# Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 20, No. 1, February 1977

# REACTION GAS-CHROMATOGRAPHY OF FISCHER-TROPSCH SYNTHESIS PRODUCTS INCLUDING THE OXYGEN CONTAINING COMPOUNDS

## Z. H. SHIRAZI

#### Government College, Lahore

# CH. STOJANOV

#### Engler-Bunte-Institute, University of Karlsruhe, W. Germany

#### (Received February 2, 1977)

Abstract. The n- and iso-alcohols are separated completely as Boresters in  $B_2O_3$  pre-column. Various test mixtures of different compositions of Fischer-Tropsch synthesis products have been examined here. The method gave for the simple test samples an error limit of 1.5 - 2.5 %.

For the complicated test mixtures and Fischer-Tropsch products (organic and watery phases), the error limits are between 3.0-5.0%. The accuracy of the method is dependent on the mixture substance and especially the selectivity of the capillary column.

The analysis of pure alcohols or alcoholic mixtures are considerably practicable, but their measurement in aqueous solution is quite difficult.<sup>1</sup> The gas chromatography even with high resolution and optimum conditions is not an adequate tool for the separation of many component mixtures. This has been endeavoured by many workers by the utilisation of combination techniques.<sup>2</sup>—19

Fischer-Tropsch synthesis products in which the oxygen containing compounds are present can best be analysed by this technique.<sup>20</sup>

For the quantitative separation of n-and iso-alcohols from the olefins, aldehydes and parafins, we have tried to separate these alcohols as non volatile boron esters in the  $B_2 O_3$  pre-column through chemical reactions. The aim of the work is summarised as : (a) In the case of adsorption properties different reaction materials should be tested. It is expected that this makes complete adsorption, *i.e.*, retention of n-and iso-alcohols or aldehydes in precolumn possible. At the same time one should calculate quantitatively the remaining components, *i.e.*, olefins, paraffins and aldehydes. (b) On account of already mentioned necessity for such pre-column filling material and their success of carried out investigations, a quantitative analytical method for gas-chromatographic analysis of Fischer-Tropsch synthesis should be proposed.

#### Experimental

Construction of the Apparatus. For these investigations we used a pre-column of steel pipe of 150 mm length and a 4 mm dia. This was enclosed in a heating jacket and was connected to a capillary separating column (PPG-100 m) of the gaschromatograph (Fig. 1).

The pre-column temperature was controlled and was held constant with iron thermoelements during the running of the experiment, *i.e.*, gaschromatographic analysis. The pre-column was connected to the gas-chromatogrpah (F - 22 Perkin-Ełmer).

Preparation of  $B_2O_3$  Pre column. For this preparation we selected  $H_3BO_3/Firebrick - 40:100$ as reaction material. This was prepared as follows: 4 g  $H_3BO_3$  was dissolved in 50 ml distilled water and then 10 g firebrick (grain size 0.4 -0.5 mm) was mixed. This mixture was placed in a rotating tank until it was completely dried. This was completely dried after being at 138-140° for 20 hr.





The dried material was then passed through the metallic sieve of pore diameter 0.066 mm. The material was collected in two different fractions: (a) Fraction 1 8.26 g ( $\geq 0.066$  mm); and (b) Fraction 2 0.83 g ( $\leq 0.066$  mm) From fraction 2 about 1.26 g substance was

From fraction 2 about 1.26 g substance was filled in the pre-column. The filled column was tested and a stream of hydrogen at 100 ml/ min was passed through the column at  $180-200^{\circ}$ . The heat converts H<sub>3</sub>BO<sub>3</sub> to B<sub>2</sub>O<sub>3</sub>. This was done for 15-20 hr. The column was ready for use.

