

Alle Sulfhydryl-Verbindungen geben orange-rote Flecken (Tabelle I). Die Nachweisgrenze liegt zwischen $2 \cdot 10^{-5}$ und $7 \cdot 10^{-7}$ g/cm². Die Farbreaktion auf dem Papier kann verstärkt werden, wenn man den besprühten und ausgewaschenen Streifen in Chlorwasserstoff-Dampf bringt.

Die Farbreaktion bleibt mehr als 24 Stunden beständig.

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¹ H. S. BENNET AND D. A. YPHANTIS, *J. Am. Chem. Soc.*, 70 (1948) 3522.

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Gas chromatographic analysis of aqueous alcohols

II. Quantitative analysis of aqueous butanol solutions containing non-volatile salts

In a previous communication¹ a procedure was reported for the qualitative gas chromatographic analysis of aqueous alcohols. The method makes use of a mixed stationary phase of sorbitol-di-(2-ethylhexyl) sebacate, the sorbitol acting as a retardant for water. Because of the very bad tailing of the water peak it was not possible to perform quantitative analyses by the peak area normalisation method. BREALEY *et al.*² overcame this difficulty in the analysis of aqueous solutions by the use of an internal standard. This technique has now been successfully applied to the analysis of aqueous *n*-butanol solutions, *n*-propanol serving as the internal standard. It has been found in this work that more accurate results were obtained when the concentration of the internal standard in the sample approached that of the component to be determined.

Peak areas for both *n*-butanol and *n*-propanol increased linearly with sample size up to a volume of 10 μ l of the pure components. For larger samples a decrease in detector (katharometer) response was noted.

The retention time of water was found to be a function of the absolute quantity injected; the larger the quantity, the shorter the retention time. For aqueous solutions of *n*-butanol, the largest sample that could be injected without obscuring the butanol peak by that of water was 100 μ l. This gave rise to a detection limit (katharometer) for *n*-butanol in water of 0.01%.

The results obtained by this method are compared in Table I with those of a colorimetric procedure based on oxidation with dichromate³, as well as with the results obtained by difference from the determination of the water content by the Karl Fisher method. The effect of the internal standard concentration on the accuracy of the results is also indicated in this table.

Peak areas were measured by triangulation and a calibration factor of 1.08 was

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TABLE I
COMPARISON OF ANALYTICAL RESULTS OBTAINED BY GAS CHROMATOGRAPHIC AND
CHEMICAL METHODS

Sample number ^a	Internal standard added %	Sample size μ l	Weight % <i>n</i> -butanol			
			Known composition	Gas chromatography	Dichromate oxidation	By difference from water content ^b
1	1.92	30		0.19	0.19	
2	2.10	30		1.48	1.54	
3	2.10	30		0.45	0.47	
4	93.1	10	88.98	88.3		88.9
5	68.5	5	94.49	94.7	94.5	94.4
	1.67	5		93.0		
6	72.5	5	86.50	86.7	87.4	87.0
	3.81	5		85.5		

^a These samples did not contain salts.

^b Water determined by Karl Fisher method.

used to normalise the *n*-butanol peak area with that of *n*-propanol. The operating conditions have been reported¹.

The chromic acid oxidation method is sensitive to interference by halide ions, so that for aqueous butanol solutions containing halide salts, it is necessary to separate the alcohol from the sample by distillation prior to analysis. As most of the solutions analysed in these laboratories contained relatively high concentrations of calcium chloride, the gas chromatographic method, therefore, proved especially suitable. However, to avoid contaminating and blocking the column with non-volatile salts it was necessary to ensure that only the vapours reached the column. Most commercial instruments are fitted with injection blocks which are intended to produce rapid volatilization of the sample. Although such injection blocks serve as traps for non-volatiles, few of these instruments are designed for ease of dismantling and cleaning. BREALEY *et al.*² designed a special, easily dismantled injection block for the analysis of pharmaceutical preparations containing non-volatiles, for use with capillary pipettes.

