

Determination of residual free epoxide in polyether polyols by derivatization with diethylammonium N,N-diethyldithiocarbamate and liquid chromatography

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Abstract

A normal-phase liquid chromatographic method is described for the determination of epoxides and particularly residual ethylene oxide and propylene oxide in polyether polyols. The residual epoxides are derivatized with diethylammonium N,N-diethyldithiocarbamate into the corresponding 1-(N,N-diethyldithiocarbamoyl)-2-hydroxyethane and -hydroxypropane. The dithiocarbamoyl esters are extracted into chloroform and separated by normal-phase liquid chromatography. Detection is done by ultraviolet at 278 nm. Total analysis time is about 45 min. Linearity (0.1–100 ppm), detection limits (0.5 ppm), recovery from spiked samples (>95%) and interferences have been studied.

1. Introduction

Epoxides such as ethylene oxide (epoxyethane, EO) and propylene oxide (1,2-epoxypropane, PO) are important chemicals for the manufacture of polyoxyalkylene substances with a large variety of industrial and pharmaceutical applications (e.g. polyurethanes, lubricants, soaps, cosmetics). Both EO and PO are classified as toxic components. EO has shown sufficient evidence for suspected carcinogenicity to animals and humans [1]. Exposure of humans to EO and PO should therefore be minimized.

The analysis of residual free epoxides can be done by gas chromatography (GC) with electron-capture detection. For this purpose, the

epoxides are first reacted with hydrobromic acid followed by further derivatization of the resulting 2-bromoalkanol with heptafluorobutyrylimidazole. Application of this approach has been described for the determination of EO in air [2]. The analysis of residual epoxides in high-molecular-mass polyoxyalkylene adducts such as polyether polyols is less straightforward with GC. In this case the epoxides need to be separated from the rest of the viscous non-volatile matrix prior to analysis, or a chromatographic multicolumn switching system is necessary. The use of the purge and trap technique followed by GC-flame ionization detection had been evaluated before, but had shown to be problematic because of the presence of small volatile molecules interfering with the determination of residual EO or PO. These by-products were often present in higher concentrations than

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the residual free epoxides and interfered with the quantitation because of partial or complete co-elution. Depending on the polyether production conditions applied, the concentration of these interfering substances varies from product to product. A second approach using GC could be the splitting of free epoxides with acid, followed by derivatization with acetic anhydride or trifluoroacetic anhydride. In the case of polyether polyols however, there can be some residual amounts of ethylene glycol and propylene glycol present in the samples as such. Besides the latter, vinyl ethers are present as well, which split into small carbonyl components by acid treatment. So a number of side reactions can take place, complicating the analysis. The nature of the polyol product and more importantly of some by-products, is thus such that they can interfere in the GC analysis. Therefore, a liquid chromatographic (LC) procedure in combination with the off-line derivatization procedure has proven to be more reliable in this case.

The present article describes the determination of residual epoxides in polyether polyols (molecular mass 1000–10 000 g/mol) using isocratic liquid chromatography in combination with a simple off-line derivatization reaction that converts the epoxides into UV-absorbing dithiourethanes. The use of N,N-diethyldithiocarbamate (DDTC) salts for epoxide derivatization has been reported before in the determination of 1,2:5,6-dianhydrogalactitol, a hexitol diepoxide, in blood plasma [3]. Sodium DDTC was used in this case to convert the drug into a UV absorbing species with higher hydrophobic character, in order to transfer it to water-immiscible solvents such as chloroform. After derivatization, the resultant dithiocarbamoyl ester was analyzed by LC with UV detection. The DDTC salts are most known for their chelation capabilities of heavy metal ions. Because of this property they have been applied in the analysis of bivalent ions such as Pb^{II} , Hg^{II} , Cd^{II} and Cu^{II} [4,5] and of Pt^{II} complexes [6,7]. Sodium DDTC has been used as well to preconcentrate heavy metal ions from aqueous solutions into non-polar solvents [4,8].