Analysis Conditions. We used  $B_2O_3$  precolumn at 120–250. The most favourable temperature for this column is about 200°. The mixture components arising from the pre-column were carried further from the carrier gas (hydrogen) into the capillary separating column (PPG/100 m) and were separated from one another with temperature 'programming or isothermally. The quantity of the sample injected was mostly (0.2–1.0 µ1).,

The watery phase of the Fischer-Tropsch products was purified by centrifuging from traces of hydrocarbons in order to obtain quantitative gas chromatographic analysis. The preparation of different test mixtures was done by an exact weighing of the individual mixture components.

#### **Results and Discussion**

Reproducibility of GC Analysis of the Test Mixture. The experimental reproducibility was checked using a test mixture of butanal, octene -1, nonane and pentanol. The individual readings obtained from 5 chromatograms showed a relative variation of the average value (for each test) of 0.25-1.35. This variation lies within the measurement accuracy of the GC analysis (Table 1).

Influence of Injection Temperature on GC Analysis. In general it is known that in GC the injection temperature does not influence the GC analysis. In our case a check of this effect in the range  $120-250^{\circ}$  was carried out using test mixture 11, since their exists a possibility that decomposition products of butanal (other aldehydes) can form at high injection temperature. We obtain no variation in the tested temperature range which corresponds with the earlier investigations to ascertain this effect (Table 2). 

 TABLE 1. GAS-CHROMATOGRAPHY OF TEST MIXTURE

 11 (WITHOUT PRE-COLUMN)

Component	Percentage *	o Absolute (%)	Relative (%)
Butanal	16.28	0.22	1.35
Octene-1	24.10	0.06	0.25
Nonane	30.25	0.10	0.33
Pentanol	29.38	0.23	0.78

\*Average of five readings

Analysis conditions: Separating column, PPG/100m; Carrier gas hydrogen; Quantity of mixture injected. 0.2  $\mu$ 1; Injection temp. 200°; Detector temp. 200° and Analysis temp. 100° (isotherm).

Determination of the Specific Correction Factors (SCF). Material specific correction factors are used in such cases where a quantitative estimation of the GC analysis is found necessary. In order to obtain unique and reliable experimental data, one must take at least 5 chromatograms for each weighing. In this work the material specific correction factors were obtained for the above mentioned substances in the injection temperature range of  $120 - 250^{\circ}$  (Table 3).

The calculation of the material specific correction factors was done with nonane as standard sample and this was found to be 1.0. While determining the average values the values given in the brackets were not taken into considerations.

GC Analysis of Test Mixture With-and Without Pre column. Using a series of experiments the method used by us had to be quantitatively checked. Hence we have analysed test mixtures of different compositions quantitatively with-and without pre-column. The following results were obtained for the test mixture from butanal, octene-1, nonane and pentanol (Table 4, Fig. 2). Analysis conditions are the same as given under Table 1. The pre-column temperature was 200°. One sees that the alcohol (pentanol) is retained completely as non volatile

TABLE 2. GAS CHROMATOGRAPHY OF THE TEST MIXTURE 11 (WITHOUT PRE-COLUMN).

Components		Ir	njection te	mperature			Average	(ơ) Absolute	(đ) Relative
	120	150	170	200	220	250	(%)	(%)	(%)
Butanal	16.02	16.18	16.06	16.28	16.13	16.03	16.12	0.09	0.57
Octene-1	24.17	24.11	23.89	24.09	24.06	23.96	24.05	0.09	0.39
Nonane	30.42	30.37	30.08	30.26	30.28	30.09	30.25	0.13	0.42
Pentanol	29.32	29.77	29.85	29.37	29.54	29.92	29.63	0.23	0.78

Analysis conditions (same as given under Table 1)



Fig. 2. GC-Analysis for test mixture No. 14 (with<sup>1</sup> and without<sup>2</sup> pre-column).



Fig. 3. GC-Analysis for the test mixture No. 20 (analysis conditions are same as given under Table 1). The analysis temperature was  $40^{\circ}/2^{\circ}/\text{min}/150^{\circ}$ , temperature programming.

