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SOLID SORBENT SAMPLING AND CHROMATOGRAPHIC DETERMINATION OF GLYCIDYL ETHERS IN AIR

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SUMMARY

Activated charcoal, Amberlite XAD-2 and XAD-7 were evaluated as solid sorbents for air sampling of isopropyl glycidyl ether (IGE), allyl glycidyl ether (AGE), *n*-butyl glycidyl ether (BGE), phenyl glycidyl ether (PGE) and *o*-cresyl glycidyl ether (CGE). IGE, AGE and BGE were determined by capillary gas chromatography and flame ionization detection, PGE and CGE by high-performance liquid chromatography and ultraviolet detection. Amberlite XAD-7 was the best sorbent for all glycidyl ethers except IGE, which showed insufficient retention on this sorbent. Activated charcoal gave good recoveries only for IGE, AGE and BGE. The storage stability was acceptable on all three sorbents, and relative humidity had little effect on retention and recovery.

INTRODUCTION

Glycidyl ethers may be considered ethers of 2,3-epoxypropanol ("glycidol"):

$$H_2C-CH-CH_2-O-R$$
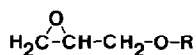
According to IUPAC nomenclature, the glycidyl ethers are derivatives of the three-membered oxirane ring. Since this ring is highly strained, epoxide-containing compounds will react with almost all nucleophilic (electron-donating) substances. Glycidyl ethers have become important because of this reactivity. The major industrial use of these compounds is as reactive diluents in epoxy resin systems, where the epoxide groups react to form cross-linkages within the resin. The glycidyl ethers most commonly used today include allyl glycidyl ether (AGE), *n*-butyl glycidyl ether (BGE), isopropyl glycidyl ether (IGE), phenyl glycidyl ether (PGE) and *o*-cresyl glycidyl ether (CGE). The oligomer with the lowest molecular weight of the glycidyl ether of bisphenol A, diphenylol propane diglycidyl ether, is probably the most common component of uncured epoxy resin[1]. In view of its toxicity, diglycidyl ether (DGE) is rarely found in industry today[1].

TABLE I

OCCUPATIONAL LIMITS FOR GLYCIDYL ETHERS IN SWEDEN AND THE UNITED STATES,
AS TIME-WEIGHTED AVERAGES FOR 8 h

Compound	Occupational limit value $(mg\ m^{-3})$	
	Sweden	U.S.A.
Isopropyl glycidyl ether	—	240
Allyl glycidyl ether	—	22
n-Butyl glycidyl ether	50	135
Phenyl glycidyl ether	60	6
o-Cresyl glycidyl ether	70	—

The primary effects of glycidyl ethers on workers are irritation and skin sensitization[2]. In 1978 NIOSH (U.S. National Institute for Occupational Safety and Health) estimated that 118 000 workers in the U.S.A. were exposed to glycidyl ethers and that an additional 1 000 000 workers were exposed to epoxy resins[1].

Table I shows the occupational limits for certain glycidyl ethers in Sweden[3] and the U.S.A.[4].

The use of solid sorbents for air sampling is preferable for the determination of workers exposure. NIOSH recommends activated charcoal for the sampling of IGE, BGE and PGE[5]. The charcoal tubes are desorbed with carbon disulphide and the glycidyl ethers are determined by gas chromatography (GC). Sampling on Tenax GC and diethyl ether desorption is recommended for AGE[6]. No recovery studies have been reported. In 1981 a method for determining $\mu g/l$ amounts of BGE, using high-performance liquid chromatography (HPLC) and ultraviolet detection at 245 nm, was published[7]. Attempts to reproduce this method failed since BGE shows practically no absorption in the ultraviolet region.

For several years we have been evaluating the Amberlite XAD porous polymers for sampling organics in workroom air[8-18]. In the present work we have evaluated XAD-2 and XAD-7, together with activated charcoal, for the sampling of industrially important glycidyl ethers in combination with chromatographic determination.

EXPERIMENTAL

Reagents

The solvents used were dichloromethane (B & J), acetonitrile (Rathburn, HPLC Grade) and water (Milli RQ-purified). The glycidyl ethers used were BGE (Fluka, purum), IGE (Merck, zur synthese), AGE (Fluka, purum), PGE (Merck, puriss) and CGE (Polysciences, purum). All were of 99% or higher purity, as determined by GC or HPLC .

