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# GLC Determination of Ethylene Chlorohydrin following Co-Sweep Extraction

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**Abstract** □ A Co-Sweep extraction method was developed for removing and concentrating trace amounts of ethylene chlorohydrin from a variety of materials which were sterilized with ethylene oxide. Samples placed inside glass tubes were extracted in an apparatus with the aid of heat, solvents, and a continuous flow of carrier gas. The volatilized solvents were condensed in a cooling coil and swept into a collection tube. The entire extraction procedure was accomplished within 35 min. GLC was used to analyze the extract for ethylene chlorohydrin in the nanogram range. An ethylene chlorohydrin recovery study was performed in the microgram per gram range on different types of samples. The results indicate that the Co-Sweep technique is reliable, simple to operate, and potentially applicable to a wide variety of materials.

**Keyphrases** □ Ethylene chlorohydrin—determination □ Ethylene oxide-sterilized materials—ethylene chlorohydrin extraction, determination □ Extraction, Co-Sweep—ethylene chlorohydrin □ GLC—analysis

Ethylene oxide is now being used extensively for the sterilization of foods, pharmaceuticals, and manufactured goods. Numerous researchers have reported on various aspects of ethylene oxide sterilization. Until 1965, the only residues found from the use of this epoxide were ethylene oxide *per se*, ethylene glycol, and diethylene glycol (1–8). Wesley *et al.* (9) showed that chlorohydrins could be formed in foods fumigated with ethylene oxide or propylene oxide in the presence of inorganic chloride. Methods for analyzing ethylene oxide-sterilized foods, plastic, and rubber materials for residual ethylene chlorohydrin (2-chloroethanol) were reported by various researchers (10–17). Spitz and Weinberger (18) recently reported on a GLC method for the determination of ethylene oxide and the simultaneous determination of ethylene chlorohydrin and ethylene glycol in cellulose-type materials.

A rapid method was developed for the extraction of trace amounts of ethylene chlorohydrin from fabrics, cellulose-type materials, and a conglomerate of various materials sterilized by ethylene oxide. An aqueous extraction of ethylene chlorohydrin was achieved with a Co-Sweep extraction apparatus using heat, solvent, and a continuous flow of nitrogen gas. The entire extraction procedure was completed within 35 min. The

aqueous extract obtained was quantitatively determined for ethylene chlorohydrin by GLC analysis.

## EXPERIMENTAL

**Apparatus**—A Kontes Sweep Co-Distiller<sup>1</sup> (No. K-500750) was employed for the extraction and was equipped with a four-bay manifold flowmeter (K-628100-000), Teflon connection tubing (K-500500-307), and specially made glass side-arm sample tubes (13 mm. o.d. × 11 mm. i.d. × 33 cm. in length, with a 4-mm. Luer joint<sup>2</sup>). The open end of the tube was wrapped with two turns of Teflon ribbon tape [1.27-cm. (0.5-in.) width] and sealed with a 13-mm. o.d. silicone septum and a 0.97-cm. (0.38-in.) stainless steel hex-nut (Swagelock). The extracts were collected in 4-ml. graduated concentrator or collection tubes with a 19/22 ground-glass joint connected to glass extenders<sup>3</sup>. The end of the Teflon coil was held at the bottom of the collection tube by passing the tubing through a one-hole silicone septum (6 mm. o.d. × 8 mm. in length) inserted into a medicine dropper which was clamped in the bracket above the cooling bath. A cylinder of compressed nitrogen gas was equipped with a two-stage regulator and a 5A molecular sieve. A gas chromatograph<sup>4</sup>, equipped with a dual-flame ionization detector and a stainless steel column [0.318 cm. (0.125 in.) × 2.44 m. (8 ft.)] packed with 10% polyethylene glycol<sup>5</sup> on 60–80-mesh acid-washed diatomaceous silica<sup>6</sup>, was employed for all the experiments. The GLC operating temperatures were: column, 115°; injector, 135°; and detector, 200°. The GLC gases and flow rates were: helium, 30 ml./min. at 40 psig.; air, 300 ml./min. at 29 psig.; and hydrogen, 45 ml./min. at 27 psig.

**Procedure**—Prior to starting the extraction, the oven was adjusted to the horizontal position and preheated to 140°; the collection tubes and Teflon cooling coils were immersed in ice water baths, and the nitrogen carrier gas flow was adjusted in each of the four bays of the manifold flowmeter to approximately 75–80 ml./min. at 10 psig. A soap bubble meter was used to adjust the flow.

