

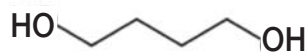
Rapid Screening of Glycols Used in the Glue Coating of a Popular Children's Toy



Introduction

In November 2007, 1,4-butanediol was discovered in a popular children's toy (shown above) instead of the expected, prescribed, safer homologue, 1,5-pentanediol, causing major public concern and a massive global recall of the affected product.

This glycol is coated onto the outer surface of small beads to make them sticky when wet and so enable interesting patterns to be created by young children by sticking them together.



1,4-Butanediol

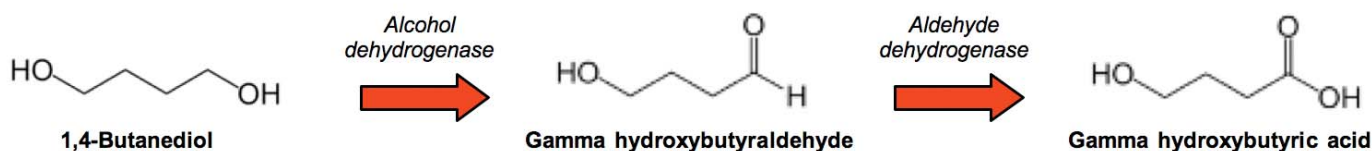


1,5-Pentanediol

1,4-Butanediol, is converted by dehydrogenase enzymes in the human body into gamma hydroxybutyric acid (GHB or the 'date-rape drug') as shown on Page 2.

Author

Andrew Tipler
 PerkinElmer, Inc.
 710 Bridgeport Avenue
 Shelton, CT 06484 USA



Since the widespread ban of GHB, 1,4-butanediol is being used increasingly as a recreational drug. Clearly, the risk of putting this type of compound into the hands (and mouths) of small children required immediate attention.

In this application note, a quick and easy method is described for using gas chromatography (GC) to identify which of the two glycols has been used in the manufacture of a given batch of beads. In addition, the use of mass spectrometry (MS) as the detection system provides the flexibility of not only identifying the glycol being used but also enables harmful impurities and other compounds to be detected.

Sample preparation

These glycols are highly polar compounds that dissolve readily in a solvent like methanol. Methanol has the added benefit that it will not interact with the polymer bead underneath the coating. Thus shaking a bead in methanol will extract the glycol but little else from the sample.

A single bead is placed directly into a GC autosampler vial, 1-mL of HPLC-grade methanol is added to the vial which is then capped and shaken. The vial is placed in the autosampler tray and the extract is analyzed chromatographically. The autosampler syringe needle does not seem to mind the single bead sample being present in the vial – the bead rolls towards the side of the vial, as shown in Figure 1.



Figure 1. Beads and extracts inside autosampler vials ready for GC analysis.

This approach makes the sample preparation very quick and simple. A minimum of glassware is required and there is no need to transfer liquid extracts between different vessels. The complete preparation time is less than one minute.

Experimental

The chromatographic conditions used throughout this work are given in Table 1.

A very polar capillary column is used to ensure good peak shape for the glycols.

Isothermal chromatography is used to ensure fast sample throughput by eliminating the need to cool and equilibrate the GC oven between runs. About 10 samples per hour can be examined using these conditions.

A mass spectrometric detector is used to provide positive and unambiguous identification of the glycol present.

Because of the large quantity of glycol present in these samples, split injection is used to reduce the amount entering the column to levels that will not overload the column or detector.

Table 1. Conditions Used for Glycol Determination.

Instrument:	PerkinElmer® Clarus® 600 GC/MS
Column:	PerkinElmer 30 m x 0.25 mm x 0.5 µm Elite-Wax Polyethylene Glycol
Oven:	220 °C isothermal for 5 minutes
Injector:	Split/splitless at 240 °C, split flow 100 mL/min
Carrier Gas:	Helium at 17 psig (1 mL/min)
Sample Injection:	0.5 µL by autosampler, fast speed
MS Mode:	EI, Full Scan
MS Scan Range:	35 to 100 amu
Scan Rate:	Scan Time: 0.2 s, Scan Delay: 0.1 s
Solvent Delay:	2 minutes
Transfer Line:	240 °C
Source Temperature:	240 °C

Results

Figure 2 shows a chromatogram from a methanol extract taken from a typical bead sample obtained from a retail outlet prior to the recall.

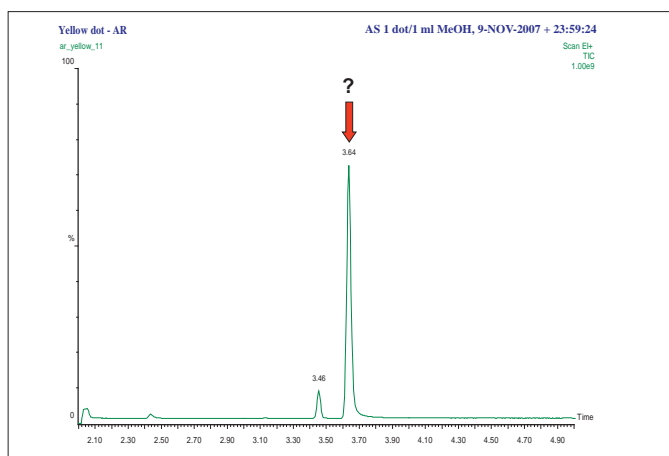


Figure 2. Chromatogram of a methanol extract taken from a typical bead.