The solid sorbents used were activated charcoal (SKC 226-01, Lot 120), Amberlite XAD-2 (SKC 226-30, Lot 285) and XAD-7 (SKC 226-30-11-07, Lot 260). The sorbents (20–40 mesh) were packed in sealed glass tubes (60 mm × 4 mm I.D.) with a 15-mm trapping section (100 mg) and an 8-mm back-up section (50 mg).

Recovery experiments

Recovery experiments were performed using air with known relative humidity. The humidified air was produced by saturation with water in gas dispersion bottles and dilution with dry air in an apparatus described previously[15]. To provide constant flow-rates for seven parallel adsorbent tubes, the humidified air was split between eight glass capillary tubes. Glass capillaries with a diameter of 0.30 mm and a length of 20 mm, giving a flow-rate of 200 ml min^{-1}, were used. One of the capillaries was connected to a relative humidity meter (Humicap 14; Vaisala OY, Helsinki, Finland). A glass tube, 80 mm × 4 mm I.D., provided with an injection port, was connected to each of the other capillaries. The glycidyl ether to be investigated was dissolved in dichloromethane (IGE, BGE) or acetonitrile (AGE, PGE, CGE), and 10 μl of this solution were injected through the injection port into the glass tube. The adsorbent tubes were directly connected to the injection tubes. When 5 or 25 l of air had been sampled, the glycidyl ether was desorbed by shaking the adsorbent beads for 30 min with 3.0 ml of dichloromethane or acetonitrile. IGE, AGE and BGE were generated at room temperature, PGE at 80°C and CGE at 125°C.

GC

The recoveries of IGE, AGE and BGE were determined by capillary GC. An Hewlett-Packard 5890 gas chromatograph and a cross-linked 5% phenylmethyl-silicone fused-silica capillary column, 25 m × 0.32 mm I.D., and film thickness 1.05 μm, were used. The splitting ratio was 1/30. The flame ionization detector temperature was 250°C for all three compounds. The column temperature was 60°C for IGE, 90°C for AGE and 130°C for BGE. Detection limits for IGE, AGE and BGE were all below 5% of the occupational limit, calculated for a 5-l air sample, a 3.0-ml desorption volume and a 2-μl injection volume.

HPLC

The recoveries of PGE and CGE were determined by HPLC. A Waters HPLC system, consisting of an M-6000 A pump, an M-710 B autosampler, an M-730 integrator and an M-440 absorbance detector, was used. The column was a Waters Radial-Pak Resolve (100 mm × 5 mm I.D., octadecylsilane, 10-μm particles). The mobile phase was 50% water in acetonitrile, and the flow-rate was 1.0 ml min^{-1}. The glycidyl ethers were detected at 280 nm with a detection limit of approximately 5 ng, corresponding to 0.3 mg m^{-3} in a 5-l air sample with an injection volume of 10 μl.

RESULTS

Recovery from activated charcoal

Since activated charcoal is the most frequently used sorbent for air sampling, it was evaluated for all five glycidyl ethers. Carbon disulphide and dichloromethane were evaluated for desorption of IGE and BGE. Both solvents gave satisfactory recoveries, but dichloromethane was chosen since it contaminated the GC detector to a smaller extent than did carbon disulphide. AGE, PGE and CGE were desorbed with acetonitrile.

Table II reports the recoveries from activated charcoal. The recoveries were determined with glycidyl ether amounts corresponding to 0.1, 1 and 10 times the

TABLE II

RECOVERY OF GLYCIDYL ETHERS FROM ACTIVATED CHARCOAL

Air volume: 5 l. Added amounts of 1200 μg, 110 μg, 250 g, 300 μg and 350 μg correspond to 240, 22, 50, 60 and 70 mg m^{-3}, respectively, in a 5-l air sample. R.S.D. = Relative standard deviation.

