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Experience with Boron Trifluoride for the preparation of the methyl esters of fatty acids for gas chromatographic analyses

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Experience with Boron Trifluoride for the Preparation of the Methyl Esters of Fatty Acids for Gas Chromatographic Analyses

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Introduction

For the gas chromatographic separation of fatty acids in oils and fats, the fatty acid is most of the time converted into its methyl ester before injection into the column. We have (1) recently checked and sometimes improved the various methylation and transesterification methods which have been recommended for this purpose. Methylation with boron trifluoride as catalyst has been known for some time (2,3). Since work with the gaseous, extremely toxic boron trifluoride is both complicated and dangerous, we gave up all investigations which use this compound. Nowadays, boron trifluoride can be obtained from the trade

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as a methanol complex and this can be handled easily. Van Wijngaarden (4) has described a simple method according to which the methyl esters of fatty acids can be obtained in elegant fashion from triglycerides by transesterification with boron fluoride-methanol reagent. We have used this method experimentally in our laboratory but occasional troubles were observed with the detector and these will be briefly reported here. p.110

Procedure

Van Wijngaarden gives the following instructions for the transesterification: about 150 mg of fat or oil are placed in a 50 ml round bottom flask with ground glass connection and mixed with 2 ml of 0.5 n methanolic sodium hydroxide

A reflux condenser is connected and the flask is heated in water until all the oil droplets have completely dissolved which, from experience, takes 2-5 minutes. 2 ml of BF_3-methanol reagent are now added through the condenser. (The BF_3-methanol reagent is a boron trifluoride-methanol complex with about 14% BF_3 content and can be obtained from British Drug Houses Ltd.). The flask is now heated for a further 2 minutes. Then 1.5 ml of heptane is added through the condenser and the mixture heated for another minute. Finally the mixture is cooled and sufficient saturated common salt solution is added until the level of the organic phase reaches the neck of the flask (ground portion). About 1 ml of

the supernatant heptane phase is pipetted out and placed in a small ground-stoppered flask. Anhydrous sodium sulphate is then added in order to extract the last traces of water. This solution is injected directly into the gas chromatograph.

Authors' Experience

By following the above method, the transesterification takes place smoothly and the mixture of esters can be cleanly separated by gas chromatography. The calculation of the fatty acids distribution by the method of height times retention time from isothermal gas chromatograms yields correct values. These agree well overall with those from other frequently verified methylation methods (see Table 1).

However, during our first preliminary tests with cocoa butter and linseed oil, we observed that the sensitivity of our flame ionization detector decreased very considerably after a few injections of the ester mixture obtained with the boron trifluoride reagent. After 4 to 6 determinations, the sensitivity amounted to only a fraction of the original value.

There was a build-up on the electrode consisting of a gray coating which seemed to adhere strongly and which is presumably a boron compound. After the electrode was cleaned by removing the coating with emery, the sensitivity returned to its original value. Schomburg (5) in his paper on "New Developments in the Field of Gas Chromatographic Detectors" had

already warned that boron residues can damage the detector. On page 30 he states: "Substances which leave solid residues during combustion in the detector, for example boron alkyls which produce boron oxide during the burning, cannot be measured in the flame ionization detector because the deposition of these oxides causes such a deterioration of the electrode insulation that measurements become impossible". We assumed the boron trifluoride-methanol complex which was used as reagent could behave in a similar fashion.

In order to clarify this situation, systematic experiments were conducted a few months later with olive oil and finally with coconut fat, using the same thoroughly cleaned detector. The oil sample was transesterified using the boron trifluoride-methanol complex while following the instructions of Van Wijngaarden precisely and the resulting mixture of esters was injected into the gas chromatograph. To our surprise, the high sensitivity of the detector remained unchanged after numerous injections of the ester mixture. During the course of three days we injected the ester mixture from olive oil 21 times and finally the ester mixture from coconut fat 11 times. All gas chromatograms were trouble-free and not the slightest disturbance of the detector was observed. The only difference in the test conditions between these tests and the preliminary experiments when the large disturbances occurred was the hydrogen to air ratio in the flame ionization detector. During the preliminary experiments the gas streams of hydrogen and air could not be

p.112

Table 1

Percentage Distribution of Fatty Acids from Oils and Fats by Various Transesterification Methods