2. Experimental

2.1. Chemicals

All solvents (*n*-hexane, methanol, tetrahydrofuran, chloroform) used were from J.T. Baker in highest purity available (HPLC grade or equivalent). Phosphate buffer solution Ready to use at pH 7.00 was obtained from Merck. Phosphoric acid (85%) was from J.T. Baker. Propanal (99 + %) was obtained from Janssen Chimica. Acetaldehyde (99 + %) and acetone (HPLC grade) were from J.T. Baker. The derivatization agent diethylammonium DDTC (98%) was from Aldrich. The sodium salt (99%) of DDTC was obtained from Merck. EO (>99%) and PO (>99%) were obtained from the production plants in Dow Benelux (Terneuzen, Netherlands) and Dow Deutschland (Stade, Germany) respectively.

2.2. Sample preparation and derivatization procedure

As most solvents and reagents are toxic and/or flammable, all sample preparation was performed in a fumehood. Epoxides are known to react with dithiocarbamic acid salts [3] according to the scheme in Fig. 1. The resulting 1-(N,N-diethyldithiocarbamoyl)-2-hydroxyethane and

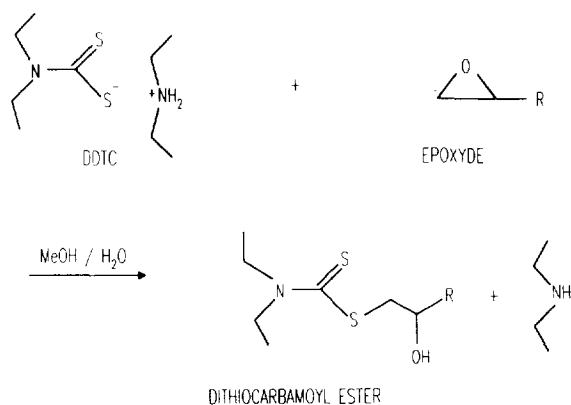


Fig. 1. Reaction of DDTC diethylammonium salt with epoxides.

-hydroxypropane (dithiourethanes) absorb UV light with a maximum at 278 nm. As an example, the UV spectrum of the epoxyethane–dithiocarbamate adduct is shown in Fig. 2.

The reagent solution was prepared by dissolving 500 mg of diethylammonium DDTC in 50 ml of buffer at pH 7.00. The solution was put in an ultrasonic bath for 5 min (the resulting solution will stay somewhat opalescent). A fresh reagent solution was made each day. The solution is stable above pH 6, below this pH rapid decomposition with carbon disulfide evolution takes place. The solid salt of DDTC was stored in a refrigerator for no longer than one month after opening.

Standard solutions containing epoxide in the amount of 1000 ppm were prepared in methanol and stored in a deep freezer. These were further

diluted in methanol to obtain epoxide concentrations of 0.1 up to 50 ppm (mg/l methanol).

The standards were derivatized by mixing 5.0 ml of standard solution (in methanol) with 5.0 ml of DDTC reagent in a pressure resistant 20-ml glass vial. The vials were closed with PTFE-lined aluminum snap-caps, shaken and put in an oven at 90°C for 30 min. As safety precaution, the vials were put into a screw-capped stainless-steel container standing permanently in the oven. After this period the vials were cooled to room temperature with streaming water. Fifteen drops of 85% phosphoric acid (about 0.3 ml) were added, followed by 10.0 ml of chloroform. The vial was shaken vigorously during 1 min. After phase separation, 10 μ l of the lower chloroform layer were subjected to LC analysis.

