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Analysis of 1,4-dioxane in ethoxylated surfactants

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Synopsis

An improved DIRECT INJECTION GAS CHROMATOGRAPHIC method has been developed for detecting 1,4-dioxane, an alleged animal carcinogen, in ethoxylated surfactants. It is a modification of ASTM Method D-3606-77 for the analysis of benzene in gasolines. The method has a detection limit of 0.5 mg/kg for alcohol ethoxylates and is suitable for routine quality control of commercial products. The ethoxylate sample, dissolved in chlorobenzene, is injected directly into a gas chromatograph equipped with two columns connected in series. The sample passes first through a column packed with a non-polar stationary phase, which separates the compounds according to boiling point. After the dioxane has eluted, the flow is reversed, flushing out the heavier ethoxylates and glycols. Dioxane and lighter components then pass through, and are separated, on a column packed with a highly polar stationary phase. Analysis of several commercial alcohol ethoxylates manufactured using a widely practiced, base-catalyzed procedure showed no detectable 1,4-dioxane using this method.

INTRODUCTION

Recently, 1,4-dioxane, an alleged animal carcinogen (1-5), was reported in trace amounts in certain polyethylene glycol food additives. In addition, there is the possibility that 1,4-dioxane is produced in the manufacture of alcohol ethoxylated surfactants. There are several methods currently used for 1,4-dioxane analysis. Birkel (6) of FDA used a closed-system vacuum steam distillation to concentrate and remove the 1,4-dioxane from Polysorbates −60 and −80 followed by gas chromatographic analysis of the distillate. The FDA procedure is tedious and time consuming as one operator can perform only two or three analyses per day. In general, other methods such as nitrogen sparging and trapping, and rotary distillation have shown poor repeatability. A headspace technique (7) being used has a detection limit of only 100 mg/kg. Another technique (7) could detect 0.5 mg/kg by sparging the sample with nitrogen and collecting the volatiles in a trap filled with a porous polymer adsorbent; however, it is time consuming and requires large quantities of the sample.

Some of the above difficulties have been overcome by the development of a direct injection gas chromatographic method with a detection limit of 0.5 mg/kg and the simplicity required for routine quality control of commercial products.

EXPERIMENTAL

APPARATUS

The gas chromatograph used in this work was a Varian Model 2440 equipped with a flame ionization detector. The schematic drawing in Figure 1 shows the column system and the flow configuration. The switching valve, a six-port medium temperature valve with 1/8-in zero-volume fittings, was purchased from Valco Instruments