Borester in the pre-column. The GC analysis of the remaining components in the mixture (octene -1, nonane and butanal) is not influenced by that. The correctness of this method, however, necessitated a further investigation of test mixtures which contain a larger number of mixture components of various compositions. Hence the test mixtures which contained mostly of aldehydes, olefins, paraflins and also alcohols were quantitatively analysed, (Tables 5-7, Figs. 3, 4). Analysis conditions are

 

 TABLE 3.
 Specific Sample Correction Factor (SCF) from 6 Different Weighings and One Injection Temperature of 170°.

Components		Y	Weighings	in (g)			Average	Absolute	Relative
	1	2	3	4	5	6		(%)	(%)
Butanal	(2.1324)	1.8928	(1.1225)	1.9439	(1.2365)	1.9068	1.9146	0.03	1.40
Octene-1	(1.1715)	1.0470	1.0488	1.0518	1.0447	1.0447	0.0476	0.003	0.27
Nonane	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.000	0.00
Pentanol	(1.7950)	(1.7363)	1.5752	1.5750	1.5536	1.5967	1.5751	0.02	1.12

Analysis conditions (see under Table 1)

TABLE 4. QUANTITATIVE COMPARISON OF THE GC-RESULTS FOR THE TEST MIXTURE 14 WITH 1 - AND WITHOUT 2 PRE-COLUMN (CHROMATOGRAMS ARE SHOWN IN FIG. 2).

5	Area (%) from		Errors			
Components	I without pre-column with		II with pre-column	△(I-II) (%)	relative (%)	
Butanal	6.15		-6.24	+0.090	+1.46	
Octene-1	15.70		15.43	-0.27	- 1.72	
Nonane	32.90		-32.90	0.00	0.00	
Pentanol	45.24		0.00	0.00	0.00	
				Average	±1.59	

3



Fig. 4. Quantitative comparison of GC-Results for the test mixture 21 (analysis conditions are as given under Table 3).

the same as given under Table 1. The analysis temperature was: 40°/2°/min/150°. *Programming*. If one compares the errors (in

**Programming.** If one compares the errors (in relative  $\frac{9}{10}$ ) of the GC analysis (per component or per total analysis) with test mixtures which have

already been analysed, it can be seen that in the case of mixture 21 (consisting mostly of aldehydes) the errors are at their largest end and have a value of  $\pm$  8.14% relative for the whole analysis (Table 6, Fig. 4). As against this the GC analysis for test mixture 20 and the paraffin test mixture showed errors of 2.37% and 1.51% respectively (Tables 5, 7). These lie within the measurement accuracy of the GC analysis.

The method was finally tested using test mixture consisting of about 19 components (olefins, paraffins, aldehydes and alcohols) (Table 8, Fig. 6). This analysis showed complete adsorption for the alcohols which were retained as non volatile Boresters in the pre-column. The error for the remaining components within the mixture and a relative value of about  $\pm$  5.75% for the total analysis (Table 8).

1

According to us this GC result for such a complicated test mixture consisting of methane and olefinic compounds containing oxygen is very satisfactory. As an exception, the errors for the mixture components, *i.e.*, butanal, propanal, dodecane and tetradecane lie outside the GC measurement accuracy determined by us ( $\pm$  5.0%). The reasons for these are:

TABLE 5. QUANTITATIVE COMPARISON OF THE GC-RESULTS FOR THE TEST MIXTURE 20 WITH <sup>1</sup> - AND WITHOUT <sup>2</sup> PRE-COLUMN (CHROMATOGRAMS ARE SHOWN IN FIG. 3).

and a second second second	Area (%) from th	Area (%) from the chromatograms				
Components	I without pre-column	II with pre-column	△(I-II) (%)	Error relative (%)		
2-Methyl-Pentene-2	18.82	18.85	+0.03		+1.60	
Hexene-1	12.51	12.14	-0.37		-2.96	
Octene-1	19.55	19.05	-0.50		- 2.56	
Nonane	20.35	20.35	-0.0		- 0.0	
Pentanol	28.77	0.0	0.0		0.0	
				Average	±2.37	

 TABLE 6. QUANTITATIVE COMPARISON OF THE GC—RESULTS FOR THE TEST MIXTURE NO. 21 WITH<sup>1</sup>—AND WITHOUT<sup>2</sup> PRE-COLUMN (REF. TO FIG. 4).