Compound	Amount added (μg)	Relative humidity (%)	Recovery (%)	R.S.D.$_{n=6}$ (%)
IGE	6000	20	98	3
		85	88	2
	1200	20	101	3
		85	100	5
		85	100	4
		85	98*	4
	120	20	100	4
		85	103	6
IGE**	1200	20	91	4
		85	94	3
AGE	550	20	98	2
		85	96	3
	110	20	98	2
		85	95	5
		85	85*	3
	11	20	96	4
		85	95	1
AGE**	110	20	87	4
		85	88	4
BGE	1250	20	96	2
		85	95	2
	250	20	95	4
		85	94	3
		85	98*	3
	25	20	93	3
		85	92	4
BGE**	25	20	93	2
		85	91	3
PGE	300	20	27	6
		85	26	5
CGE	350	20	8	8
		85	8	8

* A 25-l air sample.
** Stored for 2 weeks at room temperature in the dark.

occupational limits in a 5-l air sample. All recovery experiments were performed at 20 and 85% relative humidity. Exact breakthrough volumes were not determined, but a 25-l air sample was always taken at 85% relative humidity. A breakthrough volume > 25 l means that an 8-h sample with a flow-rate 50 ml min^{-1} can be taken without risk of breakthrough.

As Table II shows, recoveries from activated charcoal are in the range 88–103% for IGE, AGE and BGE. Recoveries at 85% relative humidity are generally somewhat lower. However, the difference is not significant in most cases.

Recoveries of PGE and CGE are considerably lower. The use of more polar or non-polar solvents for desorption did not increase the recovery.

In view of the reactivity of the glycidyl ethers, it was important to determine the storage stability of exposed sorbent tubes. The tubes were stored for 2 weeks at room temperature in the dark before desorption and analysis. Table II also shows the recoveries of IGE, AGE and BGE from charcoal after storage. There is a decrease (statistically significant) in the recovery of IGE and AGE. For BGE, the slight decrease is not statistically significant.

Recovery from Amberlite XAD-2

Table III shows the recoveries of all five glycidyl ethers from XAD-2. IGE and AGE are insufficiently retained on XAD-2. For IGE, there is a substantial

TABLE III

RECOVERY OF GLYCIDYL ETHERS FROM AMBERLITE XAD-2

Compound	Amount added (μg)	Relative humidity (%)	Recovery (%)	$R.S.D._{n=6}$ (%)
IGE	6000	85	49 (20% in back-up)	8
AGE	550	85	72* (16% in back-up)	5
BGE	1250	20	96	2
		85	96	2
	250	20	99	4
		85	97	1
		85	99*	2
	25	20	93	3
		85	99	1
BGE**	25	20	90	1
		85	89	1
PGE	1500	20	89	5
		85	91	3
	300	20	93	4
		85	94	1
		85	94*	5
	30	20	99	2
		85	97	1
PGE**	300	20	95	1
		85	94	3
CGE	1750	20	91	3
		85	77	8
	350	20	92	2
		85	79	5
		85	94*	4
CGE	35	20	90	4
		85	91	4
CGE**	350	20	83	4
		85	79	5

  * A 25-l air sample.
  ** Stored for 2 weeks at room temperature in the dark.

breakthrough, even when only 5 l of air are sampled. For AGE, 16% is found in the back-up section when 25 l of air are sampled. For BGE, the recoveries range between 93 and 99%. PGE is recovered to 89–99%, with no significant differences between 20 and 85% relative humidity. As Table III shows, CGE is recovered to more than 90% at most levels and relative humidities. At 85% relative humidity, however, there is

TABLE IV

RECOVERY OF GLYCIDYL ETHERS FROM AMBERLITE XAD-7

Compound	Amount added (μg)	Relative humidity (%)	Recovery (%)	R.S.D.$_{n=6}$ (%)
IGE	6000	85	77 (18% in back-up)	4
AGE	550	20	98	2
		85	96	3
		85	87* (5% in back-up)	3
	110	20	98	2
		85	95	5
		85	96*	1
	11	20	96	4
		85	95	1
AGE**	110	20	93	2
		85	93	3
BGE	1250	20	97	3
		85	96	2
	250	20	96	3
		85	97	2
		85	98*	1
	25	20	92	7
		85	97	4
BGE**	25	20	89	4
		85	88	2
PGE	1500	20	90	2
		85	90	5
	300	20	93	3
		85	91	4
		85	94*	4
	30	20	95	3
		85	98	3
PGE**	300	20	95	2
		85	91	3
CGE	1750	20	87	4
		85	77	7
	350	20	89	3
		85	95	2
		85	94*	3
	35	20	82	1
		85	92	1
CGE**	350	20	77	10
		85	77	2

* A 25-l air sample.
** Stored for 2 weeks at room temperature in the dark.

a decrease in recovery at 1750 and 350 μg. This decrease is not due to a breakthrough.

