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Note

High-performance liquid chromatographic determination of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether in water

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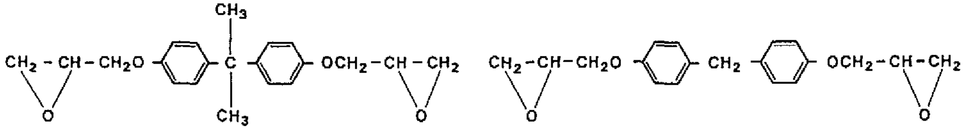
The condition of the water distribution system in the United Kingdom is of increasing concern to the water industry. The total length of water distribution pipe is in the region of 320 000 km and pipes made from cast-iron account for 70–80% of this figure. In many areas, corrosion of cast-iron pipes has resulted in poor flow, low pressure, discoloured water and an increase in the frequency of bursts and consumer complaints. The growing awareness of this progressive corrosion and the high cost of laying new pipes has led to the development of *in situ* renovation techniques[1].

The development of a renovation technique based on epoxy-resin began in 1977. During field trials on the process in 1980–1981, analytical work was carried out on samples of water which had been in contact with epoxy-resin lining[2]. In this work, gas chromatography–mass spectrometry and field-desorption mass spectrometry were used to show that certain organic compounds, known to be in the epoxy-resin formulation, were present in these water samples. Due to the nature of this work it was not possible to give reasonably accurate estimates of the concentration of most of the compounds detected. A realistic assessment of any risk to public health due to the presence of these compounds in drinking water could not be made without more information on the levels present. Therefore, it was necessary to develop methods of analysis for these compounds, to be used to monitor *in-situ* epoxy-resin relining operations and which would enable reasonably accurate quantitation down to a level of about 1 $\mu g\ l^{-1}$.

Epoxy-resins used for the renovation of water pipes are based on either bisphenol A diglycidyl ether or a mixture of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether. Residues of these compounds in water appear to be due to incomplete polymerisation. The structures of both of these compounds are shown in Fig. 1. The use of high-performance liquid chromatography (HPLC) for the characterisation of bisphenol-type epoxy resins has been described previously[3–7]. Re-



Bisphenol A diglycidyl ether

Bisphenol F diglycidyl ether

Fig. 1. Structure of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether.

versed-phase systems using either water–tetrahydrofuran[3], water–*p*-dioxane[4], water–acetonitrile[3,5,6] or water–methanol–dichloromethane[7] as eluent have been shown to give good separation of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether oligomers.

In this paper, a method for the analysis of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether in water is reported. Extraction from water is carried out by adsorption on to C_{18} bonded silica with separation and quantification using reversed-phase HPLC.

EXPERIMENTAL

Materials

Bisphenol A diglycidyl ether was obtained courtesy of Shell Chemical Company and bisphenol F diglycidyl ether courtesy of Sandalin International Ltd. Both compounds were of unspecified purity although only minor impurities were observed by HPLC separation of standard solutions. Methanol and dichloromethane (glass distilled grade) were obtained from Rathburn Chemicals and water used for HPLC eluent was deionised, double-distilled grade. Sep-pak cartridges (C_{18} silica) were obtained from Waters Assoc. New cartridges only were used. These were prepared for use by elution with methanol (20 ml), dichloromethane (20 ml), methanol (20 ml) and de-ionised double-distilled water (2 ml).

Concentrated solutions (1 mg ml^{-1}) of bisphenol A diglycidyl ether were prepared in methanol and of bisphenol F diglycidyl ether in methanol–dichloromethane (9:1). Dilute solutions were prepared as required by addition of methanol. All standard solutions were stored in the dark at −18°C. Although no specific experiments were carried out on the stability of solutions, no deterioration of concentrated solutions was observed for at least six months after preparation when the solutions were stored in this way.

The equipment used consisted of a Varian 5060 solvent delivery system and a Varian UV 50 variable-wavelength detector operating at 275 nm or a Hewlett-Packard 1040A scanning diode-array UV detector. Injections were made using a Rheodyne valve (Model 7125). The column (25 cm × 4.6 mm I.D.) was packed in our laboratory with 5 μm particle size Spherisorb ODS (Phase Separations) by a slurry procedure using acetone as slurry medium. Elution conditions were isocratic elution with water–methanol–dichloromethane (20:50:30) at a flow-rate of 1 ml min^{-1}.