	Area (%) from the	he chromatograms	△(I-II)	Errors relative (%)	
Components	I without pre-column	II with pre-column	(%)		
Ethanal	0.85	0.75	-0.10	-11.76	
Propanal	6.11	6.76	+0.65	+10.63	
Acetone	15.07	15.38	+0.31	+2.06	
Nonane	51.43	51.43	0.0	0.0	
Butanal	5.27	5.80	+0.53	+10.06	
Pentanol	14.50	0.0	0.0	0.0	
Pentanal	6.77	6.35	-0.42	- 6.20	
			Average	+8.14	

	Area (%) from the	△(I-II)	Error	
Components	I without pre-column	II with pre-column	(%)	relative (%)
Pentane	22.56	22.10	-0.28	-1.25
Hexane	17.56	17.70	+0.14	-0.79
Heptane	12.49	12.68	+0.19	+1.52
Octane	12.10	12.30	+0.20	+1.65
Nonane	12.45	12.67	+0.22	+1.77
Decane	9.59	9.53	-0.06	-0.63
Undecane	13.42	13.02	-0.40	- 2.98
		A SULLET Pade 10000 Not part in the use	Average	±1.51

 TABLE 7. QUANTITATIVE COMPARISON OF THE GC—RESULT FOR THE TEST MIXTURE OF PARAFFINS (WITH<sup>1</sup> – AND WITHOUT<sup>2</sup> PRE-COLUMN)

TABLE 8. QUANTITATIVE COMPARISON OF THE GC – RESULTS FOR THE TEST MIXTURE NO. 25 WITH—AND WITHOUT PRE-COLUMN; ANALYSIS CONDITIONS ARE SAME AS GIVEN UNDER TABLE 3 (REF. TO FIG. 5).

	A	rea (%) f	rom the	rams	스(I-II)	Error	
Components	wi	I without pre-column		II with pre-column		(%)	relative (%)
Methanol		2.05		0.0		0.0	0.0
Ethanol		2.35		0.0		0.0	0.0
ropanol		6.93		0.0		0.0	0.0
entanol		3.01		0.0		0.0	0.0
Iexanol		4.46		0.0		0.0	0.0
leptanol		2.23		0.0		0.0	0.0
Octanol		2.26		0.0		0.0	0.0
ropanal		3.25		3.48		+0.23	+7.06
utanal		5.22		4.78		- 0.44	- 8.43
lexene-1		6.38		6.29		- 0.09	- 1.41
octene-1		7.14		7.20		+0.06	+0.84
entane		19.09		18.69		-0.40	- 2.10
leptane		8.78		8.56		-0.22	- 2.51
lonane		5.56		5.56		0.0	0.0
odecane		10.27		9.44		0.83	- 8.08
etradecane		11.03		9.31		- 1.72	- 15.60

Average  $\pm 5.75$ 

(a) As can be seen by Tables 6 and 8, The aldehyde showed a higher error between the analysis with and without pre-column. This could be due to the instability of aldehydes during mixing with other mixtures (propanal; ref. Table 4). In the case of the check for the reproducibility of GC analysis of aldehydes only with pre-column we ob-

tained satisfactory results (except for butanal) as can be seen from Table 9.

