SOME OBSERVATIONS ON THE SWOBODA TECHNIQUE
FOR ALCOHOL ANALYSIS
IN DILUTE AQUEOUS SOLUTIONS BY
ARGON IONIZATION CHROMATOGRAPHY
by J. B. ENTICKNAP*

Gas-liquid chromatography is probably the method of choice for analytical separations of volatile substances, since it permits reasonably certain identification of the material investigated as well as demonstrating the presence or absence of similar substances. This is of particular importance when ethanol is suspected, as comparable pharmacological effects can be produced by drugs such as methyl pentynol and methanol of quite different significance. Argon ionization detectors are perhaps the most widely used in this country, but are adversely affected by water vapour. Swoboda (1960) has described a technique in which a precolumn of diglycerol is used to trap the water from aqueous solutions while permitting the passage of the volatiles into an analytical column of polyethylene glycol. Chundela and Janak (1960) have described a similar method.

A modification of the Swoboda apparatus is available from W. G. Pye of Cambridge, England. It incorporates a flow valve which can reverse the flow through the precolumn while maintaining an identical flow through the main column without interruption.

Qualitatively the method is excellent. Clear separations of methanol, ethanol, propanol, butanol and methyl pentynol, in that order and without any overlapping of the relative peaks, have been obtained in several hundred tracings. The peak of iso-propanol overlaps that of ethanol, and that of di-ethyl ether precedes methanol.

Integrals are unequivocal and easy to read within 2% but quantitatively the method lacks precision for four main reasons:

1. The amount of water vapour present after multiple readings causes the soluble stationary phase to bleed into and contaminate the detector. This is much reduced if the temperature is kept down to 50°C., but changes in the responsive characteristics of the detector may still be encountered.

![Integram of EtOH 1.6 µg.](image1)

FIG. 1. Showing the change in detector response to 1.6 µg. of ethanol in 5 µl. of water with time elapsing before reversing flow through precolumn. Flow-rate 100 ml./min. (The units in the ordinate are millivolts of response of an integrating amplifier attenuated ×10)

2. The precise time of gas flow in a forward direction through the precolumn critically affects absolute response to a

![Area of Peak](image2)

FIG. 2. Showing that the relationship between detector response and concentration of ethanol in aqueous solution is a complex function. The points are average values of from 2 to 20 estimations at each concentration. Ordinate units as in Fig. 1

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given weight of ethanol. Response increases linearly and rapidly up to the time that ethanol leaves the analytical column, and then slowly until water appears, when it begins to fall (Fig. 1). Similar results are obtained with butanol.

A calibration curve was drawn by fitting a smooth line to the mean results of about 100 analyses of 10 standard solutions prepared gravimetrically. Results were comparable on any one day, but varied widely from day to day. Seven readings during two weeks on a standard of 165 mg./100 ml. gave results from this curve of 148–210 mg./100 ml., and 20 readings on a standard of 331 mg./100 ml., gave results from 280–400 mg./100 ml.

Thus, the results obtained from a calibration curve were unacceptable, and accordingly butanol was employed as an internal standard. As precise calculations could not be made because of the complex mathematical relationships between the variables, a compromise method was adopted using the most stable parts of the parameters. These were:

1. A column temperature of 50°C. varying by <1°C. along the column.
2. A 15 cm. precolumn of 20% diglycerol on 120–150 μ particle size cellite (B.S. sieves 100–120) with a 100 cm. analytical column of 10% polyethylene glycol on cellite.
3. Precolumn time of 3 minutes 20 seconds at a flow rate of 100 c.c./min.; this was the time the ethanol tracing began to appear on the recorder.
4. The amount of internal standard was made very close to the amount of the unknown ethanol.
5. 5 μL sample size.
6. 1.45 mg. butanol was held to be equivalent to 1.0 mg. of ethanol. This is
the ratio observed at an ethanol concentration of 170 mg./100 ml., and provides the best fit for all my data. Under these conditions 80 analyses on 11 samples gave mean errors of −25% to +20% (−60 to +34 mg./100 ml.) and maximum errors of −25% to +24% (−60 to +36 mg./100 ml.). The maximum errors occurred in the samples in which the concentration of internal standard added varied most from that of the ethanol being estimated. Seven readings on a standard of 165 mg./100 ml. gave a range of results from 168–177 mg./100 ml. and 20 readings on a standard of 331/100 ml. gave a range of 274–306 mg./100 ml. Analyses on five artificial samples gave the standard deviations shown in the table.