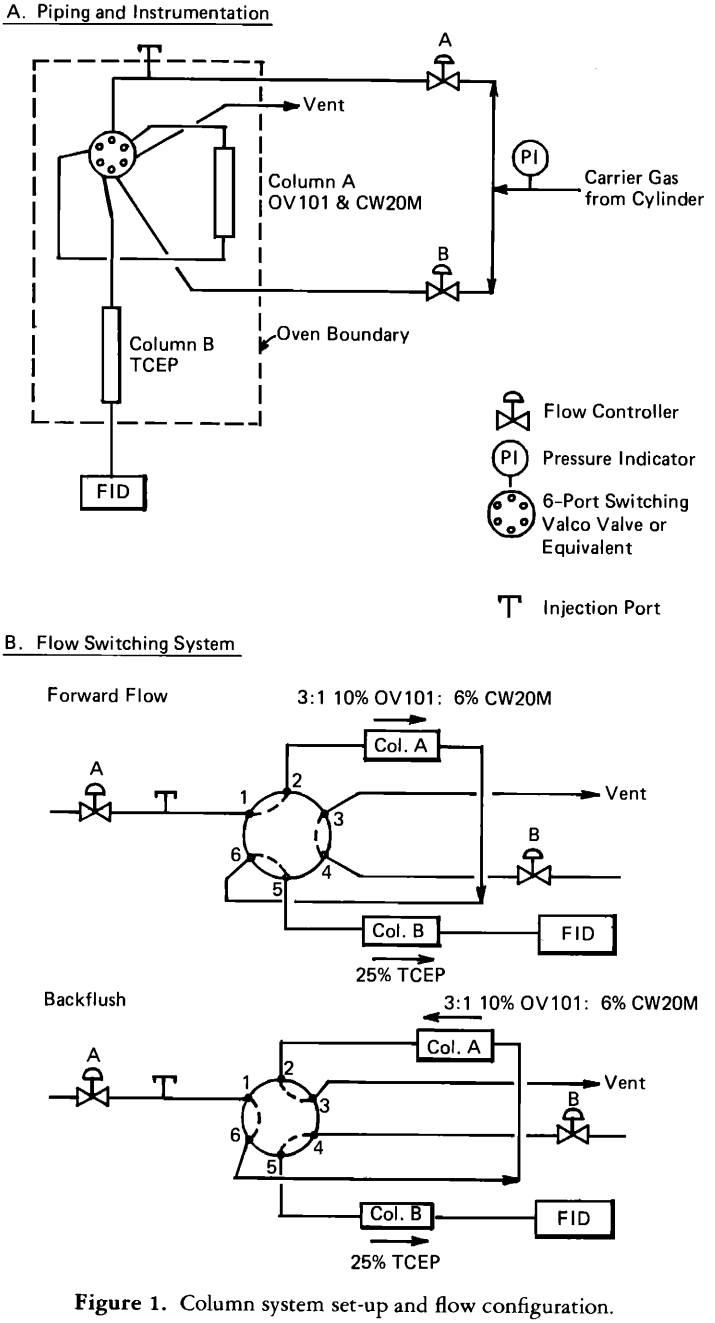

Figure 1. Column system set-up and flow configuration.

Table I
Gas Chromatographic Operating Conditions

Column Temperature:	70°C or appropriate temperature to efficiently separate 1,4-dioxane and chlorobenzene.
Carrier:	Helium
	Carrier: 30 cc/min NORMAL VALVE POSITION Auxillary: 30 cc/min NORMAL VALVE POSITION
	Carrier: 30 cc/min BACKFLUSH VALVE POSITION Auxillary: 30 cc/min BACKFLUSH VALVE POSITION
Air:	300 cc/min
Hydrogen:	30 cc/min
Valve Time to Backflush:	125 seconds; or appropriate time to efficiently separate 1,4-dioxane and chlorobenzene.
Detector Temperature:	200°C
Injector Temperature:	150°C
Sensitivity:	Range: 10^{-12} AFS
Attenuation:	Appropriate to keep 1,4-dioxane peak on scale.

Co., Houston, TX. Operating conditions are listed in Table I. The 15-ft × 1/8-in column containing 25% TCEP (1,2,3-TRIS [2-cyanoethoxy] propane) on Supelcoport 80/100 mesh was purchased from Supelco Inc., Bellefonte, PA, and the 2.5-ft × 1/8-in column containing a 3:1 mixture of 10% SP2100 (or OV-101) on Supelcoport 80/100 mesh and 6% Carbowax 20M on Gas Chrom Q 80/100 was prepared in the laboratory using materials also purchased from Supelco Inc.

CHEMICALS

The solvent, chlorobenzene, was purchased from J. T. Baker Chemical Co., Phillipsburg, PA, and 1,4-dioxane was purchased from Chemical Samples Co.

PREPARATION OF 1,4-DIOXANE STANDARD SOLUTIONS

The standard solutions were prepared by making a stock solution of 1g of 1,4-dioxane in 100g of chlorobenzene (1%). Then, the stock solution was diluted according to

Table II
Dilutions of the 1% 1,4-Dioxane in Chlorobenzene Stock Solution for the Preparation of Calibration Standard Solutions

Conc.	Amount 1,4-Dioxane Solution	Diluted with Chlorobenzene to
3,000 mg/kg	3.0 g of 1% Solution	10 g
1,000 mg/kg	1.0 g of 1% Solution	10 g
300 mg/kg	3.0 g of 1000 mg/kg Solution	10 g
100 mg/kg	1.0 g of 1000 mg/kg Solution	10 g
30 mg/kg	3.0 g of 100 mg/kg Solution	10 g
10 mg/kg	1.0 g of 100 mg/kg Solution	10 g
5 mg/kg	0.5 g of 100 mg/kg Solution	10 g
1 mg/kg	1.0 g of 10 mg/kg Solution	10 g

Table II to obtain standard solutions with concentrations from 1 mg/kg to 10 g/kg (1%). All solutions containing 1,4-dioxane were handled in a ventilation hood.