Extraction

The water sample (500 ml or 50 ml) is eluted through a clean Sep-pak cartridge using a 50-ml luer-lock glass syringe at a flow-rate of approximately 20 ml min^{-1}. The cartridge is then eluted with methanol–dichloromethane (1:1, 1 ml) at a flow-rate of approximately 2 ml min^{-1}. The first 0.5 ml eluted is discarded and the remainder collected. The cartridge is then eluted with methanol–dichloromethane (1:3, 1 ml) at a flow-rate of approximately 2 ml min^{-1}, collecting all of the eluate. The eluates are combined and concentrated to 0.5 ml under a stream of nitrogen.

TABLE I
RESULTS FROM SPIKING EXPERIMENTS

Sample volume (ml)	*Concentration ($\mu g\ l^{-1}$)*	*Recovery (%)*
Bisphenol A diglycidyl ether		
500	1	91
500	10	96
500	100	93
500	500	93
50	1000	88
Bisphenol F diglycidyl ether		
500	1	82
500	10	80
500	100	92
500	500	91
500	1000	66
50	1000	82
Bisphenol A diglycidyl ether–bisphenol F diglycidyl ether (1:1)		
500	1000*	80 (bisphenol A diglycidyl ether) 72 (bisphenol F diglycidyl ether)
50	1000*	92 (bisphenol A diglycidyl ether) 97 (bisphenol F diglycidyl ether)

* Total concentration.

RESULTS AND DISCUSSION

Recovery efficiencies for bisphenol A diglycidyl ether and bisphenol F diglycidyl ether from water were determined by analysing samples of tap water spiked at levels between 1 and 1000 $\mu g\ l^{-1}$. Several determinations were carried out within this range to determine whether reasonable recoveries could be obtained. Results from these experiments are given in Table I. Recoveries of 80% or better were always obtained for both components, with 500 ml samples, at concentrations up to 500 $\mu g\ l^{-1}$. Experiments carried out on samples spiked at 1000 $\mu g\ l^{-1}$ gave lower recoveries than expected, possibly indicating breakthrough of the determinands through the cartridge. The improved recoveries obtained from analysis of 50-ml samples spiked at 1000 $\mu g\ l^{-1}$ support this. The method was developed to enable reasonably accurate quantification at concentrations down to 1 $\mu g\ l^{-1}$. The recovery figures indicate that this objective was fulfilled with high recoveries being obtained with a variation of around ± 10%. The detection limit of the method is lower than this, and concentrations of about 0.5 $\mu g\ l^{-1}$ can be monitored although we have no information on the precision at this level. An HPLC chromatogram from the separation of a standard solution containing bisphenol A diglycidyl ether and bisphenol F diglycidyl ether is illustrated in Fig. 2. It should be noted that small variations in the

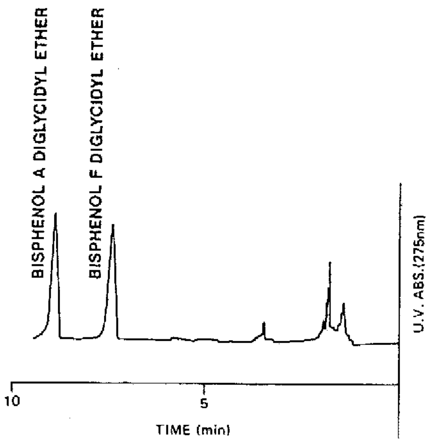


Fig. 2. HPLC separation of a standard solution of bisphenol A diglycidyl ether (300 ng) and bisphenol F diglycidyl ether (300 ng). Conditions; column, Spherisorb-ODS (5 μm); eluent, water–methanol–dichloromethane (20:50:30); flow-rate, 1 ml min^{-1}; detection, UV 275 nm, 0.05 a.u.f.s.

amount of dichloromethane in the eluent can lead to changes in the retention times of both compounds. Retention of both compounds is increased with a slightly reduced amount of dichloromethane in the eluent and decreased with more dichloromethane present. In our experience, baseline resolution of the two compounds is always obtained; however, this should be confirmed, by analysis of standard solutions, for each batch of eluent prepared. After equilibration of the column with each batch of eluent the retention time of both compounds is stable. This variation is illustrated in Figs. 2 and 3 where the retention time of bisphenol A diglycidyl ether changes from 8.8 min to 7.5 min.