It is concluded that the method is not sufficiently precise for medico-legal purposes but, in experimental work and as a screening test, the speed with which results are obtained greatly offsets their large error. It also provides a useful method of confirming the identity of an intoxicating agent, and of estimating similar agents in presence of one another. It does not approach the accuracy of the alcohol dehydrogenase method of estimation which has an error in my laboratory of about 5%.

### Table Showing that the Standard Deviation of Measurements made with an Internal Standard are Proportional to the Concentration of Ethanol

<table>
<thead>
<tr>
<th>Actual concentration of ethanol mg./100 ml</th>
<th>No. of tests</th>
<th>Standard deviation mg./100 ml.</th>
<th>Mean error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>11</td>
<td>1</td>
<td>−1</td>
</tr>
<tr>
<td>85</td>
<td>6</td>
<td>3</td>
<td>+8</td>
</tr>
<tr>
<td>165</td>
<td>7</td>
<td>3</td>
<td>+7</td>
</tr>
<tr>
<td>331/100</td>
<td>20</td>
<td>8</td>
<td>−17</td>
</tr>
<tr>
<td>391</td>
<td>14</td>
<td>8</td>
<td>+5</td>
</tr>
</tbody>
</table>

**DISCUSSION**

**Dr. Lester** (U.S.): I would like to know what the material is in the precolumn. What material do you use to separate water from alcohol?

**Dr. Enticknap**: The precolumn is 20% dehy-droglycerol on 120 to 150 micron cellite, and the analytical column is 10% polyethylene glycol with a molecular weight of 400. I have also used polyethylene glycol with molecular weight of 1,000 on the analytical column which, if anything, improves the separations of some of the rather difficult mixtures like the aldehyde-methanol one that you were mentioning. This column is the difficult one. This material is extremely soluble, it is heat labile, and it causes that wavy baseline.

**Professor Harger** (U.S.): I am not clear on the second line there; is that sieve size 120 to 150?

**Dr. Enticknap**: Yes, those are microns. It is the actual particle size. It is 100 to 120, British standard sieves.

**Professor Harger**: What is the cellite—is it a mineral?

**Dr. Enticknap**: Yes, it is from Johns Mansville, an American powder.

**Professor Harger**: If you can make that separation work you have really got something. We worked for years to find something that separates alcohol and moisture.

**Dr. Enticknap**: I am sure it can be done, but by the time I had collected these figures, it seemed that one was going to need a computer to work out a formula. I could not see any ordinary mathematical relationship. Dr. Lester said his response was log log. Mine wasn't.

**Dr. Lester** (U.K.): I can confirm that in the flame ionization detection of alcohol, taking simply the current from the flame ionization detector, the current is proportional to the quantity of alcohol passing into the flame per unit time over an enormously wide range, 1,000 to 1 or more.

**Dr. Enticknap**: This ionization detector is usually linear and on most things over quite a wide range. But the water vapour, I think, is responsible here for a lot of this confusion. Some of it must be getting through. You can't standardise this thing with pure ethanol; it has to be standardised with aqueous solution, because curiously enough the response to alcohols, and this goes for ethanol, propanol, isopropanol—about six or eight of them, is between three and six times as high in aqueous solution as it is in its pure form.

**Professor Harger**: On this matter of separating alcohol and water, maybe you recall years ago, when Thomas of England was studying the distribution of alcohol between air and water at different temperatures, he ran his gas through calcium carbide and the alcohol wouldn't react with it, but water would and, of course, produced acetylene. Then he simply caught his alcohol in concentrated sulphuric acid and reweighed it, but he claimed a very good separation that way because the solubility of acetylene there would not amount to anything. I think he flushed it out pretty well, but he claimed that calcium carbide would do it.