The mass spectrum for the main peak in Figure 2, labeled '?', is given in Figure 3.

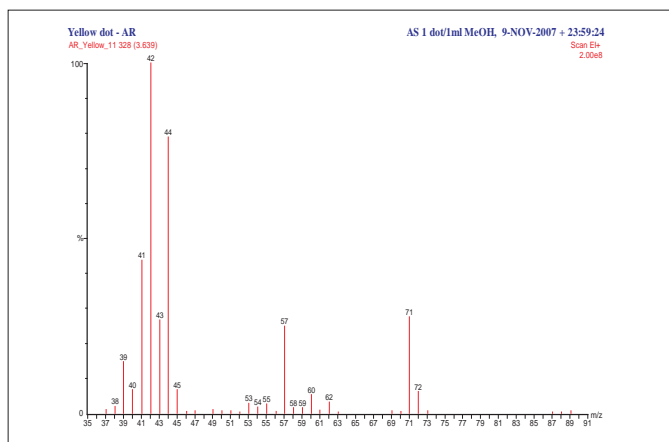


Figure 3. Mass spectrum of main peak in Figure 2.

Yellow dot - AR						
Hit	REV	for	Compound Name	M.W.	Formula	CAS
1	999	996	1,4-BUTANEDIOL	90	C4H10O2	110-63-4
2	992	990	1,4-BUTANEDIOL	90	C4H10O2	110-63-4
3	990	983	1,4-BUTANEDIOL	90	C4H10O2	110-63-4
4	814	783	6H-PYRAZOLO[1,2-A][1,2,4,5]TETRAZINE, HEXAHYDRO-2,3-DIMETHYL-	156	C7H16N4	70517-50-9
5	801	771	OXIRANE, ETHYL-	72	C4H8O	106-88-7
6	772	743	OXIRANE, ETHYL-	72	C4H8O	106-88-7
7	765	761	BUTANAL, 3-METHYL-	86	C5H10O	590-86-3
8	754	730	BUTANAL	72	C4H8O	123-72-8
9	746	734	BUTANAL	72	C4H8O	123-72-8
10	745	710	FURAN, TETRAHYDRO-	72	C4H8O	109-99-9

Figure 4. Results of spectral library search from spectrum in Figure 3.

A search of the standard NIST spectral library was performed and the results are shown in Figure 4.

The top three matches in this search show a near-perfect match for the compound 1,4-butanediol, confirming its presence in this sample of the toy. This conclusion is further reinforced by a visual comparison between the sample spectrum and the NIST reference spectra of the two glycols, as shown in Figures 5 and 6.

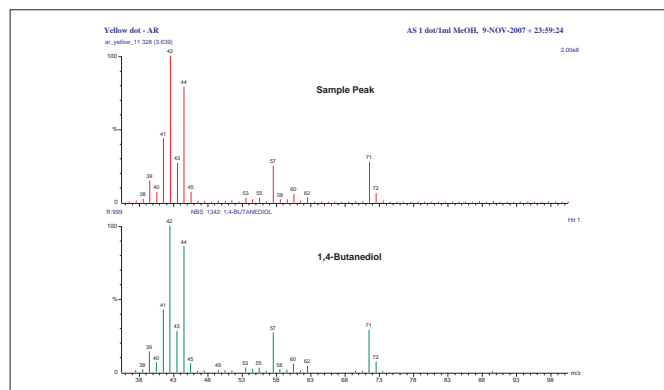


Figure 5. Comparison between sample peak and 1,4-butanediol spectra.

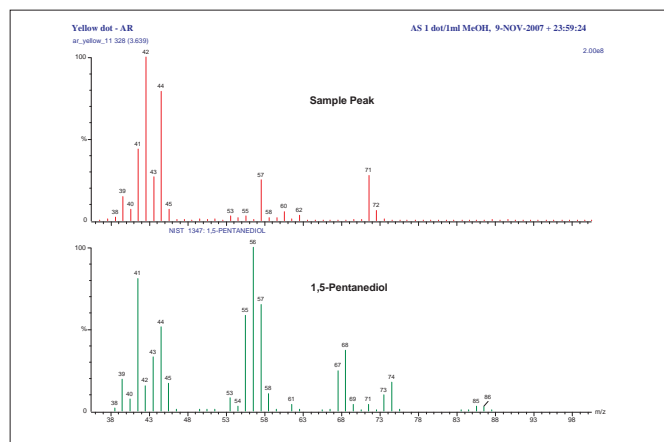


Figure 6. Comparison between sample peak and 1,5-pentanediol spectra.

Figure 7 shows a chromatogram of a standard mixture of 0.5% v/v 1,4-butanediol and 0.5% v/v 1,5-pentanediol in methanol run under the conditions given in Table 1. This chromatogram was used to calibrate the system so that the amount of glycol extracted from each bead sample could be determined. It also provides additional confirmation of peak identity from the retention times.