Four samples were extracted simultaneously in the Co-Sweep apparatus. The sample materials to be extracted were cut, weighed, and placed inside the glass sample tubes. A hex-nut and silicone rubber septum were used to seal each tube. Approximately 1 ml. of purified water was injected into the sample tubes with a hypodermic syringe and needle. The sample tubes were placed inside the preheated oven (140°) and connected to the Teflon cooling coil and then to the nitrogen carrier gas flow. The extraction time was started at this point. After 15 min. of sweeping carrier gas through the

<sup>1</sup> Kontes Glass Co., Vineland, N. J.

<sup>2</sup> Drawing No. 002172-29, Kontes Glass Co., Vineland, N. J.

<sup>3</sup> Kontes No. K-570050-0425 and K-570100, part 355.

<sup>4</sup> F & M model 5750.

<sup>5</sup> Carbowax 20M, Union Carbide, New York, N. Y.

<sup>6</sup> Chromosorb W, Johns-Manville, New York, N. Y.

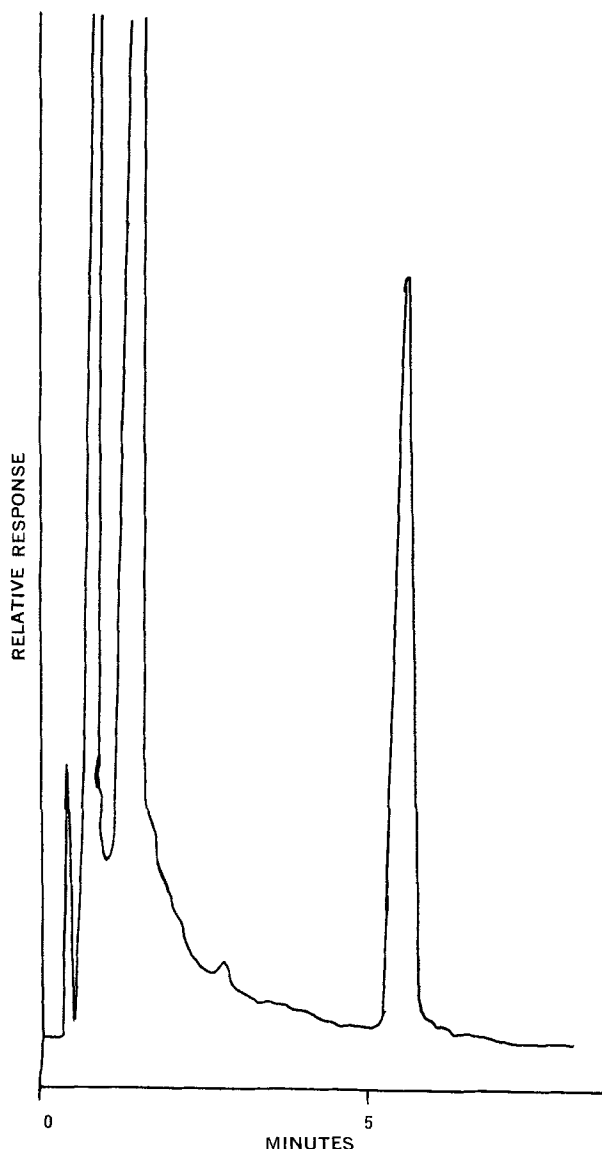


Figure 1—Gas chromatogram of a standard aqueous solution of ethylene chlorohydrin, representing 40 ng. Retention time = 5.5 min. Injection volume = 1  $\mu$ l. Attenuation range = 1 $\times$ 4.

sample tubes and Teflon cooling coils, a 1-ml. injection of isooctane<sup>7</sup> was made into each sample tube through the septum using a 5-ml. hypodermic syringe and needle. Two additional 1-ml. injections of isooctane were performed at 5-min. intervals. After 30 min. of extraction, each cooling coil was disconnected from the sample tube and rinsed with 0.5 ml. of isooctane. The Teflon cooling coil was then connected again to the sample tube so that the carrier gas flow could force the rinse into the collection tube. The extraction was terminated after 35 min., and the collection tubes were removed from the water bath. The tubes were centrifuged at 1500 r.p.m. for 1 min. to remove any water droplets trapped in the isooctane layer. The volume of aqueous phase (bottom layer) in each tube was read to the nearest 0.01 ml. from the graduations on the tube. The Co-Sweep aqueous extracts were then quantitatively analyzed for ethylene chlorohydrin by GLC analysis on 1.0- $\mu$ l. injections.

