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Note

Determination of water content in toluene using a novel method of calibration

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Toluene is used as a solvent for many polymerization processes and the water content can affect the rate of polymerization, microstructure and molecular weight distribution¹.

Among the published methods of water content analysis²⁻⁷, the calibration procedure is always the limiting factor for the accuracy of water determinations. Approximate measurements have been made by relating the water peak area to the solvent peak area^{3,5}. Internal standardization requires an internal standard with a known moisture content⁶. Another method involves analysing mixtures in which water is the major component⁴. External standard methods^{2,7} involve blending various amounts of water with toluene, previously dried using molecular sieves. However, the calibration curves show significant responses at a water content supposedly of zero, indicating that the molecular sieves did not dry the toluene completely^{2,7}.

To overcome these problems a more accurate calibration method for the determination of water content in toluene using gas chromatography was investigated. Various volumes of water vapour with known quantities were used as calibration standards. To recover moisture adsorbed on the syringe walls, each sample of standard required re-injections with carrier gas.

EXPERIMENTAL

Apparatus and method

A Hewlett-Packard 5710A gas chromatograph with a thermal conductivity detector was used. A nickel column (0.5 m × 3 mm I.D.) packed with Porapak R (100-120 mesh) was used to separate air, water and toluene. The column temperature was 90°C and the helium flow-rate was 40 cc/min. Porapak R, with an upper temperature limit of 250°C, allowed rapid column clearing of higher-boiling-point components by temperature programming to 240°C. The retention time for air was 5 sec, for water 56 sec and for toluene 236 sec. The complete temperature-programme cycle ran for 12 min.

For the water calibration standards, saturated water vapour at a known temperature was used. Various volumes of saturated water vapour were drawn from a flask with 100- and 250- μ l gas-tight syringes. Before sampling, the syringe was dried by flushing several times with carrier gas. Complete dryness was ensured by re-

injecting this carrier gas into the gas chromatograph, and observing the response. Sampling involved drawing up the syringe plunger to the exact level required and then injecting this sample into the gas chromatograph. In order to recover material adsorbed on the walls of the barrel, a volume of dry carrier gas equal to the sample volume was immediately redrawn into the syringe. The syringe was left in this state, in the injection port, until the water peak of the initial injection had appeared. Then, the syringe contents were injected into the gas chromatograph and dry carrier gas was again redrawn into the syringe. This redrawing procedure was repeated several times until all the moisture in the sample had been recovered. For the analysis of the moisture content in toluene, samples were injected with a 10- μ l liquid syringe.

RESULTS AND DISCUSSION

Toluene samples in the 44.6–601.4 ppm water-content range were analysed. The accuracy of these determinations ranged from ± 2.4 to $\pm 16.8\%$, as shown in Table I.

TABLE I
CONFIDENCE INTERVALS FOR TOLUENE ANALYSES

<i>Toluene batch</i>	<i>Sample number</i>	<i>Sample volume (μl)</i>	<i>Water content (ppm)</i>	<i>Mean water content (ppm)</i>	<i>Calibration standard error (ppm)</i>	<i>Sampling standard error (ppm)</i>	<i>Overall standard error</i>	<i>Error (%)</i>
A	1	7.2	47.4	47.4	4.6	—	—	16.8
	2	7.2	42.4	44.9	3.4	3.5	4.9	
	3	7.2	41.9	43.9	3.0	3.0	4.2	
	4	7.2	44.6	44.1	2.7	2.5	3.7	
B	1	8.0	122.6	122.6	4.0	—	—	5.4
	2	8.0	119.8	120.9	3.0	2.4	3.8	
	3	8.0	119.2	120.5	2.5	1.8	3.1	
	4	8.0	117.4	119.8	2.3	2.2	3.2	
C	1	7.0	207.6	207.6	4.5	—	—	3.4
	2	7.0	210.9	209.3	3.3	2.4	4.1	
	3	7.0	211.3	209.9	2.8	2.0	3.4	
	4	7.0	213.7	210.9	2.5	2.5	3.5	
D	1	8.2	353.3	353.3	3.8	—	—	2.4
	2	8.2	355.0	354.2	2.8	1.3	3.1	
	3	8.2	357.7	355.3	2.3	2.2	3.2	
	4	8.2	349.1	353.8	2.1	3.6	4.2	
E	1	8.3	521.3	521.3	4.0	—	—	3.0
	2	8.3	539.2	530.3	3.0	12.7	13.0	
	3	8.3	530.8	530.4	2.6	9.0	9.4	
	4	8.3	530.5	530.5	2.4	7.3	7.7	
F	1	6.1	588.8	588.8	5.2	—	—	4.0
	2	6.1	612.2	600.5	3.9	16.5	17.0	
	3	6.1	603.3	601.4	3.3	11.8	12.3	