The standard curve was obtained by injecting 2 μl aliquots of each standard solution into the gas chromatograph using the conditions described in Table I. Four standard curves were drawn using peak height measurements for the 0-10, 10-100, 100-1000 and 1000-10,000 mg/kg ranges. Figure 2 shows the standard curve for 0-10 mg/kg range. Figure 3 shows the chromatogram obtained from the analysis of a 1 mg/kg standard solution. A different standard solution was analyzed each day to check the validity of the curve.

PREPARATION AND ANALYSIS OF SAMPLES

Three grams of sample were weighed into a 10-ml volumetric flask and diluted to the mark with chlorobenzene. The samples were analyzed by injecting a 2 μl aliquot into the gas chromatograph operated as described in Table I. After 120 s with the valve in the normal position, the valve is switched and the high boiling and non-polar components are backflushed (reverse flow) from the first column (SP2100 (or OV101)/Carbowax 20M mixed phase). At the same time, the low boiling and polar components, including 1,4-dioxane, are separated on the second, or analytical column (TCEP).

The 1,4-dioxane peak height was measured and converted to concentration in mg/kg in the sample by using the appropriate standard curve. Figure 4 shows the gas chromatographic curve of an ethoxylate sample which was spiked with 5 mg/kg dioxane.

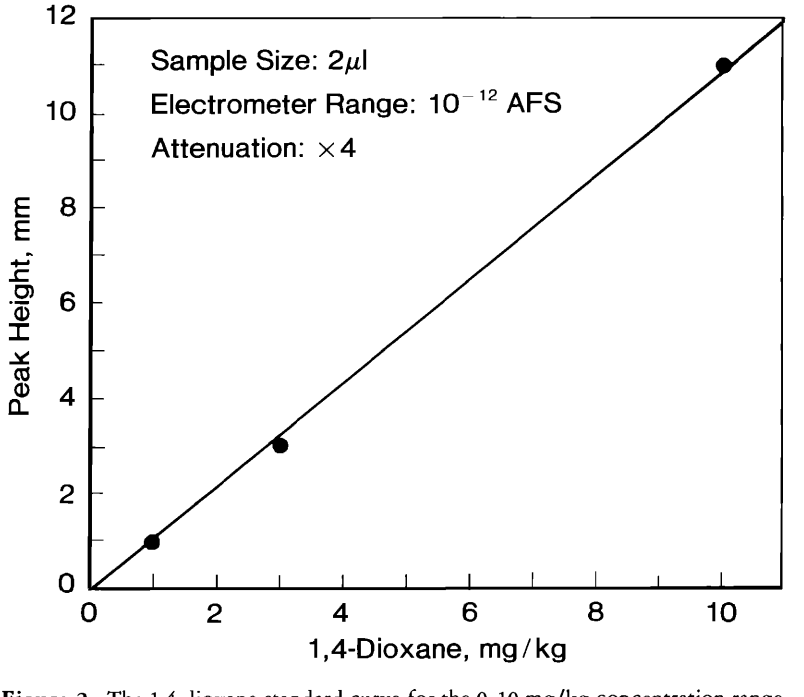

Figure 2. The 1,4-dioxane standard curve for the 0-10 mg/kg concentration range.