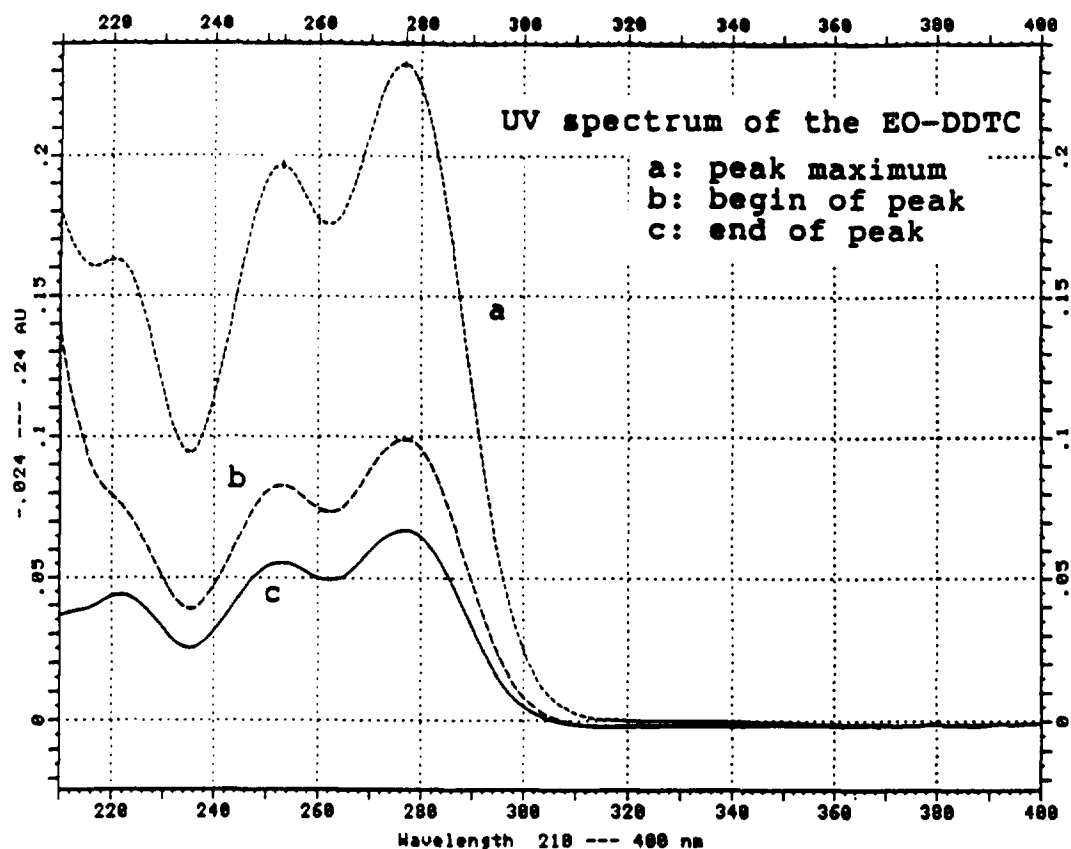


Fig. 2. UV spectrum of 1-(N,N-diethyldithiocarbamoyl)-2-hydroxyethane.

Samples were derivatized by accurately weighing approximately 500 mg of polyether polyol in a 20-ml glass vial, after which 4.5 ml of methanol and 5.0 ml of DDTC reagent were added. Further sample preparation was identical as described above. The polyether polyol distributes over the two layers giving rise to a hazy appearance of both the chloroform and methanol layer (after about half an hour, the polyether polyol has completely migrated into the methanol layer, giving a clear chloroform layer). After methanol–chloroform phase separation, 10 μ l of the chloroform layer was injected into the liquid chromatograph. No chromatographic problems such as pressure increase or baseline drift were observed with this procedure for a period of at least 5 days. The blank was prepared by mixing 5.0 ml of the DDTC solution with 5.0 ml of methanol, followed by the procedure as described above.

2.3. Chromatographic conditions

A Shimadzu LC-9A pump and Shimadzu SPD-6AV UV-Vis detector (278 nm and 0.02 AUFS) were used. A 10- μ l volume of the chloroform layer was injected by a Valco 6-way valve. Quantitation was done on peak area using Nelson 6000 software on a HP1000 computer. A Zorbax-NH₂ column (25 cm \times 0.46 cm I.D.) from DuPont was used. The eluent consisted of 89% (v/v) of *n*-hexane, and 11% (v/v) of methanol–tetrahydrofuran (2:1). Flow-rate was set to 1.0 or 2.0 ml/min. At the end of each week the column was rinsed with about 200 ml of tetrahydrofuran to remove adsorbed polymers.

3. Results and discussion

3.1. Quantitative aspects

The precision of the derivatization and analysis procedure was studied by derivatizing and analyzing one sample 10 times spread over two successive days. The data are presented in Table

1. The relative standard deviations (R.S.D.s) on PO and EO determination were 3.2 and 5.3%, respectively (at levels of 2.9 and 1.5 ppm, respectively).

