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DETERMINATION OF METHYL ALCOHOL IN TETRAHYDROFURAN BY GAS CHROMATOGRAPHY

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DEVELOPMENT DIVISION

JULY - SEPTEMBER 1976

Normal Process Development
Endeavor No. 107

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ABSTRACT

A gas chromatographic method is described for the quantitative analysis of methyl alcohol in tetrahydrofuran.

DISCUSSION

The need to maintain a methyl alcohol-tetrahydrofuran (MeOH/THF) solution of constant composition during the synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) prompted the development of the analytical method described herein. This technique permits sampling of the solution at will.

EXPERIMENTAL

APPARATUS

The gas chromatograph used was a Tracor Inc., MT-150 series instrument, equipped with dual hydrogen flame ionization detectors, a Westronics MT-21 strip chart recorder, and an Infotronics Model CRS-100 integrator.

The column used was a stainless steel tube (1.524 m x 0.0032 m i.d.) packed with 80/100 mesh Chromosorb 102. The column was preconditioned for six hours at 150 C while maintaining a helium flow of 0.25 $\mu m^3/s$. A ten microliter Hamilton syringe (701-N) was employed for sample injection. The size of the injected samples ranged from 0.5 to 1.0 nm^3.

PROCEDURE

The operating conditions were as follows: temperatures for the injection port, column oven, and detectors were maintained at 150, 210 and 220 C, respectively. The helium flow was controlled at 0.5 $\mu m^3/s$ and the hydrogen and air flows were regulated at 0.83 $\mu m^3/s$ and 5.0 $\mu m^3/s$, respectively.

Preparation of samples: Only one standard, of exact composition, is required in this analytical procedure.

A twenty-five percent (by weight) stock solution was prepared by introduction of 5 g MeOH (ρ = 0.792 g/cc) into 15 g THF (ρ = 0.888 g/cc). Each component was weighed to the nearest 0.0001 gram. Employing measuring pipettes, 1 mℓ of the above solution and 10 mℓ of toluene (ρ = .866 g/cc) were transferred into a sample vial to give the following composition:

Toluene	787.3 μg/μℓ
THF	60.5 μg/μℓ
MeOH	18.0 μg/μℓ

The samples to be analyzed must likewise be diluted with toluene (1 to 10).

Peak areas or peak counts of components are not proportional to percent composition, i.e., different compounds have different detector responses; therefore, it is necessary to determine correction factors to obtain quantitative results from the GC trace. The amount of correction is a function of the response of a compound to the detecting device(*1*). Once determined, these correction factors can be used to calculate percentage composition. Under the same detector conditions these factors can be employed repeatedly to calculate the weight percent of 'b', 'c', 'd', etc. relative to toluene(*2*).

The procedure for calculating the flame ionization detector (FID) response factor involved preparation of a standard solution of known weight composition, of methyl alcohol, tetrahydrfuran and toluene. One microliter of the standard solution produced the chromatogram in Fig. 1. The weights 'W' were known and the peak counts 'A' for each component were recorded. The ratio A/W was calculated for each peak. The correction factor 'F' was calculated by dividing the A/W of each peak by the A/W of toluene. These factors are relative to toluene whose factor is arbitrarily set equal to 1 (Table I).

Table I. Procedure for Calculation of FID Factors

Peaks	W Wt. Injected (μg)	A Peak Counts	A/W	F Correction Factors
(a) Toluene	787.3	390900	496.5	1.00
(b) THF	60.5	7166	118.4	0.24
(c) MeOH	18.0	1070	59.4	0.12

From these results the weight of an unknown 'b' can be calculated from its peak count

$$W_b = \frac{W_a \cdot A_b}{F_b \cdot A_a} = \mu g \text{ 'b'}$$

where

W_b = weight of component 'b' (μg)
W_a = weight of standard 'a' (μg)
A_a = peak counts of standard 'a'
A_b = peak counts of component 'b'
F_b = correction factor of compound 'b' relative to compound 'a' at equal weights

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(1) Dietz, W. A., Journal of Gas Chromatography, 5, 68)1967).