RESULTS AND DISCUSSION

A rapid procedure that could be applied to very small experimental samples was desired for the analysis of 1,4-dioxane in alcohol ethoxylates. Early attempts at direct injection gas chromatographic procedures using various single columns were unsuccessful due to interferences from other components eluting with the dioxane. The nature of the two required separations—1) that of separating volatile components from the heavy ethoxylates and 2) separation of polar volatile components from each other, suggested that a dual-column system with column switching might be applicable. This is the type of column-valve configuration described in ASTM Method D-3606-77 (8) for the analysis of benzene in gasolines. Several modifications were made to this method. A flame ionization detector was used instead of the prescribed thermal conductivity detector. To achieve baseline resolution of 1,4-dioxane and the chlorobenzene solvent, a 3:1 mixture of 10% methyl silicone stationary phase (SP2100 or OV-101) and 6% Carbowax 20M was required as the packing in the stripper column (Column A, Figure 1).

The alcohol ethoxylates dissolved in chlorobenzene are injected directly into the gas chromatograph. When the light components including dioxane and the chlorobenzene solvent have eluted from the SP2100/Carbowax 20M column, the six port valve is switched, and the heavy components are backflushed from the first column by reversing the flow. The use of an auxiliary carrier gas allows continued analysis on the polar analytical column while the first column is being backflushed. It was found that

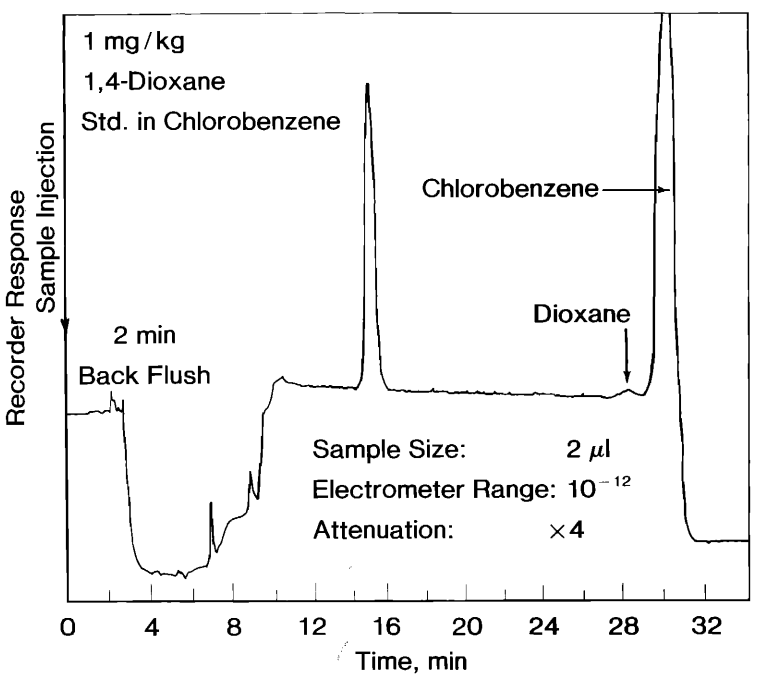

Figure 3. Chromatogram for a 1 mg/kg standard.