Table III also shows the storage stability data for the glycidyl ethers BGE, PGE and CGE on XAD-2. The exposed tubes were stored for 2 weeks at room temperature in the dark. In the case of BGE there is a 10% decrease ib recovery. PGE is unaffected by storage, but for CGE the decrease is approximately 10%.

Recovery from XAD-7

The recoveries of IGE, AGE, BGE, PGE and CGE are given in Table IV. IGE is not sufficiently retained on XAD-7; a 18% breakthrough to be back-up section is observed. The retention of AGE is excellent, but a small breakthrough is noted at 85% relative humidity at the 550-μg level when 25 l of air are drawn through the sorbent tube. BGE is well retained under all conditions studied, with a mean recovery of 96%. The recoveries of PGE are in the range 90–98%, with a mean of 93%. For CGE, there is a decrease in recovery at 85% relative humidity at the highest level. The mean recovery at all levels and relative humidities for CGE is 88%.

Table IV also shows the results of storage of AGE, BGE, PGE and CDE on XAD-7. For AGE and PGE, there is no significant decrease in recovery following storage in the dark for 2 weeks at room temperature. A 5–10% decrease is observed for BGE, and the decrease in recovery of CGE is 10–20%.

DISCUSSION

The use of solid sorbents is the most important method for monitoring harmful organic substances in workplace atmospheres. The most frequently used method is sampling on an activated charcoal sorbent, followed by carbon disulphide desorption and GC determination. Reactive organic compounds like the glycidyl ethers often decompose or absorb irreversibly on activated charcoal. For such compounds, sorbents of the porous polymer type, *e.g.*, Amberlite XAD, Tenax, Porapak and the Chromosorb 100 series, are useful alternatives.

We have previously shown that phenols[8,18], polychlorinated aromatics[9], glycol ethers[11], polycyclic aromatics[12], organic nitro compounds[13], nitrates[14], amines[16] and ketones[17] are examples of compounds that may adsorb irreversibly or decompose on activated charcoal but may be successfully sampled on XAD polymers. The XAD polymers which have proved most useful are XAD-2, a styrene–divinylbenzene polymer with an active surface of 330 m^2 g^{-1}, XAD-4, the same polymer with an active surface of 750 m^2 g^{-1}, and XAD-7, a more polar polyacrylic ester with a surface area of 450 m^2 g^{-1}.

From Table II it is evident that PGE and CGE show low recoveries from activated charcoal. The poor recoveries are not caused by low retention; no breakthroughs are observed. It is likely that PGE and CGE are adsorbed strongly on, or react with, active sites on the charcoal sampling bed. The aliphatic glycidyl ethers, IGE, AGE and BGE all show recoveries in the range 90–100% if the sorbent tubes are desorbed and analyzed immediately. All three compounds show a decrease in recovery on storage, probably owing to their reactivity. They may, however, be stored for 2 weeks at room temperature in the dark with a loss that is not greater than approximately 10%.

Amberlite XAD-2 retains only 49 and 72% of IGE and AGE, respectively. The

breakthrough volumes of these compounds are less than 5 l on XAD-2, owing to the low polarity and small active surface of this adsorbent. The less volatile BGE, PGE and CGE are quantitatively retained. PGE shows good storage stability, but BGE and CGE show a small decrease in recovery on storage.

Amberlite XAD-7 has a larger surface area and is more polar than XAD-2. Accordingly, the glycidyl ethers should be better retained on this adsorbent. This can indeed be seen from Table IV. Only IGE, the most volatile of the glycidyl ethers, shows a significant breakthrough at the highest level. A 5% breakthrough was noted for AGE at 85% relative humidity at the highest level. Like the other sorbents, on XAD-7 there is some decrease in recovery on storage, especially in the case of CGE. The occasional lower recoveries noted for CGE may, however, be a result of difficulties in the generation of this high-boiling compound.

In summary, the best overall adsorbent appears to be Amberlite XAD-7. Except for the most volatile, IGE, all glycidyl ethers are effectively retained on XAD-7, and can be recovered in high yields. The relative humidity has little influence on recovery. As a rule, no more than 5–10% is lost if the samples are stored no longer than 2 weeks in the dark at room temperature. In addition, activated charcoal enables good recoveries and acceptable storage stability for the aliphatic glycidyl ethers (IGE, AGE, BGE).

ACKNOWLEDGEMENT

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