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Note

Determination of residual epichlorohydrin in middle cut alkylglycidyl ethers by headspace gas chromatography

ALAN H. ULLMAN* and ROBERT HOUSTON
The Procter & Gamble Company, Sharon Woods Technical Center, 11530 Reed Hartman Highway, Cincinnati, OH 45241 (U.S.A.)
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Epichlorohydrin (1-chloro-2,3-epoxypropane) has been determined in a variety of matrices by extraction followed by infrared spectrophotometry[1,2], colorimetry[3–5], and by direct injection gas chromatography (GC)[6–8]. When the need developed to determine low levels of residual epichlorohydrin (epi) in some middle cut (C_{12} to C_{16}) alkylglycidyl ethers, also known as alkylglyceryl ethers (AGE), these methods were considered and rejected as too long and involved, too insensitive, and/or unsuited to our matrix. We needed a method which could quantitate epi concentrations below 100 μg/g and be fast as well as simple enough to install in a manufacturing plant laboratory.

Headspace (GC)[9] was the method of choice since it is quite sensitive and reasonably interference-free. The fairly volatile epi (boiling point 118°C), is determined in the vapor above the high-boiling (high-molecular-weight, >200) glycidyl ethers which are the main components of the sample. This simplifies GC conditions by reducing analysis time and lowering column temperatures, and increases the sensitivity of the determination, compared to direct injection of the liquid sample.

EXPERIMENTAL

A Valco (Houston, TX, U.S.A.) zero dead-volume, stainless-steel, 6-port liquid chromatography valve (Model CV-6-UHPa-N60) was attached to the external portion of the injection port of a Perkin-Elmer 3920 gas chromatograph using 1/8-in. Swagelok fittings. The dead volume of the injection port was substantially reduced by placing a glass insert in the injection port and extending a PTFE-lined 1/8 in. O.D. (0.070 in. I.D.) stainless-steel tube from the valve body through the glass insert to the rear of the injection port. The PTFE lining of the tubing prevented decomposition of the analyte due to contact with any hot metal surfaces in the injection port and reduced the dead volume. The valve body and sample loop were also lined with or fabricated of an inert fluorocarbon "Valcon-H". The valve configurations are shown in Fig. 1. For temperature control, we wrapped the valve and loop with heating tape (attached to a Variac) and mounted a thermocouple temperature probe on it. By adjusting the Variac, the temperature could be controlled from approximately 50°C to 150°C. Valco literature indicated the valve could tolerate 175°C.

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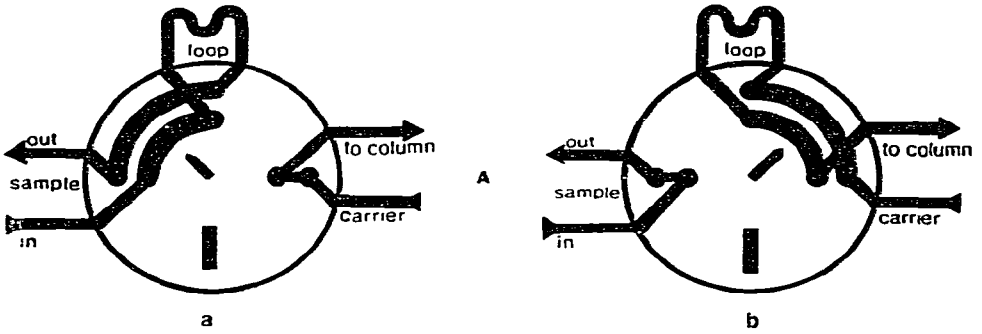

Fig. 1. Internal configuration of the valve in "fill" (a) and "inject" (b) positions. The syringe is attached to "in" during "fill". "Out is connected to a water aspirator, which is used to purge the system between samples. Redrawn from Valco Instrument Company Sales literature, with permission.

Samples (1 ml) of AGE were equilibrated for 15 min at 60°C in 10 ml serum vials (Wheaton Scientific, Millville, NJ, U.S.A.) sealed with PTFE-faced rubber septa. Vapor samples were removed from the vials and introduced to the valve-loop assembly with a heated Hamilton gas-tight syringe. GC conditions are summarized in Table I. Epichlorohydrin was purchased from Matheson, Coleman and Bell (East Rutherford, NJ, U.S.A.).

TABLE I

GC CONDITIONS USED FOR THE DETERMINATION OF EPICHLOROHYDRIN

Instrument	P-E 3920 modified for headspace
Detector	Flame ionization
Integrator	P-E Sigma 10
Carrier gas	Nitrogen; 20 ml/min
Valve–sample loop assembly temperature	60°C
Injection port temperature	200°C
Oven temperature	80°C for 8 min, then 32°/min to 140°C
Interface temperature	200°C
Detector temperature	250°C
Column	10 ft. × 1/4 in. O.D. (2 mm I.D.) glass packed with 100–120 mesh Ultra-Bond PEGS (RFR Corp., Hope, RI, U.S.A.)
Transfer syringe	5 ml, Hamilton, gas-tight, *ca.* 60°C
Approximate retention time of epichlorohydrin	4.6 min

Epi-free AGE was prepared by bubbling nitrogen through a stirred portion of the AGE which was heated to approximately 45°C, until the sample analyzed by the method described here did not show the presence of an epi peak. An attempt to verify independently the absence of epi in the blank using a modification of the method of ref. 3 was not successful, presumably due to a matrix effect. The sparged material was

used as the blank for epi determinations and for preparation of standards. Standards were made by adding weighed amounts of epi to the blank and diluting these with additional blank AGE to reach the desired epi concentration.