(b) The errors encountered for the case of dodecane and tetradecane are due to the unsatisfactory separation capacity of PPG-capillary column. Because of this, dodecane and tetradecane were not considered during the evolution of Z. H. SHIRAZI and CH. STOJANOV





Components		Numbe	rs of readin (%)	Average from 5 chromato-	( <b>o</b> )	(Ø)			
	1	1 2 3 4		4	5	grams (%)	Absolute (%)	Relative (%)	
Ethanal	4.50	4.53	4.55	4.55	4.50	4.53	0.03	0.55	
Propanal	22.89	22.83	22.96	22.75	22.71	22.82	0.11	0.47	
Butanal	3.14	3.09	3.09	2.84	3.86	3.04	0.12	3.95	
Pentanal	19.50	19.62	19.23	18.64	19.14	19.22	0.39	1.97	
Hexanal	50.00	49.94	50.21	51.35	50.29	50.42	0.02	0.04	

TABLE 10. QUANTITATIVE COMPARISON OF THE GC-Results, with<sup>1</sup> - and without<sup>2</sup> Pre-column for the Test Mixture No. 19; Analysis Conditions are the Same as Given Under Table 3 (Ref. to Fig. 6).

Components	Area (%) from the	Adsorption in the pre-column in (%)		
components	I without pre-column	II with pre-column	n-alcohols	iso-alcohols
Methanol	2.44	0.00		
Ethanol	5.02	0.00		
n-Propanol	7.82	0.00		
Iso-Propanol	1.92	0.00		
Pentanol	18.70	0.00		
Hexanol	6.44	0.00	67.68	7.82
Heptanol	10.20	0.00		
Octanol	10.12	0.00		
Nonanol	13.54	0.00		
Nonane	24.50	24.50		

the chromatograms for the paraffinic test mixtures (Table 7). The aim of this work was, however, to find a reaction material which has the characteristics to retain or adsorb quantitatively alcohols or aldehydes in the pre-column from the GC analysis carried uptil now. On different ma-



terial mixtures it can be seen that the  $B_2O_3$  precolumn has satisfied this requirement with respect to n-and *iso*-alcohols. In order to experimentally support this quantitative statement we analysed test mixtures which contained mostly of nand *iso*-alcohols (ref. to Table 10).

As can be seen from Table 10 and Fig. 6 that the n-and *iso*-alcohols in the pre-column were completely retained or adsorbed in the precolumn as Borester. The mixture ratio of the n- and *iso*alcohols was 8.65: 1.0 by weight percentage. As against this the standard (nonane) added can be clearly recognised from the chromatogram with and with-out pre-column (ref. to Fig. 6). With this it was shown that the samples mixtures with an alcohol content (n- and *iso* - alcohols) of 95.5 % by weight can be quantitatively analysed.

GC Analysis of Fischer - Tropsch Reaction Pro-

ducts. The GC analysis which was successful on the test mixtures of different compositions was utilised also for the analysis of the Fischer – Tropsch reaction products. As can be seen from Fig. 7. We observe hardly any difference between the chromatograms with – and without precolumn for the organic phase of the product of synthesis.

7

It was expected that the alcohols eventually present in the organic phase of the product would lead to different GC analysis. As already mentioned this is not been experimentally varified. Since the PPG-capillary column does not have sufficient power of resolution for higher alcohols and since the product under test contained very small quantities of alcohols. The identification of the hydrocarbons registered on the chromatogram (olefins, *cis*-and *trans*-compounds paraffins etc., with-and without pre-column) offered



Fig. 7. Quantitative comparison of the GC-Results for the organic phase of the Fischer-Tropsch-Synthesis Products. (analysis conditions are the same as given under

Table 3). The analysis temperature was  $30^{\circ}/0$ ,  $6^{\circ}/min/150^{\circ}$  temperature programming, with 1 and without 2 pre-column.



Fig. 8. GC-Analysis of Fischer-Tropsch-Synthesis Products (watery phase : 1 without centrifuging, 11 with centrifuging ; only without pre-column. (analysis condition are the same as given under Table 7).

no difficulties since such an evaluation of the above mentioned products was already known (done by the help of retention indices and partly by the addition of standard samples with the product). A comparison of the chromatograms with the pre-column for the organic and watery phase of the Fischer-Tropsch synthesis products is shown in Fig. 7, and Fig. 8, I, II.

