

Moisture Determination in Plasticizer-Pigment Formulations by Gas Chromatography

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Synopsis

A rapid quantitative method has been developed for the determination of small amounts of water present in plasticizer-pigment and epoxy resin-pigment dispersion used in polyurethane formulations. Specific dispersions examined have been the systems diisooctyl phthalate-titanium dioxide and titanium dioxide-epichlorhydrin-Bisphenol A. The samples examined contained 50-70% titanium dioxide.

Introduction

Microporous polymer beads Poropak Q (Applied Science Labs, State College, Pa.) have been demonstrated by Hollis et al.^{1,2} and by other workers^{3,4} to be suitable for the determination of water in a variety of materials. In the present work the relatively nonvolatile components are retained on the column. The gradual accumulation of nonvolatile components only slightly alters the column characteristics, so that many determinations can be completed before the accumulation of nonvolatiles interfere with experimental results.

Procedure

Ethanol containing 0.025% water as determined by gas chromatography was used as the solvent for the diisooctyl phthalate-titanium dioxide mixture. Acetone of 99 mole-% was used for the epichlorhydrin-Bisphenol A-titanium dioxide mixture. The acetone was dried over molecular sieve pellets (13X) and the clear solvent was decanted as soon as the drying agent had settled. Methanol, 4 mg/ml solvent, was used as an internal standard.

Approximately 1 g of the dispersion was placed in a tared screw-cap vial, the vial sealed, and shaken until the mixture appeared homogenous. Then 2 μ l of the diluted dispersion was withdrawn and analyzed by gas chromatography.

A Beckman GC-5 gas chromatograph equipped with a thermal conductivity detector was used for this work. The conditions were as follows: Columns, 6 ft, $\frac{1}{8}$ in. O.D. stainless steel, filled with 80/100 mesh Poropak Q (Applied Science Labs, State College, Pa.); flow rate, 50 ml/min helium;

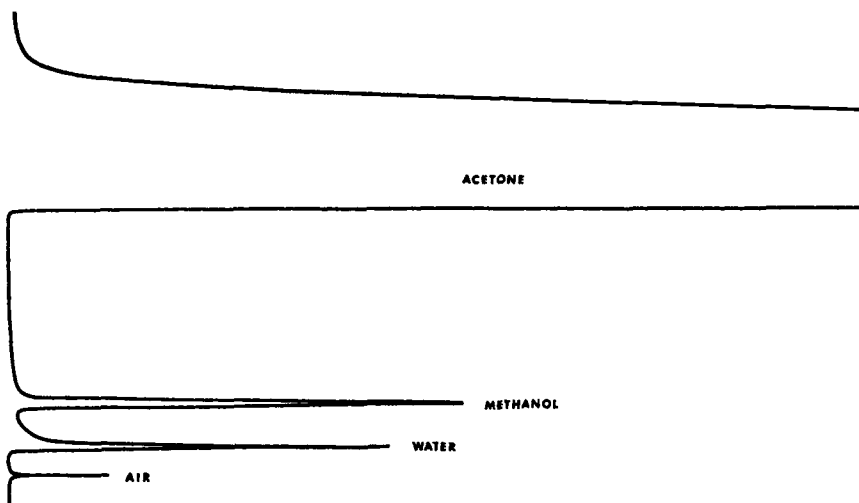


Fig. 1. Chromatograph of a titanium dioxide and epichlorhydrin-bisphenol A mixture. Acetone was used as the solvent and methanol was the internal standard.

column temperature, 130°C; injector temperature, 200°C; detector temperature, 150°C; detector filament current, 275 ma.

Results and Discussion

A typical chromatogram is shown in Figure 1. The adjusted retention time for water was 0.3 min; methanol, 0.7 min; for ethanol, 1.8 min; and for acetone, 2.6 min.

TABLE I
Determination of Water in Plasticizer Dispersions

Sample	Weight, g	Dispersion type	Solvent	H ₂ O content		
				H ₂ O, %	Average, %	Standard deviation
37	1.158	Epoxy	Acetone	0.39	0.40	0.012
38	1.745	Epoxy	Acetone	0.39		
40	1.409	Epoxy	Acetone	0.41		
46	0.758	Epoxy	Acetone	0.29	0.29	0.017
47	1.134	Epoxy	Acetone	0.31		
50	0.965	Epoxy	Acetone	0.28		
51	1.139	Epoxy	Acetone	0.24	0.24	0.000
54	0.981	Epoxy	Acetone	0.24		
9	1.570	Phthalate	Ethanol	0.66	0.68	0.033
10	1.183	Phthalate	Ethanol	0.67		
11	0.736	Phthalate	Ethanol	0.72		
17	1.235	Phthalate	Ethanol	0.208	0.209	—
18	1.220	Phthalate	Ethanol	0.210		

In the construction of a calibration curve, known amounts of water and methanol were combined. Aliquots containing 0.4–2.5 mg/ml of water and 0.15–4.0 mg/ml of methanol were examined. The injection volume was 2 μ l. Each injected sample gave two peaks, one for methanol and one for water, plus the solvent peak. Peak heights of the methanol and water were plotted against the concentrations injected. The resulting calibration curves were straight lines passing through the origin. The curves are shown in Figure 2. Each point on the calibration curves is an average of two determinations. The determinations were reproducible within $\pm 2\%$ or better.