RESULTS AND DISCUSSION

Quantitation of epi in AGE depends upon equilibrium being attained between the liquid and gas phases. While only a portion of the epi contained in the headspace was measured, the absolute amount of epi was not known or desired. Since we carefully controlled equilibration and sampling conditions, the amount of epi in the vapor was proportional to the original concentration in the liquid phase and therefore could be used to determine the level of epi in the sample. Based on our experiments with epi in AGE and epi dissolved in ethylene glycol we estimated the distribution coefficient for epi–AGE to be 3% vapor–liquid phase.

The equilibration temperature of 60°C was chosen because it was high enough to provide the required sensitivity by vaporizing reasonable amounts of epi in the headspace, but low enough to prevent vaporization of higher boiling components in the sample. Higher and lower equilibration temperatures gave poorer results.

Optimum equilibration time was determined experimentally by analyzing the same sample repeatedly using different equilibration times. An equilibration time of 15 min was chosen for all analyses because, under our conditions, there was little increase in peak area after that length of time (Fig. 2).

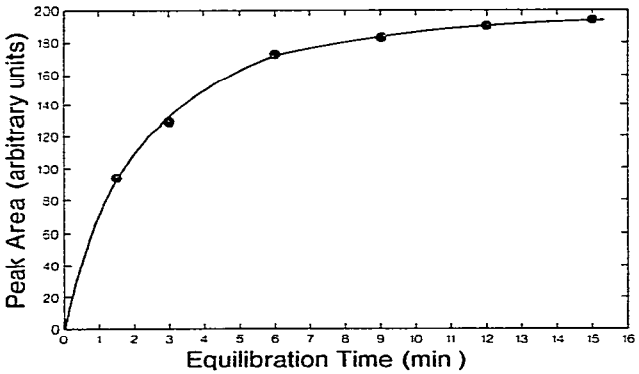

Fig. 2. Equilibration of epichlorohydrin between the liquid and vapor phases. Equilibrium is reached after approximately 12 min, as the epi vapor reaches a maximum and levels off.

A typical chromatogram is given in Fig. 3. The epi peak retention time and calibration curve were checked daily. Adequate separation was attained with an isothermal program, but to prevent possible carry-over from run to run, the temperature was increased to 140°C at 32°C/min after 8 min at 80°C. Average analysis time was approximately 20 min per sample since the start of each equilibration was staggered, to coincide with the GC run.

The calibration curve was linear (correlation coefficient 0.999) for at least three orders of magnitude above the limit of detection. Fig. 4 is the low concentration portion of the calibration curve. No attempt was made to determine whether linearity

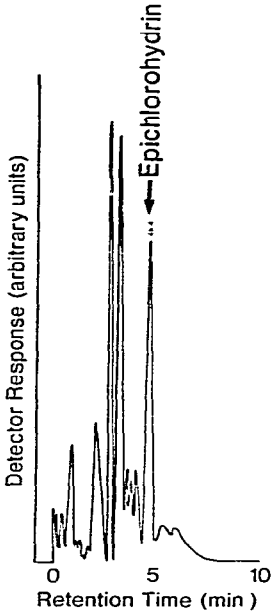

Fig. 3. Typical gas chromatogram of a middle cut alkylglycidyl ether from the headspace GC determination of epichlorohydrin.

extended above approximately 2000 μg/g. The limit of detection was approximately 2 μg/g based on a signal-to-noise ratio of 3; this might be lowered further by using a larger volume sample loop. The reproducibility of the method at several concentration levels is shown in Table II.

Experience with this method for more than a year and hundreds of samples indicates that it is both a simple and reliable method for determining epichlorohydrin

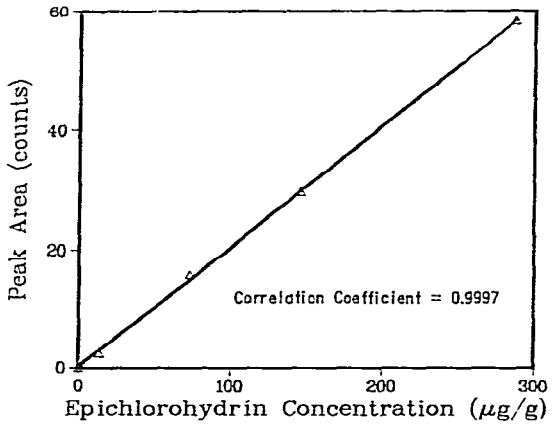

Fig. 4. Calibration curve for epichlorohydrin in a middle cut alkylglycidyl ether as determined by headspace GC. Linearity extended from the detection limit (approximately 2 μg/g) up to at least 2000 μg/g.

TABLE II

PRECISION OF THE HEADSPACE GC EPICHLOROHYDRIN METHOD

Number of replicates	*Mean concentration (μg/g)*	*Standard deviation (S.D.) (μg/g)*	*Relative S.D. (%)*
7	847	16	1.8
8	100	2.6	2.6
10	7	0.93	12.5

in mid-cut alkylglycidyl ethers. It is capable of providing precise results at epi concentrations as low as *ca.* 2 μg/g and can do so on simple, inexpensive equipment in a short period of time.

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