We also ascertain that the watery phase of paraffins and olefins traces will be contaminated. These were removed fully by centrifuging of the products as shown in Fig. 8. II). If one compares the chromatograms (with-and without pre-column) for the watery phase of the synthesis products, one observes that a direct analysis of the product without pre-column only helps to register methanol and ethanol (ref. Fig. 8 II). Even an analysis of larger samples (*i.e.*  $0.5 \ \mu$ 1) gave the same results. In contrast in the case of the analysis of the watery phase of the products with  $B_2O_3$  pre-column, non-alcoholic (methanol and ethanol) contents were registered, since these were retained by the  $B_2O_3$  as non-volatile Boresters. Finally, one can say that a quantitative comparison between the chromatograms with-and without pre-column for the watery phase is only then possible when the analysis of this can be done with a PPG-capillary column without precolumn. This was not known and hence it had to be confirmed.

According to our experience the PPG column is not advisible for the GC analysis for alcohols from watery solutions.

Since its resolution capacity is disturbed by water. Hence for further investigations the Carbowax 20M/100m – capillary column was tested (ref. to Fig. 9). The investigations have been successfull but not yet complete.<sup>21</sup>

#### Conclusions

With the help of the  $B_2O_3$  pre-column which was connected to the PPG-capillary separating column it was shown that the n-and *iso*-alcohols can be retained as non volatile boresters from the



Fig. 9. GC-Analysis of the watery phase of the Eischer-Tropsch-Reaction Products without pre-column (separated on the carbowax 20M / capillary column / 100m). (a) Fig. 9/1-alcohols, pur., (b) Fig. 9/2-90°, water : 10°, alcohols. (c) Fig. 9/3-watery phase of the Fischer-Tropsch-Products (1, $\mu$ ) (d) Fig. 9/4-10  $\mu$ l watery phase of the Fischer-Tropsch Product. Temperature Programming : 50°/2°/min/170°.

rest of the components (olefins, paraffins and aldehydes). This technique was used for the GC analysis of test mixtures of different compositions and finally for the analysis of the Fischer-Trophsch reaction products. As can be seen from Table 11 that the analysis of the different test mixtures gave satisfactory result (Table 11).

With this, the quantitative techniques adopted by us within the range of GC analysis of various test mixtures of different compositions, is satisfied. The error of  $\pm$  8.14 % corresponding to mixture 21 is a specific case depending upon the mixture components (ref. P-11). All the other recorded values lie within the accuracy of GC analysis. Using this technique for the quantitative analysis of Fischer-Tropsch reaction products (organic and

		Error limits for		Adsorption in the pre-column (% relative)			
	Mixture whole analysis area number (%) for 5 chroma- tograms		n-alcohols	iso-alcohols			
Paraffi	ns miz	ture	±1.50				
Test m	ixture	14	±1.59	45.24			
*	"	20	$\pm 2.37$	28.77	· · · · · · · · · · · · · · · · · · ·		
		21	$\pm 8.14$	14.50			
	#	25	$\pm 5.75$	23.29			
"		19	± -	67.68	7.82		
FTP (c	organic	phase)	$\pm 3.00-5.00$	whole	whole		
		phase)	± -	11	"		

 TABLE 11.
 CLASSIFICATION OF THE RESULTS FOR THE GC—ANALYSIS WITH VARIOUS TEST MIXTURES OF FISCHER—TROPSCH—REACTION PRODUCTS WITH—AND WITHOUT PRE-COLUMN (REF. TO TABLE 4—11 AND FIG. 2—10).

x) FTP=Fischer-Tropsch-Product









watery phase), we obtained the following results :

(a) The organic phase of the synthesis products could be analysed very well with a temperature programming (ref. Fig. 7). Viewed qualitatively and quantitatively the chromatograms with and without pre-column do not differ much from one another. For the experiments conducted on the organic phase with the carbowax 20 M/100 m-capillary column without precolumn, one can infer that higher alcohols are present in the product which could not be recorded by the PPG-capillary column. The contents of *cis*-and *trans*-olefinic and

The contents of cis- and trans-olefinic and Paraffinic were satisfactorily recorded by the PPG separating column (with- and without precolumn). The identification of the separated components from the organic phase was done by the help of the retention indices and partly with the mixing of standard samples to the synthesis products. (Fig. 7).