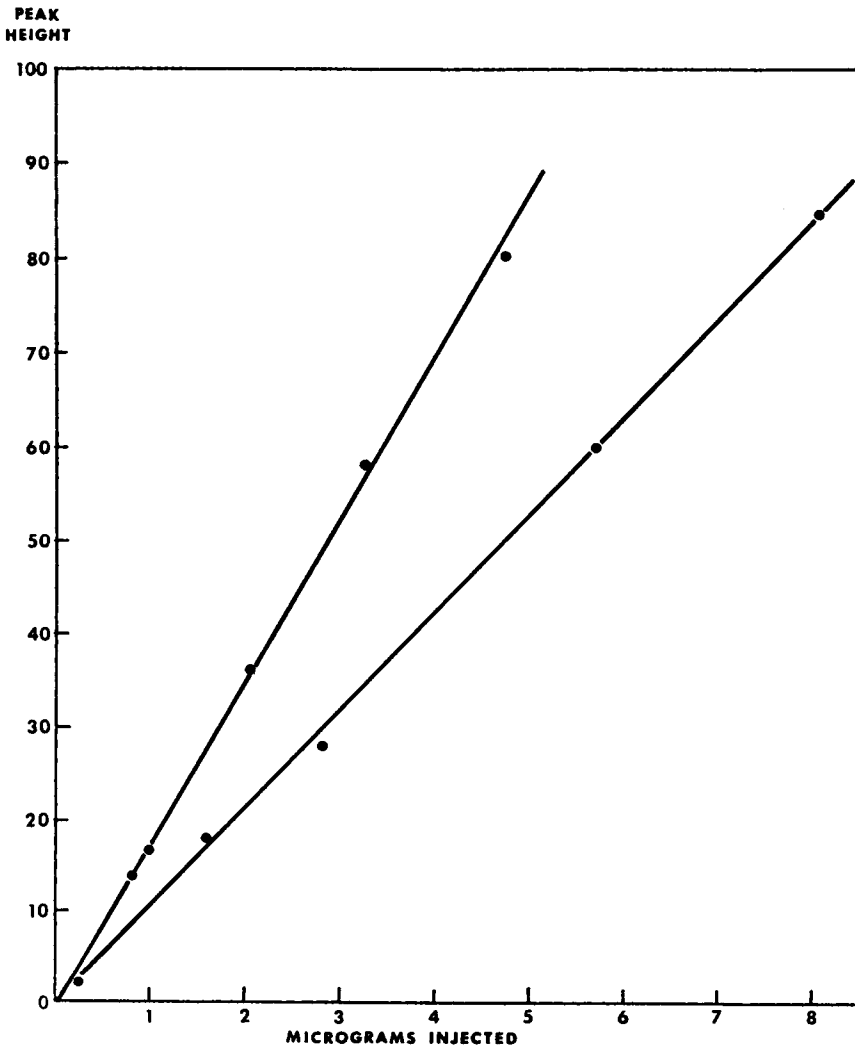


Fig. 2. Calibration curve for the determination of methanol and water.

TABLE II
Recovery of Added Water from Plasticizer Dispersions

Sample	Weight, g	Type	Solvent	Calculated			Water recovery, mg	Recovery, %
				original water, mg	Added water, mg	Total water, mg		
42	1.487	Epoxy	Acetone	5.95	2.30	8.40	2.45	107
48	1.076	Epoxy	Acetone	3.12	2.30	5.48	2.36	103
49	1.060	Epoxy	Acetone	3.07	2.30	5.46	2.39	109
52	0.984	Epoxy	Acetone	2.36	2.30	4.58	2.22	97
55	0.804	Epoxy	Acetone	1.93	2.30	4.23	2.30	100
56	1.304	Epoxy	Acetone	3.13	2.30	5.25	2.12	92
26	1.060	Phthalate	Ethanol	0.64	2.17	3.01	2.37	109
30	1.160	Phthalate	Ethanol	0.73	2.17	2.87	2.14	99
31	1.290	Phthalate	Ethanol	0.83	2.17	3.11	2.28	105

The sample dilution caused by the addition of solvent was corrected as follows:

$$\frac{\text{Concentration of MeOH in extracting solvent}}{\text{Concentration of MeOH found in sample}} \times 2 \text{ ml} \\ = \text{Final sample volume}$$

To establish the reproducibility of the method, a series of determinations was carried out on epoxy dispersions and on phthalate dispersions, each containing various amounts of water. The results obtained are shown in Table I. The figures in the table show that the standard deviation within particular sample sets ranged from 0.012 to 0.033.

A series of determinations was carried out on phthalate and epoxy-type dispersions where known amounts of water were added. The per cent recovery of the added water is shown in Table II. The figures in the table show an average recovery of 102.3%.

Calibration curves were constructed daily. After three days of using the column, a gradual tailing of the water peak was observed. This was probably due to the accumulation of noneluted plasticizer on the column packing. A similar effect has been reported by Castello and Munari⁴ when Poropak Q was treated with relatively non-polar liquids.

This column could be used for at least 250 analyses of plasticizers containing water.

References

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