The elution time for ethylene chlorohydrin from the time of injection was approximately 5 min. Standard aqueous solutions of ethylene chlorohydrin<sup>8</sup> were prepared in the same concentration range as present in the samples. The peak height method was used to calculate the ethylene chlorohydrin content. Recovery studies were performed by carrying out the same extraction procedure on

<sup>7</sup> Matheson Coleman & Bell.  
<sup>8</sup> Aldrich Chemical Co.

Table I—Recovery of Ethylene Chlorohydrin

Material <sup>a</sup>	Micrograms Added	Percent Recovery <sup>b</sup>
Plastic <sup>c</sup> , cotton, and rayon	0	0
	1.5	101
	2.35	102
	4.60	93.5
Wood pulp nonwoven fabric	0	0
	11.5	94.7
	23.0	92.9
Rayon nonwoven fabric	0	0
	57.8	91.7
	48.0	91.7

<sup>a</sup> Weight of material ranged from 1.0 to 1.6 g. <sup>b</sup> Average value based on duplicate sample injections. <sup>c</sup> Polyvinyl chloride plasticized with dioctyl phthalate; sheet thickness = 0.1524 mm. (0.006 in.).

1-ml. aliquots of aqueous standard solutions of ethylene chlorohydrin which were pipeted onto unsterilized samples of material inside the sample tube. Ethylene oxide-sterilized counterparts of the sample materials were also subjected to the Co-Sweep technique and analyzed for ethylene chlorohydrin by GLC analysis.

## RESULTS AND DISCUSSION

The recovery of ethylene chlorohydrin obtained with the Co-Sweep extraction method on various spiked materials is presented in Table I. The high recoveries obtained for ethylene chlorohydrin in the range of 1.5–57.8 mcg. seem to indicate that no appreciable adsorption took place on the spiked materials. Unspiked samples of materials were also extracted to eliminate the possibility of interfering peaks having the same retention time as ethylene chlorohydrin; for this reason, unsterilized counterparts of ethylene oxide-sterilized materials should also be extracted and analyzed for ethylene chlorohydrin as a precautionary measure. Table II shows the concentration of ethylene chlorohydrin found in ethylene oxide-sterilized counterparts of the sample materials used in Table I.

The rate of removal of ethylene chlorohydrin from an aqueous solution seems to be directly related to the nitrogen gas flow rate through the solution with time. A 13% loss of ethylene chlorohydrin occurred from a 50-mcg./ml. solution after bubbling nitrogen gas into the collection tube at a flow rate of 120 ml./min. for 1 hr. At a nitrogen flow rate of 50 ml./min., the loss of ethylene chlorohydrin was 3% in 1 hr. Therefore, to minimize the possible loss of ethylene chlorohydrin, a short extraction time of 35 min. and a low nitrogen flow rate of 75–80 ml./min. were chosen for the Co-Sweep extraction method.

Table III shows the recovery of ethylene chlorohydrin obtained from spiked rayon samples under different conditions of Co-Sweep extraction. Lower recoveries of ethylene chlorohydrin were obtained at extended extraction times and higher nitrogen flow rates (and, also, when helium was substituted for the carrier gas). Higher extraction temperatures above 140° caused additional volatiles to show up on the gas chromatogram of some samples which interfered with the analysis.

The isooctane injected into the sample tube does not affect the aqueous volume and was used to drive the condensed water droplets

Table II—Ethylene Chlorohydrin Found in Ethylene Oxide-Sterilized<sup>a</sup> Materials by Co-Sweep Extraction

Material <sup>b</sup>	Percent Weight/Weight Ethylene Chlorohydrin <sup>d</sup>
Plastic <sup>c</sup> , cotton, and rayon	0.00017
Wood pulp nonwoven fabric	0.00046
Rayon nonwoven fabric	0.00003

<sup>a</sup> Samples of materials were previously sterilized in a commercial ethylene oxide sterilization cycle. <sup>b</sup> Weight of material analyzed ranged from 1.0 to 2.9 g. <sup>c</sup> Polyvinyl chloride plasticized with dioctyl phthalate; sheet thickness = 0.1524 mm. (0.006 in.). <sup>d</sup> Average value based on duplicate injections.