Fig. 1 shows a similar injection block designed for use with syringes carrying a two-inch needle. The basic principle is the same as that of BREALEY *et al.* but the design has been simplified. The injection block, which attaches directly to that of the commercial instrument, consists essentially of an electrically heated copper block in which a small removable brass cup, filled with glass wool, is seated. To clean the block, the four securing bolts (not shown in the diagram) are opened, the head removed, and the glass wool replaced. The 100 W heating element, the details of which are not shown in the diagram, produces a maximum temperature of 300°. Temperature control was achieved by means of a rheostat.

As water is not measured directly by this method the extent of the hydration of the calcium chloride residue left in the injection block would not affect the analytical result. However, a partially hydrated residue could undergo slow dehydration by the carrier gas stream, a condition which could be expected to give rise to an unstable base line. Although the calcium chloride-calcium chloride monohydrate equilibrium temperature is reported to be 260°, an injection block temperature of 220° was found sufficient to give a stable base line.

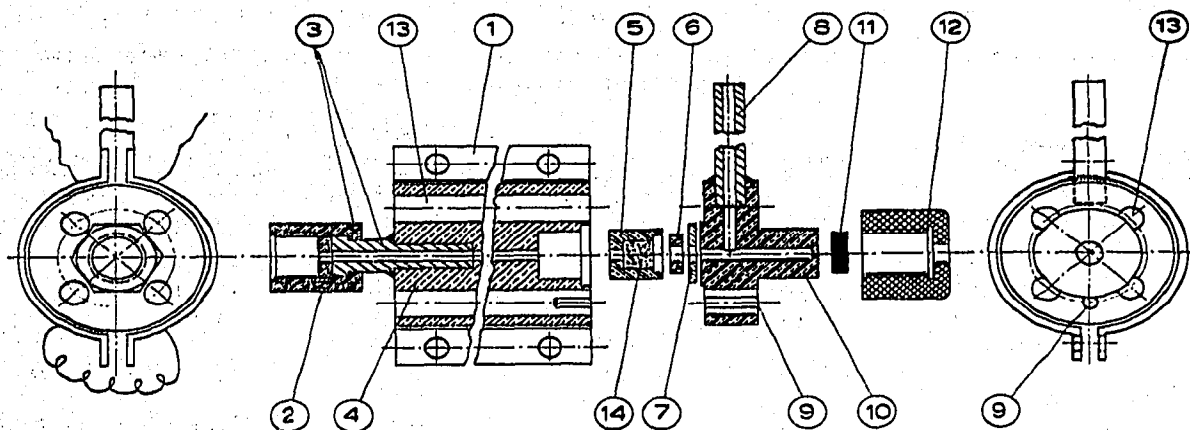


Fig. 1. Injection block designed for use with syringes carrying a two-inch needle.

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|--|------------------------------------|
| 1. Electrical heating jacket retainer | 8. Carrier gas inlet |
| 2. Annealed copper gasket | 9. Thermocouple well |
| 3. Connection to instrument injection port | 10. Removable head |
| 4. Copper block | 11. Silicone rubber septum |
| 5. Brass cup for glass wool | 12. Transite cap (septum retainer) |
| 6. Brass retainer for glass wool | 13. Holes for securing bolts |
| 7. Annealed copper gasket | 14. Glass wool |

The trapping efficiency for non-volatiles of this injection block was examined after several days of operation. The original injection block of the instrument was rinsed with distilled water—no chlorides could be detected in these washings.

We are indebted to Messrs. BREALEY, ELVIDGE AND PROCTOR for furnishing us with further information on their injection block, to Messrs. OFER AND GLASBERG of the Instrumentation Department for constructing and assisting in the design of the injection block, to the Analytical Department for the chemical analyses, and to the Israel Mining Industries for permission to publish this work.

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