	C_{10}	C_{12}	C_{14}	C_{16}	$C_{16:1}$	C_{17}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$ $C_{20:1}$	C_{20}
Cocoa butter											
a) Sodium methylate method	-	Tr.	0.1	29.1	0.2	0.2	31.1	35.0	3.5	0.2	0.6
b) Boron trifluoride method	-	Tr.	0.1	29.9	0.2	0.2	30.9	34.3	3.4	0.3	0.6
Linseed oil											
a) Sodium methylate method	-	0.3	0.1	6.1	0.1	Tr.	3.2	16.6	14.7	59.0	0.1
b) Boron trifluoride method	-	0.3	0.1	6.4	Tr.	0.1	3.5	16.5	14.7	58.1	0.3
Olive oil											
a) Sodium methylate method											
1st Injection	-	Tr.	Tr.	12.4	0.8	0.1	2.0	70.8	12.5	0.8	0.3
2nd Injection	-	-	Tr.	12.3	0.8	0.1	2.0	70.7	12.6	0.9	0.4
3rd Injection	-	-	Tr.	12.6	0.8	0.1	2.0	69.7	13.1	1.0	0.4
b) Boron trifluoride method											
3rd Injection	-	-	-	12.1	0.8	0.1	2.0	71.9	11.6	0.8	0.4
19th Injection	-	-	-	12.7	0.8	0.1	2.1	71.6	11.3	0.8	0.4
20th Injection	-	-	-	12.2	0.8	0.1	2.0	72.4	11.5	0.6	0.3
Test mixture made up of:											
1/3 coconut fat											
1/3 cocoa butter											
1/3 linseed oil											
a) Sodium methylate method	3.0	19.9	6.6	12.9	0	0	12.6	18.1	7.3	19.6	-
b) Sodium propylate method	2.8	19.0	6.5	13.0	0	0	12.8	17.9	7.6	20.5	-
c) Boron trifluoride method	3.1	22.1	7.0	13.4	0	0	12.1	17.4	7.0	18.0	-

measured accurately. The hydrogen stream amounted to about 30 ml/min and the air quantity approximately 300 ml/min. For the second series of experiments the hydrogen stream was exactly 30 ml/min and the air stream was adjusted in such a way that the detector reached maximum sensitivity. With a constant hydrogen stream the air supply was adjusted at the regulator valve so that the background signal showed a maximum deflection, and this occurred at 430 ml of air per minute. The operating conditions for the second series of experiments were as follows:

Separation column: 15'x 1/8", stainless steel.

Column packing: 10% polyethylene glycol succinate EGS from Aerograph A.G., Basel, on Chromosorb W, acid washed and treated with dimethylchlorosilane.

Detector: hydrogen flame ionization detector.

Gas streams: nitrogen measured at the column outlet 25 ml/min
Hydrogen for the detector 30 ml/min
Air for the detector 430 ml/min

Temperatures: Injector with glass inset 275°C.
Detector oven 275°C.
Column oven 175°C. isothermal

Injection volume: 0.5 µl

Sensitivity: 16 to 64 x 10^{-10} amperes

Evaluation: manual, height times total retention time.

Conclusions

Van Wijngaarden's method for transesterification with the boron trifluoride-methanol complex as reagent is very

simple and fast. It yields correct results. The occasionally observed disturbances which showed up as a strong reduction in the detector's sensitivity did not appear during a later series of experiments. Whether the disturbances which resulted from the formation of a gray deposit on the electrode and which led to a loss of sensitivity are due to the geometry of the detector or to the hydrogen-air ratio in the detector could not be clarified. It would be interesting to find out whether similar disturbances in the flame ionization detector were observed in other laboratories after transesterification with boron trifluoride.

Summary

The method described by van Wijngaarden for the preparation of methyl esters with BF_3 reagent in the gas chromatographic analysis of fats and oils has been tested.

The fatty acid distributions were computed from the gas chromatograms obtained; they are in agreement with the results obtained by different, proved transesterification methods. p.114

Initial trouble with the FID resulting in loss of detector sensitivity was resolved by the choice of an optimum H_2/air ratio.

After more than 30 injections, no loss of sensitivity of the detector could be observed.

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