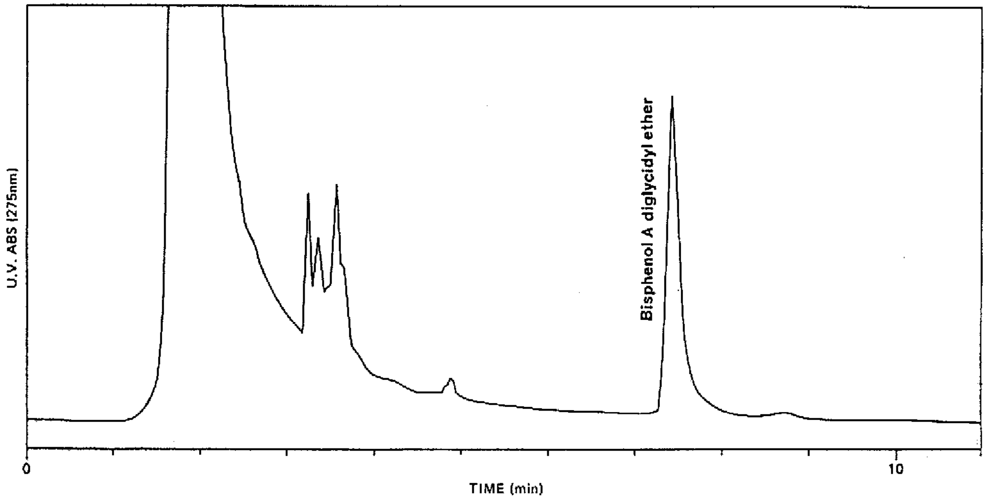


Fig. 3. HPLC separation of an extract of water which has been in contact with an epoxy-resin lining. Conditions as in Fig. 1 except a detector attenuation of 0.02 a.u.f.s.

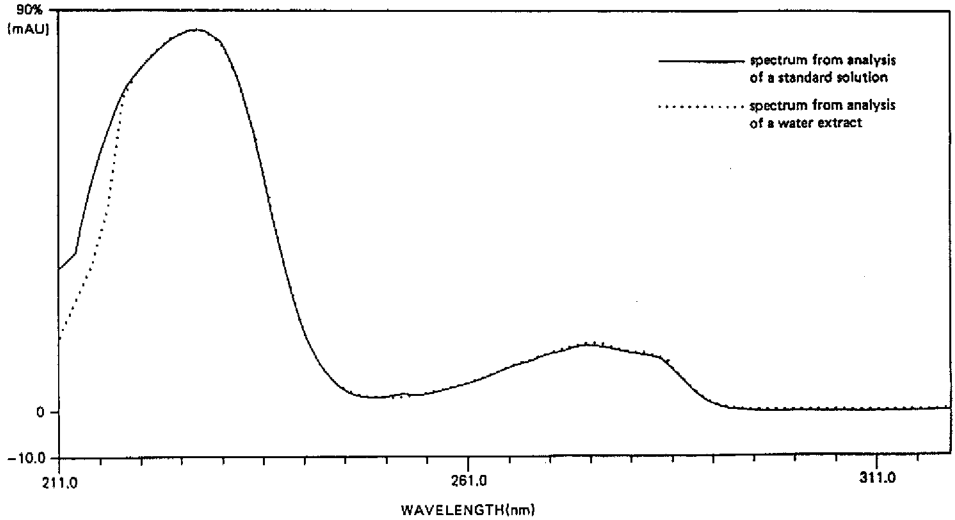


Fig. 4. UV spectra of bisphenol A (or F) diglycidyl ether recorded using a photodiode array detector.

A chromatogram from analysis of a sample taken from a water pipe which was lined with epoxy-resin is shown in Fig. 3. The presence of the two bisphenol diglycidyl ethers in this sample is clearly demonstrated. Confirmation of peak identity can be obtained by a comparison of UV spectra recorded using the photodiode-array detector. Fig. 4 shows a UV spectrum of the two bisphenol diglycidyl ethers recorded from analysis of a water extract and, for comparison, a UV spectrum from the separation of a standard solution. The UV spectra of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether are identical. Two maximum are observed, at 225 nm and 275 nm. Routine monitoring of water extracts was carried out at 275 nm rather than 225 nm even though this results in some loss of sensitivity. However, since many more compounds absorb at 225 nm compared to 275 nm, the possibility of interference from other compounds present in the water extract is reduced.

This method thus provides a way of monitoring concentrations of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether down to 1 $\mu g\ l^{-1}$ in water following *in-situ* epoxy-resin relining.

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