak area and the concentration of developing agents. In order to simplify the measurements, the peak height was

used to make calibration curves in Figure 2.

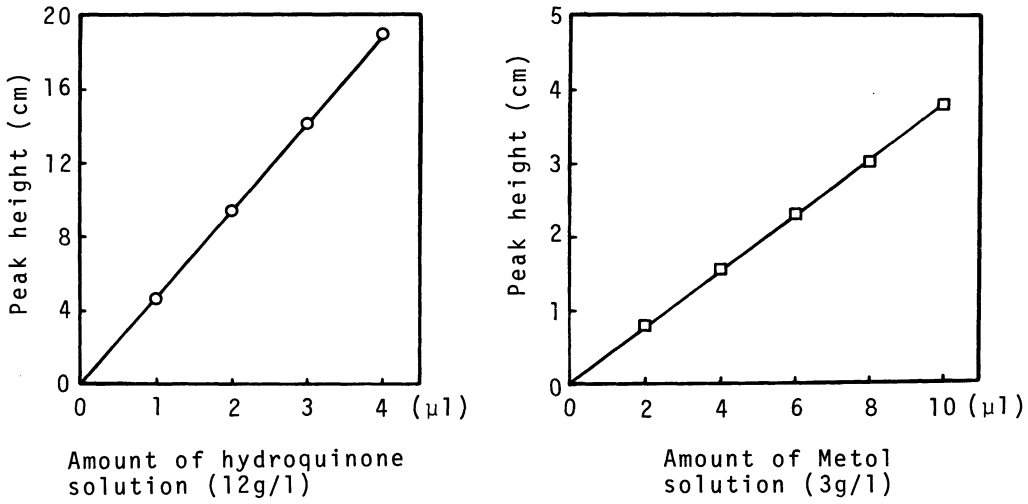

Fig. 2 Calibration curves of hydroquinone and Metol

Figure 3 shows that Metol and hydroquinone in Kodak D-72 developer were satisfactorily determined. The chromatograms of the exhausted developer by aerial oxidation are also shown in Figure 3. As the aerial oxidation increased, hydroquinone was gradually oxidized, but Metol was not oxidized when hydroquinone was present in the developer. Their oxidation products also could be detected by the liquid chromatography as shown in the chromatograms. This anion exchange resin is able to use many times without any special regeneration under this analytical con-

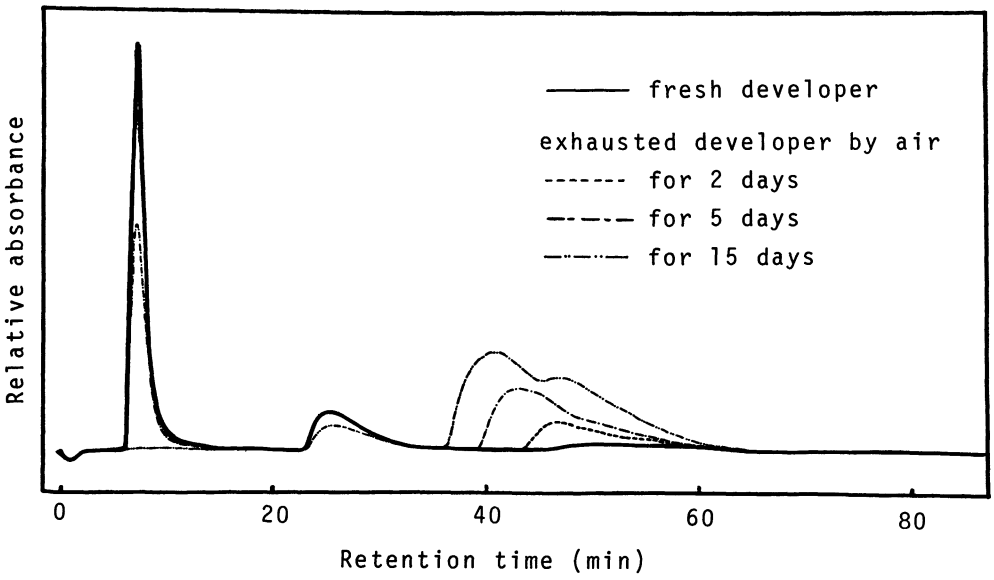

Fig. 3 Chromatograms of Kodak D-72 developer and its exhausted developer by aerial oxidation

ditions. The resin is useful in separating Metol, hydroquinone and their oxidation products.

Figure 4 shows the chromatogram of the exhausted developer by film processing. A pre-column was used to determine the developing agents in exhausted developer by film processing. The pre-column was connected in series to the analytical column. A strip of film was placed in the pre-column and the developer was injected into the pre-column through the septum injector. When the film is placed to the developer, the silver halide in the emulsion serves as the oxidizing agent in preference to oxygen. It shows that Metol was not consumed when hydroquinone existed in the developer during the processing.

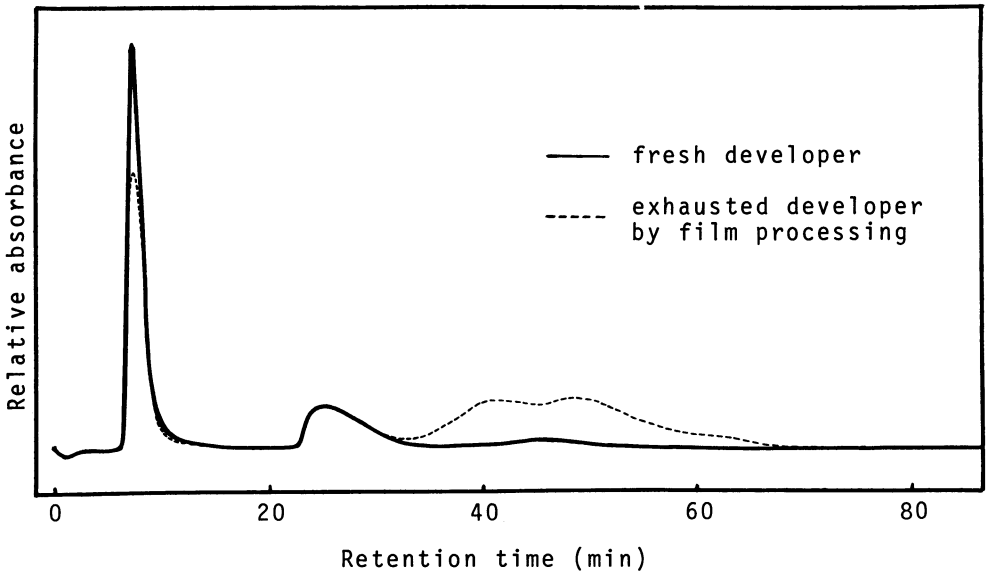

Fig. 4 Chromatograms of Kodak D-72 developer and its exhausted developer by film processing

It is said that hydroquinone is preferentially oxidized in a mixture of Metol and hydroquinone, either during development or by reaction with oxygen.

The present results suggest that this method may be applicable to determination of Metol, hydroquinone and their oxidation products in a photographic developer without any pre-treatment of the developer.

References and notes

1) p-methylaminophenol sulfate, this compound is known by several trade names, most commonly Metol.

2) G. Russell, "Chemical Analysis in Photography" Focal Press, London and New York (1965), pp 205-230.

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