Results obtained by calibrating with water vapour are shown in Table II. A 250- μ l syringe was used for samples larger than 100 μ l. For the other samples, a 100- μ l syringe was used. The relative standard deviation on the repeats ranged from ± 0.2 to $\pm 3.2\%$. Approximately 85% of the water vapour per sample was recovered with the first injection. Water adsorbed on the walls of the syringe was recovered in subsequent re-injections. Fig. 1 shows water peaks in a series of re-injections. Air peaks were also present on re-injections. The air must be retained on the syringe walls by adsorption because it does not condense at room temperature.

By calculating the water vapour moisture content per unit volume, the data of Table II were used to construct a calibration curve (Fig. 2). Inspection of the calibration curve indicates a straight line passing very near the origin. A slope of 1559 and intercept of -147 were calculated by linear regression. Confidence intervals for the calibration curve were computed using eqn. 1, an approximation of Fieller's Theorem⁸, assuming negligible error in the water vapour standards:

$$\text{C.S.E. } (X_0) = \frac{\sigma}{b} \sqrt{\left\{ \frac{1}{m} + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 S_{xx}} \right\}} \quad (1)$$

where C.S.E. (X_0) is the standard error for X_0 , n is the number of samples used for the calibration, σ is the standard deviation based on $n - 2$ degrees of freedom, b is the slope of the standard curve, m is the number of samples used for the analysis, \bar{y} is the

TABLE II
WATER CALIBRATION DATA

Nominal sample volume (μ l)	Corrected sample volume (μ l)	H_2O (μ g)	Injection number				Total	Mean	σ (%)
			1	2	3	4			
40	40	0.6481	762	86	—	—	848	842	3.2
			742	70	—	—	812		
			777	89	—	—	866		
60	60	0.9721	1237	109	—	—	1346	1366	1.2
			1238	138	—	—	1376		
			1265	110	—	—	1375		
80	80	1.2961	1762	160	—	—	1922	1889	1.8
			1722	133	—	—	1855		
			1738	152	—	—	1890		
100	100	1.6202	2195	192	—	—	2385	2400	1.2
			2184	197	—	—	2381		
			2238	195	—	—	2433		
150	149.9	2.4286	3077	390	82	42	3591	3665	1.7
			3117	432	98	62	3709		
			3128	407	90	40	3665		
200	199.1	3.2257	3923	762	143	69	4897	4852	0.9
			4040	601	131	80	4852		
			3930	690	137	51	4808		
250	248.6	4.0277	5113	751	185	79	6128	6143	0.2
			5258	649	161	79	6147		
			5269	683	124	78	6154		