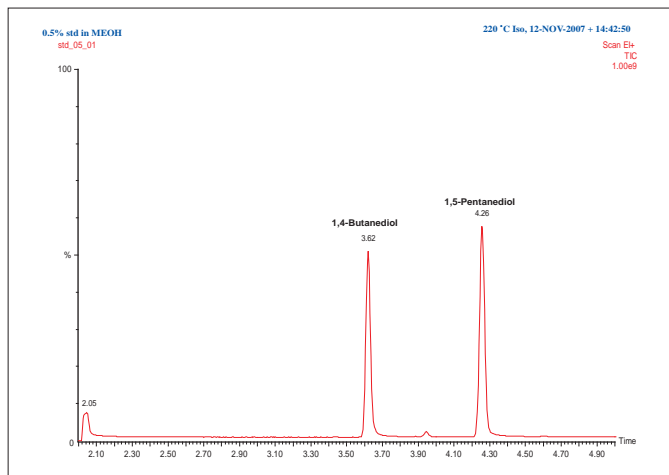


Figure 7. Chromatogram of a standard mixture of 0.5% v/v 1,4-butanediol and 0.5% v/v 1,5-pentanediol in methanol.

Tables 2 and 3 show the quantitative results obtained from the bead samples contained in two retail boxes of the toys. All contained 1,4-butanediol and none contained the prescribed 1,5-pentanediol.

The results in Tables 2 and 3 assume that none of the glycol is left in the sample bead after the extraction and all has passed into the methanol solvent. To see if this was true, a previously analyzed bead that had already been through the extraction procedure was analyzed again to determine the levels of any residual glycols left in it.

Table 2. Levels of 1,4-Butanediol Extracted from Beads in Box 1.

Bead Color	1,4-Butanediol (mg)
Yellow	7.36
Pink	8.12
Black	8.30
Blue	7.62
Purple	8.00
White	12.08
Red	8.10
Green	7.79

Figure 8 indicates that the residual level of the glycol left in the bead after analysis is about 2% – thus 98% of the extractable glycol is present in the initial extract and so the results shown in Tables 2 and 3 should be representative of the amounts in the coating.

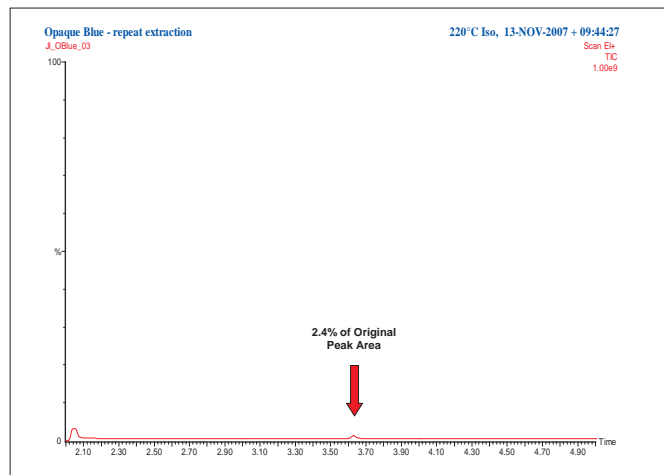


Figure 8. Repeat analysis of a sample bead to determine efficiency of first extraction.

Table 4 (Page 5) shows the quantitative precision obtained from repetitive injections of a single sample bead extract. A value of 3.20% for the relative standard deviation is very good and indicates high confidence in the sample results obtained.

Table 3. Levels of 1,4-Butanediol Extracted from Beads in Box 2.

Bead Color	1,4-Butanediol (mg)
Opaque Blue	3.64
Clear Red	3.03
Opaque Green	3.68
Clear Purple	5.54
Black	3.24
Opaque Purple	3.72
Clear Yellow	5.27
Light Green	4.19
Clear Blue	5.48
Rose	4.23
Clear Pink	5.16
White	5.09
Opaque Yellow	6.40
Opaque Pink	5.68

Table 4. Quantitative Precision from Repetitive Runs of Extract Taken from Yellow Bead Sample from Box 1.

Run No.	1,4-Butanediol (mg)
1	7.36
2	7.31
3	7.60
4	7.64
5	7.11
6	7.54
7	6.91
8	7.28
9	7.48
10	7.15
Mean	7.34
RSD%	3.20

Conclusion

This method is very quick and easy – both for sample preparation (add bead to vial, add methanol, seal and shake) and the chromatographic analysis (5-minute isothermal run). The sample throughput should be about 10 samples per hour so that large numbers of samples can be processed quickly.

The identity of the glycol in each bead sample is unambiguously established through the use of a mass spectrometric detector, giving great confidence in the results with a negligible chance of making a mistake. In addition, the use of the MS detector allows for the detection of other possible problem components.

Although this particular analysis is somewhat specialized, it could be adapted for similar applications. It demonstrates very effectively the extreme flexibility of the GC technique in its ability to enable good methods to be developed very quickly to analyze many types of organic samples as the need arises.