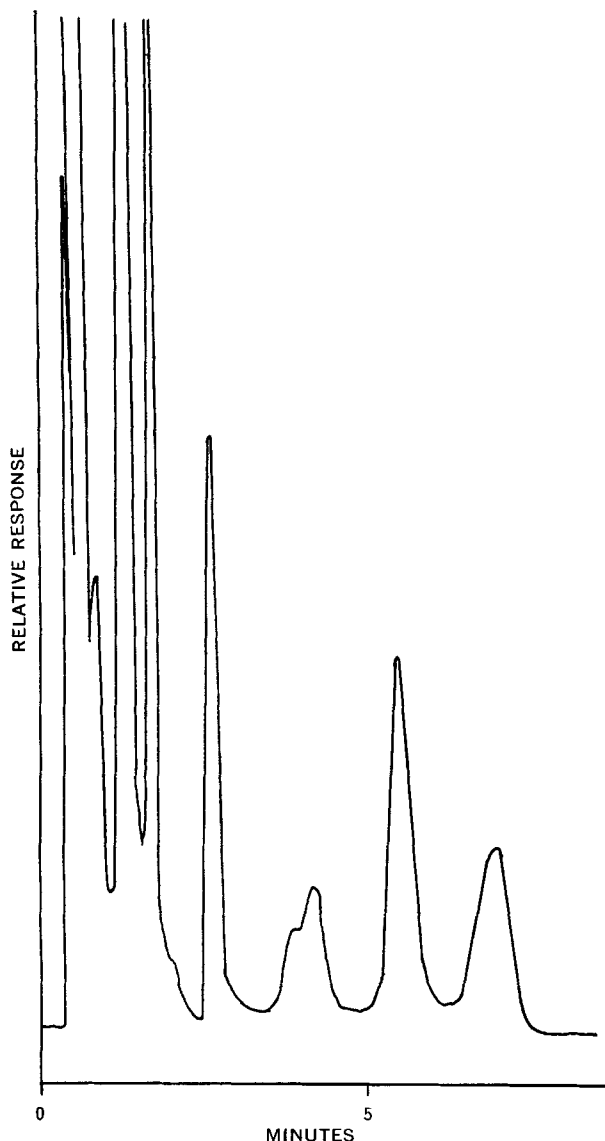


Figure 2—Typical gas chromatogram obtained from a Co-Sweep extract of an ethylene oxide-sterilized material composed of plastic, cotton, and rayon. Retention time of ethylene chlorohydrin = 5.5 min. Injection volume = 1  $\mu$ l. Attenuation range = 1 $\times$ 4.

into the collection tube. The extracted ethylene chlorohydrin remains preferentially in the aqueous layer; this was determined by GLC analysis on both layers. A gas chromatogram of a standard aqueous solution of ethylene chlorohydrin, representing 40 ng., is shown in Fig. 1. A typical gas chromatogram obtained from a Co-Sweep extract of an ethylene oxide-sterilized material composed of plastic<sup>9</sup>, cotton, and rayon is shown in Fig. 2. The complexity of the gas chromatogram in Fig. 2 as compared to the aqueous standard (Fig. 1) is due to additional components extracted from the plastic material.

The sensitivity of the GC instrument for ethylene chlorohydrin is approximately 0.2 ng./ $\mu$ l. injection. Therefore, the total weight of sample to be extracted by the Co-Sweep technique must contain more than 0.2 mcg. of ethylene chlorohydrin for a positive detection by GLC analysis (based on a 1- $\mu$ l. injection from 1 ml. of aqueous extract). The amount of water used in the extraction can be reduced below 1 ml. for samples containing a high moisture content or, if desired, to lower the ethylene chlorohydrin detection level.

<sup>9</sup> Polyvinyl chloride sheet [thickness 0.1524 mm. (0.006 in.)] plasticized with dioctyl phthalate.

Table III—Recovery of Ethylene Chlorohydrin from Rayon Staple<sup>a</sup> under Varying Conditions of Co-Sweep Extraction<sup>b</sup>

Carrier Gas	Flow Rate, ml./min.	Minutes	Number of Injections, 1 ml. —		Percent Recovery <sup>c</sup> , Range
			Water	Isooctane	
Helium	120	60	1	5	78–83
Nitrogen	120	60	1	5	82–90
Nitrogen	120	45	1	5	82–84
Nitrogen	66	45	1	5	86–87
Nitrogen	120	35	1	3	85–87
Nitrogen	80	35	1	3	89–95

<sup>a</sup> Recovery based on spiking samples with 48 mcg. of ethylene chlorohydrin/g. <sup>b</sup> The oven temperature was 140°. <sup>c</sup> Based on duplicate injections from replicate sample extractions.

The Co-Sweep extraction method achieves a low level for determining ethylene chlorohydrin by increasing the sample weight relative to the aqueous extract volume. The method is potentially applicable to a wide range of materials and achieves a detection level for ethylene chlorohydrin at the micrograms per gram range in ethylene oxide-sterilized materials. In view of the foregoing results, the Co-Sweep extraction technique may be adaptable for the determination of various trace quantities of compounds or impurities in a wide variety of materials.

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