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Note

Determination of trace phenol and isomeric hydroxybenzoic acids in aqueous benzoic acid solutions by aqueous liquid chromatography

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A study of the radiolytic oxidation of benzoic acid required a development of a rapid sensitive method for ultra-trace determinations of phenol and three isomeric hydroxybenzoic acids formed in irradiated dilute ($\leqslant 10^{-3}$ *M*) benzoic acid solutions. Aqueous liquid chromatography is an excellent tool for the trace determinations of polar organics in aqueous solutions[1]. A separation of benzoic acid and *o*-hydroxybenzoic acid on an anion-exchange column (2.1 mm × 1 m; DuPont, Wilmington, Del., U.S.A.) using an eluent made up of borate buffer, pH 9.2, and 0.05 *M* ammonium nitrate has been reported[2]. We determined that this method was not applicable for the trace determination of *p*-hydroxybenzoic acid because *p*-hydroxybenzoic acid was oxidized on the column by the nitrate in the eluent. Moreover the peaks due to benzoic acid and *m*- and *p*-hydroxybenzoic acids were not sufficiently resolved to allow reliable determinations of individual components. We report here our method that allows satisfactory results.

The chromatograph used in this study is described elsewhere[1]. A spectrophotometric detector (Model 1205; Laboratory Data Control, Riviera Beach, Calif., U.S.A.) operated at a wavelength of 254 nm was used. A separation (Fig. 1) of a five-component dilute ($\leqslant 3.7 \times 10^{-3}$ *M*) aqueous solution was conveniently realized on a column (2.1 mm × 2 m) packed with pellicular anion-exchange material (H. Reeve Angel, Clifton, N.J., U.S.A.) using water (buffered to pH 4.2 with 7 m*M* ammonium chloride) as the eluent. The column, pH 4.5, at 40°, was eluted at a flow-rate of 1 ml/min, which produced a pressure drop of 670 p.s.i. across the column. This chromatogram was recorded at an attenuation of 20, therefore *ca.* 5×10^{-5} *M* *o*-hydroxybenzoic acid and *ca.* 6×10^{-7} *M* *p*-hydroxybenzoic acid could be readily determined at a signal-to-noise ratio of >2. The detection limit for other components was between these two limits. The ultra-trace determination of individual components was best realized by optimizing the chromatographic separation conditions and monitoring the peaks at a wavelength of maximum absorption. The monitoring of *o*-hydroxybenzoic acid at 303 nm ($\varepsilon_{max.}$ 3600) would improve the sensitivity at least by an order of magnitude.

A comparison of the performance characteristics of columns packed with polystyrene (H. Reeve Angel) and methylmethacrylate (DuPont) based anion-exchange material indicated that only those columns packed with polystyrene-based material

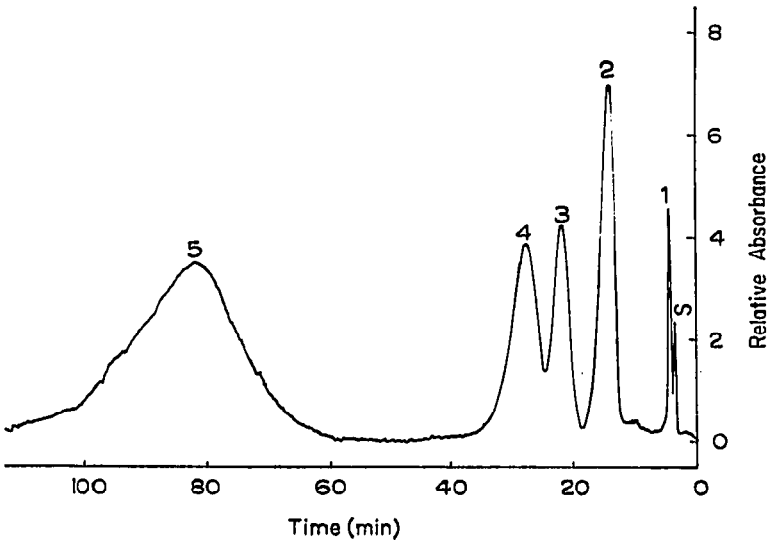

Fig. 1. Separation of phenol, benzoic acid and isomeric hydroxybenzoic acids using a polystyrene-based strong anion-exchange column (2.1 mm × 2 m) at 40° and water (buffered to pH 4.2 with 7 m*M* NH_4Cl) at a flow-rate of 1 ml/min as the eluent. 1 = Phenol (1×10^{-4} *M*); 2 = benzoic acid (5×10^{-4} *M*); 3 = *p*-hydroxybenzoic acid (5×10^{-4} *M*); 4 = *m*-hydroxybenzoic acid (5×10^{-4} *M*); 5 = *o*-hydroxybenzoic acid (3.7×10^{-3} *M*); S = solvent.

were stable to operations for extended periods at elevated temperatures (up to 60°) and with aqueous alcoholic eluents. A column at 40° packed with methylmethacrylate material lost its separation ability because of a loss of the coated material upon injection of a sample (0.2 ml) of ethanol.

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