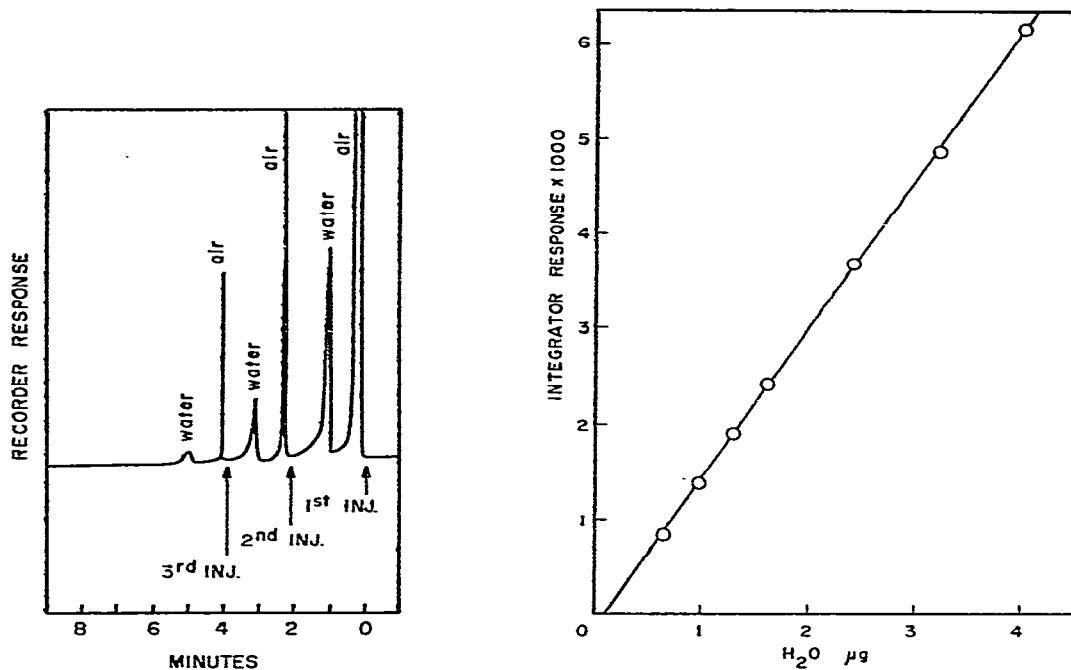


Fig. 1. Recovery of total water vapour sample by re-injection using Porapak R column packing.

Fig. 2. Calibration curve constructed using water vapour standards.

mean value of the calibration response, y_0 is the mean value of the analyses response, and S_{xx} equals $\Sigma(x - \bar{x})^2$.

The calibration curve data were obtained using relatively large gas-tight syringes whereas toluene samples were analysed with a 10- μ l liquid syringe. Lesser readability and thus reproducibility with the liquid syringe led to uncertainties in the toluene analysis which could not be estimated by eqn. 1 alone. The overall standard error was estimated using eqn. 2,

$$\text{O.S.E. } (X_0) = \sqrt{\text{C.S.E. } (X_0)^2 + \sigma(X_0)^2} \quad (2)$$

where O.S.E. (X_0) is the overall standard error, C.S.E. (X_0) is the standard calibration error and $\sigma(X_0)$ is the standard deviation of the toluene analysis.

The number of re-injections required to completely recover adsorbed water depended on a number of factors and varied from 1 to 5. Cleaning and silanizing the syringes reduced the number of re-injections required; however, more than one re-injection was always necessary. The results are shown in Table III.

The gas-tight syringes were calibrated by weighing, using pure mercury of known density. When taking water vapour samples, the plunger was brought exactly to the required level on the first draw. Drawing a sample larger than required and expelling the excess sample prior to injection resulted in a higher water response. By

TABLE III
EFFECTS OF VARIOUS TREATMENTS ON SYRINGE WATER ADSORPTION

Syringe A was new; syringe B was previously silanized.

<i>syringe A (100 µl sample)</i>					<i>Syringe B (100 µl sample)</i>				
<i>Injection number</i>					<i>Injection number</i>				
<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>Total</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>Total</i>
1373	521	106	65	2065	1437	583	77	—	2097
1027	738	142	42	1945	1197	659	91	38	1985
1454	502	113	80	2149	1228	630	99	—	1957
1372	508	106	74	2060	1047	772	102	49	1970
<i>5% NaOH treatment</i>									
1335	473	137	68	2013	2041	216	—	—	2257
1387	790	203	76	2456	1993	283	—	—	2276
1455	481	139	64	2139	2071	236	—	—	2307
1191	664	184	61	2100	2075	216	—	—	2291
<i>Organosilane treatment</i>									
1586	454	117	66	2223	1785	385	52	—	2222
1723	390	97	28	2238	1762	338	56	—	2156
1774	358	67	30	2260	1898	351	39	—	2288
1919	322	78	49	2368	1839	386	54	—	2279
<i>5% NaOH treatment</i>									
2091	301	66	—	2458	2193	192	—	—	2385
2040	304	80	—	2424	2184	197	—	—	2381
2201	243	67	—	2511	2238	195	—	—	2433