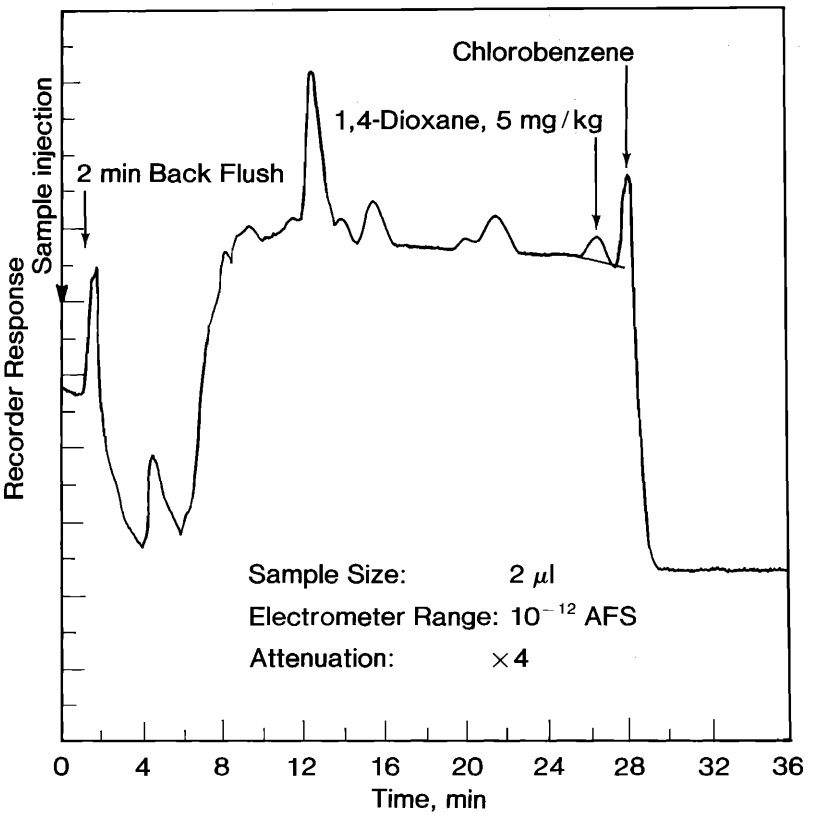

Figure 4. Chromatogram of an ethoxylate spiked with 5 mg/kg dioxane.

variation of the flow rates given in Table I causes the dioxane peak to co-elute with the solvent peak or to be backflushed. A glass injection port insert, which reduces peak tailing, is replaced daily to prevent polymer migration onto the column head.

Even though the total analysis cycle time is 2.0 hr, only 15 min of technician time are required and four to five analyses can be performed in an eight-hour day. The column switching and backflushing can be automated for installation in a quality control laboratory. Since the ethoxylates are dissolved in chlorobenzene and injected directly, the method is applicable to alcohol ethoxylates ranging from low molecular weight liquids to high molecular weight solids.

The limit of detection for 1,4-dioxane in ethoxylates using this method is 0.5 mg/kg with a linear range of up to 10 g/kg (1%). Quantification is accomplished by relating peak height measurements to an external standard curve, which is checked daily by a standard analysis. The coefficient of variation of the standards was 4.2% based on 80 standard solution analyses. Figure 3 shows a typical chromatogram obtained for the analysis of a 1 mg/kg 1,4-dioxane in chlorobenzene standard solution.

The recovery of the method was determined by analyzing an ethoxylate sample spiked with 1, 3, and 5 mg/kg, respectively, of 1,4-dioxane using the above procedure (Figure 4). In all cases the recovery was 100% at these levels. The repeatability of the method,

Table III
Recovery and Comparison of Direct Injection Gas Chromatographic and Birkel-FDA Procedures for Analysis of 1,4-Dioxane

Dioxane Added, mg/kg	Dioxane Found, mg/kg	
	Birkel-FDA	Direct GC
1.25	1.2	2
2.50	2.5	3
5.00	4.8	5

determined by analyzing spiked samples seven times each, was found to be 25% of the 1,4-dioxane level.

Fifty-five alcohol ethoxylates, all manufactured using a base-catalyzed procedure and analyzed by this dual-column direct injection gas chromatographic method, did not contain a detectable level of 1,4-dioxane. These results have also been compared to those obtained using the FDA-sanctioned Birkel Method (6). As Table III shows, for alcohol ethoxylates spiked with dioxane and analyzed by both procedures, there is good agreement and recovery at the very low mg/kg level.

CONCLUSION

The above procedure has been used to screen a wide range of primary alcohol ethoxylates manufactured by Shell Chemical Company (NEODOL® Alcohol Ethoxylates. CTFA Adopted Name (9) PARETH). The ethoxylates tested were based on alcohols ranging from a $C_9/C_{10}/C_{11}$ blend to a C_{14}/C_{15} blend, and had ethylene oxide contents ranging from an average of 2.25 to 13 moles/mole of alcohol. The ethoxylates were manufactured using a base-catalyzed procedure believed to be broadly practiced in the industry. No 1,4-dioxane could be detected in these products using either the above procedure or the Birkel FDA method. Both methods have a detection limit of 0.5 mg/kg 1,4-dioxane.

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