(2) McNair, H. M., and Bonell, E. J., Basic Gas Chromatography, 5th ed., Berkeley, CA, Consolidated Printers (1969).

The weight percent of component 'b' can likewise be established

$$\text{'b' (wt \%)} = \frac{W_b}{W_b + W_c} \times 100$$

Chromatograms of solutions containing 25, 30 and 40 percent methyl alcohol in tetrahydrofuran were obtained. The analyses of these solutions are listed below:

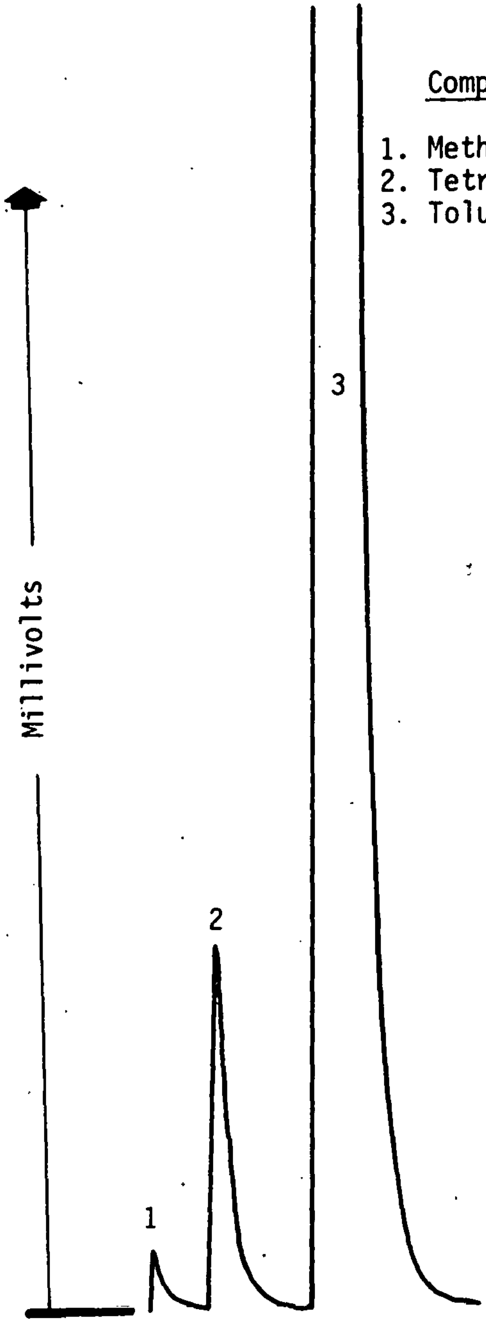
Methyl Alcohol (%)	Found (%)
25	24.6
25	25.2
30	29.2
30	29.1
40	39.26
40	40.05

Within the range of the methyl alcohol concentrations above (25 to 40%), the mean ($\overline{X}$) for the observed error is -0.4316 with a standard deviation (S) of 0.4652. Fig. 2 gives the plot of the data with error bands around the best fit line.

With toluene as the diluent for the MeOH/THF composition 5 to 6 minutes are required per analysis, depending on the size of the injected aliquot.

FUTURE WORK, COMMENTS, CONCLUSIONS

While there are several types of detectors employed in gas chromatography, most instruments employ either the flame ionization or thermal conductivity detectors. The response of the FID is independent of temperature, carrier gas, or flow rates which makes the flame ionization detector the best suited for most quantitative analysis; however, this detector is irresponsive to water and will not detect its presence. Since both methyl alcohol and tetrahydrofuran are hygroscopic, water will be present in some concentration. If its content is desired it must be determined by other analytical methods.