expelling the excess sample, the walls of the syringe came into contact with and adsorbed more water than required. This same effect made the use of a sampling valve unacceptable. Water response was much higher than that obtained with a syringe of the same volume and peak tailing was observed.

Calibration using various volumes of water-saturated toluene was unsuccessful. Results were not reproducible because it was difficult to prevent the formation of a suspension of small water droplets in the toluene. This may explain the scattered literature values for water content in saturated toluene. Also, toluene rapidly absorbs moisture from the atmosphere.

CONCLUSIONS

Accurate gas chromatograph calibration, for low levels of water, is performed with water vapour standards. This can be applied to toluene water-content analysis or other organic solvents in the ppm range.

Sorption of water and air on the syringe walls, with water vapour standards, is significant. This material is recovered by re-drawing dry carrier gas into the syringe and re-injecting into the chromatograph. This method of recovering sample adsorbed on the syringe walls finds application in all types of gas analyses.

APPENDIX

Sample calculations

Calibration parameters for eqn. 1 using data from Table II.

$$n = 21$$

$$\bar{y} = \frac{848 + 812 + \dots + 6154}{21} = 3021$$

$$\bar{x} = \frac{0.6481 + 0.9721 + \dots + 4.0277}{7} = 2.031$$

$$b = 1559.57 \text{ (by linear regression)}$$

$$\sigma = 41.482$$

$$S_{xx} = 27.94$$

For toluene batch D of Table I

$$m = 4$$

$$y_0 = \frac{3786 + 3804 + 3835 + 3739}{4} = 3791$$

$$x_0 = 2.5239 \mu\text{g H}_2\text{O}$$

$$\text{C.S.E.}(2.5239) = \frac{41.482}{1559.57} \left[\frac{1}{4} + \frac{1}{21} + \frac{(3791 - 3021)^2}{6.796 \cdot 10^7} \right]^{1/2} = 0.0147 \mu\text{g H}_2\text{O} \quad (1)$$

$$\text{Now, } \frac{2.5239 \pm 0.0147 \mu\text{g H}_2\text{O}}{8.2 \mu\text{l toluene}} = 353.8 \pm 2.1 \text{ ppm H}_2\text{O (C.S.E.)}$$

Overall standard error calculation:

$$\text{C.S.E. (353.8)} = 2.1 \text{ ppm}$$

$$\sigma = 3.6 \text{ ppm}$$

$$\text{O.S.E. (353.8)} = [(2.1)^2 + (3.6)^2]^{1/2} = 8.4 \text{ ppm} \quad (2)$$

Therefore 353.8 ± 4.2 ppm.

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REFERENCES

- 1 D. H. Lee and C. C. Hsu, *J. Appl. Polym. Sci.*, 25 (1980) 2373.
- 2 S. Ahuja et al., *Anal. Chem.*, 37 (1965) 840.
- 3 J. F. Haskin et al., *Anal. Chem.*, 30 (1958) 217.
- 4 H. G. Nadeau and D. M. Oaks, *Anal. Chem.*, 32 (1960) 1760.
- 5 L. C. Browning and J. O. Watts, *Anal. Chem.*, 29 (1957) 24.
- 6 J. M. Hogan et al., *Anal. Chem.*, 42 (1970) 249.
- 7 Supelco. Inc., *Bulletin*, 1975, 747E.
- 8 O. L. Davies and P. L. Goldsmith, *Statistical Methods in Research and Production*. Hafner, New York, 4th ed., 1972.