(b) In the case of the GC analysis of the watery

Fig. 10/3. Distribution of total olefins of the Fischer-Tropsch-Products (organic phase, ref. to Fig. 7).



Fig. 10/4/I, II. Distribution of the chemical composition of Fig. 10/4/1, fl. Distribution of the chemical composition of the Fischer—Tropsch—Products (organic, gas and watery phase), Acids (S), Wax (W), Gas (G), Ketons (K)-Aldehydes (A°), Alcohols (A\*), Paraffins(P), Olefins (O), Fraction (F), ref. to Fig. 7 and Fig. 10/1-2(I) and 10/4(II). Distribution of paraffins and olefins with (+VS) and without (-VS) pre-column.

phase of the synthesis products our method could be adopted only within limits since the PPGcapillary column did not permit a direct analysis of the products because its resolution power is weakened by water. The analysis of water phase withand without pre-column was carried out in order to check the applicability of the PPG column for such purposes.

As can be seen from Fig. 8. I, II only methanol and Ethanol were registered (without pre-column) on chromatogram. Increase in the quantity of the sample (0.5 µl) did not bring any satisfactory result.

The analysis of the same product using a precolumn showed a quantitative adsorption of the alcohols (methanol and ethanol) which was clearly recognised in the case of the analysis with-out precolumn. These were retained as non volatile Boresters in the pre-column as already mentioned.

The complete GC Analysis of the Fischer-Tropsch-Product (organic and watery phase) can be seen in Fig. 10/4. I, II. The experimental GC results have shown that the  $B_2O_3$  precolumn is ideal for the adsorption of n-and iso-alcohols. Its capacity can be precalculated if one follows the stocheometric rule (one mole of B2O3 for 3 moles of alcohols).

# References

- 1. E. Bayer Gas-chromatographie, Springer-Verlag, Heidelberg, (S. 80 u. 124, (1959).
- 2. B. Smith et al., Acta Chem. Scand., 17, 801 (1963)
- 3. R. M. Ireda, et al., J. Agr. Food Chem., 10, 98 (1962).
- 4.
- H.J. Schulz, Chem. Ing. Tech., 46, 2, 79 (1974).
  W. M. Ruckendorf, Z. Anal. Chem., 175, 5. 350 (1960).
- 6. J. Nikelly et al., Anal. Chem., 34, 472 (1962).
- 7. Y. G. Osokin, Neftekhimiya, 6, 333 (1966).
- 8. D. A. Bierl, Mikrochimica. Acta (Wien), 637 (1969).
- 9. H. J. Schulz und N. Sedighi, Erdöl und Kohle-Erdgas-Petrochemie mit Brennstoffchemie, 27, 345 (1974).
- J. Anon, Chem. Eng. News, 38, 16, 114 (1960).
   F. Drawert, et al., Chem. Ber., 93 3066 (1960).
   F. Drawert, Angew. Chemi., 72, 385, 555
- (1960).
- 13. D.A. Gronin, J. Chromatography, 64, 25 (1972).
- 14. H. J. Schulz and H. O. Reitemeyer, Chromatographia, 1, 315, 364 (1968).
- 15. W. E. Haris, et al., Anal. Chem., 31, 1, 114 (1959)
- 16. F. W. Hefendhel, Naturwissenschaften. 51, 138 (1964).
- 17. W. Brandenberg, et al., J. Am. Chem. Soc., 72, 3275 (1950).
- 18. C. Hungneny, Bull. Soc. Chim., France, S. 497 (1965).
- 19. F. Drawert, Angew. Chem., 72, 33 (1960).
- 20. H. G. Struppe, Chem. Tech. (Berlin), 14, 114 (1962).
- 21. Ch. Stojanov and Z. H. Shirazi, in preparation.