Component	Wt. (μg)	Peak Count
1. Methyl Alcohol	18.0	1070
2. Tetrahydrofuran	60.5	7166
3. Toluene	787.3	390900

Fig. 1. Calculation of FID Response Factors

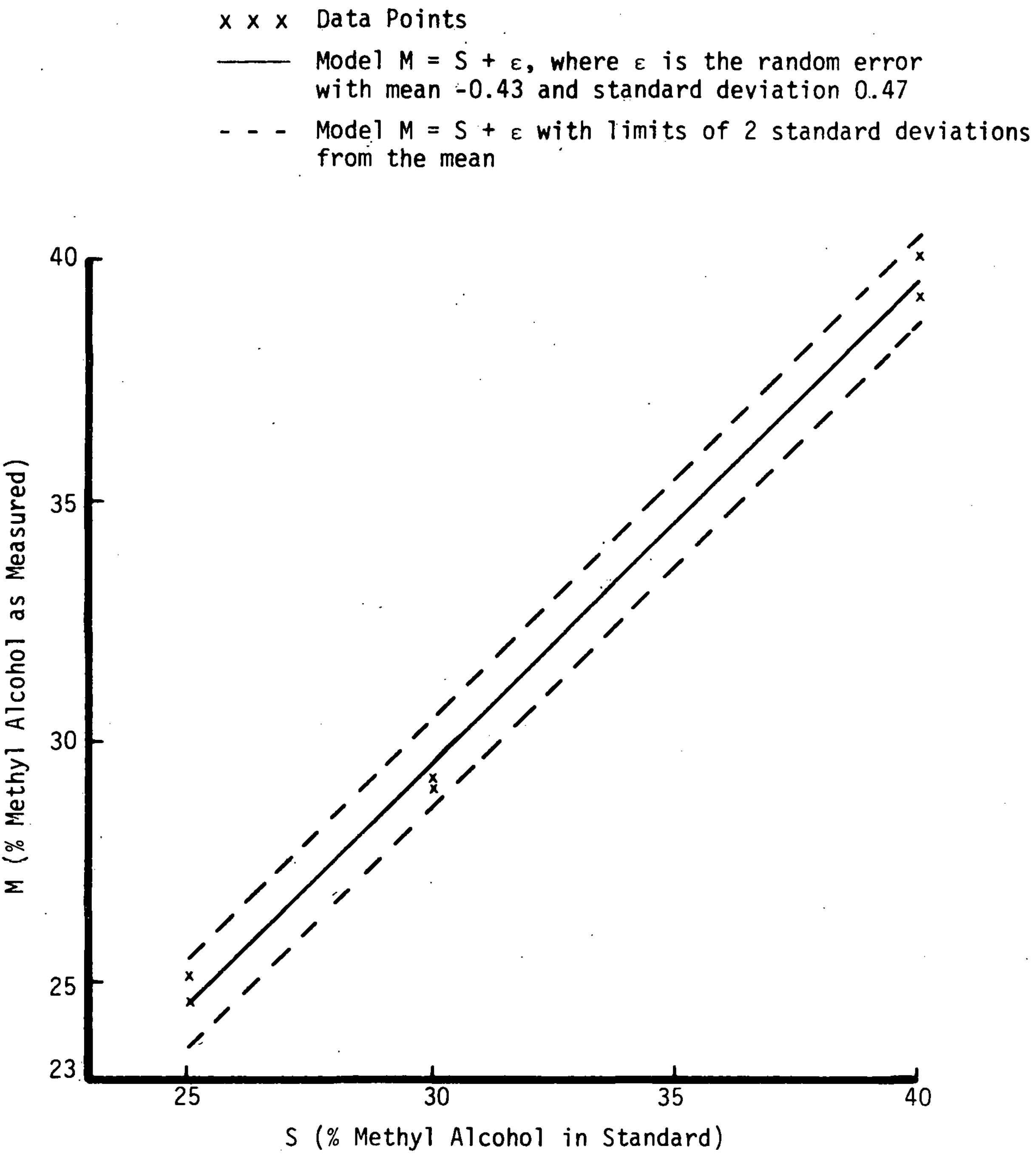


Fig. 2. Plot of Methyl Alcohol (Percent Measured Versus Percent Standard)