Calibration lines of concentration versus detector response were linear in the range from 0.1 to 100 ppm. These concentrations refer to the epoxide standard solutions in methanol of which 5 ml were used in the derivatization procedure. The linear regression coefficients were 0.99998 and 0.99992 for EO and PO, respectively. With the 10- μ l injection, the detection limits for both epoxides were about 50 ppb (signal/noise = 3). This corresponds to a level of 0.5 ppm in the samples if 500 mg were used in the final procedure. When lower concentrations need to be determined a larger injection volume can be used.

The recovery from spiked samples was studied with different amounts of polyether taken into account. Samples were fortified with varying amounts of the standard solution prepared as described above. Low recoveries at low concentrations were measured when 1000-mg sample amounts were used. However when 500 mg of polyether polyol was used, complete recovery was observed down to sub-ppm level. The data are presented in Table 2.

Table 1
Precision of derivatization and analysis

Analysis	Day	PO counts	EO counts
1	1	9 819	5 520
2	1	9 729	5 409
3	1	9 887	5 703
4	1	10 138	5 748
5	1	10 663	6 505
6	2	9 636	5 632
7	2	9 953	5 813
8	2	10 186	6 060
9	2	9 631	5 658
10	2	9 802	5 712
Average		9 944	5 776
S.D.		314	309
R.S.D. (%)		3.2	5.3

Table 2
Ethylene oxide recovery from spiked samples

Sample amount (g)	Spike (ppm)	Counts		Recovery (%)
		Theory	Found	
0.98	1	22 432	17 501	78
1.00	4	61 984	54 830	88
0.97	10	141 088	129 446	92
0.98	20	272 928	258 507	95
0.99	40	536 608	515 260	96
0.50	0.4	6 413	6 975	109
0.50	0.8	14 023	14 365	102
0.50	1.0	18 828	18 853	100
0.50	2.0	36 853	38 939	106
0.50	10.0	188 828	208 384	110

3.2. Interferences

The possible interference of traces of small molecule aldehydes and ketones present in samples was studied. To see whether such contaminants give rise to DDTC adducts eluting at similar retention times as the epoxides, small carbonyl components such as propanal, acetone and acetaldehyde (1500, 1200 and 900 ppm in methanol, respectively) were subjected to the same derivatization procedure as described in the experimental part. No interfering peaks were observed on the position of the epoxide-DDTC adducts. Residual EO and PO were also determined in polyether polyol based on aromatic initiators (e.g. phenols). In most products co-elution of the EO-and/or PO-DDTC adducts with low-molecular-mass polyether oligomers was observed. This makes the determination of residual free epoxides in such products at the above described conditions impossible.

3.3. DDTC sodium salt versus diethylammonium salt

In order to study the effect of the DDTC cation on the epoxide-dithiocarbamate reaction yield, 1% (w/v) solutions of both sodium and diethylammonium DDTC were used for the derivatization of epoxide standards. The ob-

tained responses for EO and PO were 45 and 10%, respectively, higher when the diethylammonium salt was used, despite the higher molar concentration of the sodium DDTC reagent. Due to this higher yield, the ammonium salt was used further.

3.4. Stability of derivatized standards

After the derivatization procedure, the chloroform layer was routinely analyzed within 8 h. However, the obtained dithiocarbamoyl esters in chloroform slowly decay in time. A derivatized 1 ppm ethylene oxide solution was reanalyzed after standing 4 days at room temperature. The area counts of the adduct after this time period decreased to about 85% of its original value, directly measured after derivatization. Normally, no corrections were made on the quantitation, because samples were analyzed directly after derivatization.

3.5. Effect of derivatization temperature on reaction rate

The reaction rate and yield between the epoxide and DDTC ammonium salt was studied at 25, 70, 90 and 100°C. At room temperature the final equilibrium concentration was only reached after 24 h. At 70°C the same equilibrium con-

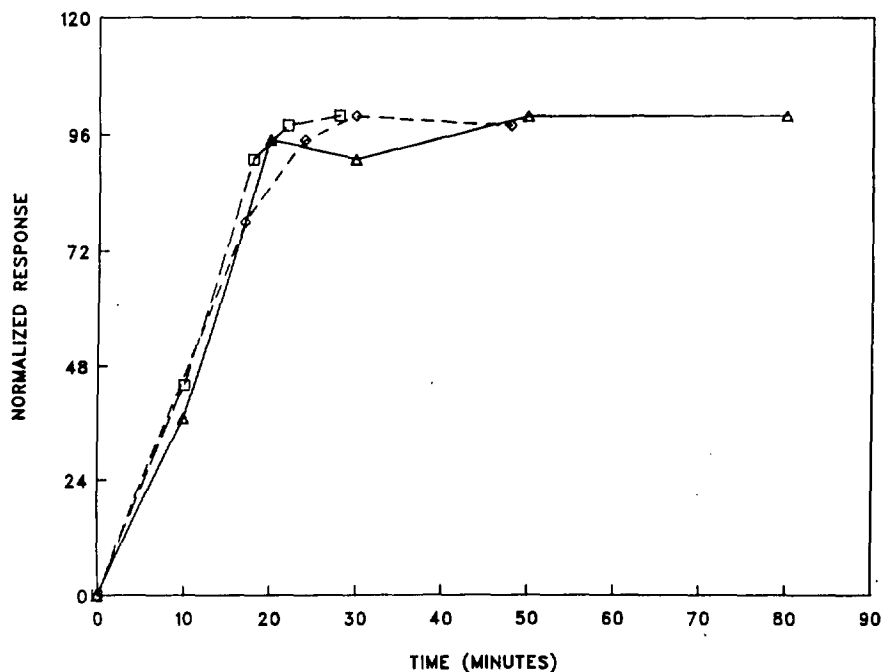


Fig. 3. Time to reach equilibrium concentration (EO) at different derivatization temperatures: \triangle = 70°C; \diamond = 90°C; \square = 100°C.

centration was found after about 25 min. At 90 and 100°C an identical response was measured after this same time period. As final temperature 90°C was chosen for convenience and because fluctuations in reaction time do not have an influence on the final response. The results of this equilibrium study are shown in Fig. 3.

3.6. Analysis of polyether polyols from different sources

Table 3 shows residual epoxide content in different commercially available industrial lubricants, being polyether adducts, from various manufacturers. A typical chromatogram is shown

Table 3
Residual free epoxide in commercial lubricants

Product	Epoxyethane (ppm)	Epoxypropane (ppm)
Lubricant A	2.5	3.5
Lubricant B	N.D. ^a	N.D. ^a
Lubricant C	2.3	N.D. ^a
Polyether D	2.9	5.8
Product E		
5 min after EO addition	1350	—
30 min after EO addition	150	—
45 min after EO addition	10.0	—
60 min after EO addition	3.9	—

^aN.D. = Non-detected, detection limit 0.5 ppm.

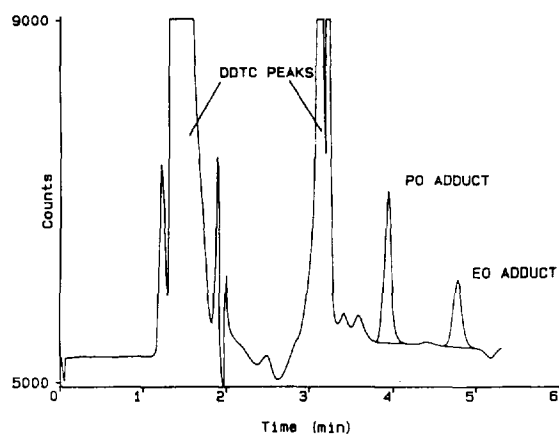


Fig. 4. Typical chromatogram of PO-DDTC and EO-DDTC adducts in a commercial sample. column: Zorbax-NH₂ (25 cm); eluent: 89% (v/v) *n*-hexane, 11% (v/v) methanol-tetrahydrofuran (2:1); flow-rate: 2 ml/min; detection: UV at 278 nm and 0.02 AUFS; injection volume: 10 μ l.

in Fig. 4. The product E refers to an experiment in a pilot plant to study reaction rates. Samples were taken at different times after completion of the addition of EO to the pre-heated reaction mixture. Optimum production cycles can be established in this way.

4. Conclusions

Residual EO and PO can be determined down to sub-ppm level in polyether polyols using DDTC as an off-line derivatization agent. The methodology is simple and requires only standard LC instrumentation.

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