DANIELE NAVIGLIO
RAFFAELE ROMANO

Dipartimento di Scienza degli Alimenti
Università degli Studi di Napoli "Federico II"
Via Università 100 - 80055 Portici (NA) - Italy

GERARDINA ATTANASIO

DICA - Dipartimento di Ingegneria Chimica e Alimentare - Università degli Studi di Salerno - Via Ponte Don Melillo 8 - 84084 Fisciano (SA) - Italy

Rapid determination of ethanol content in spirits and in beer by high resolution gas chromatography

SUMMARY

The study of the determination of ethanol content in spirits and beer by a HRGC method is carried out. The suggested method requires a short time of analysis and it is an alternative to the official method of analysis both Italian and international, that provide the determination of alcohol content by distillation of the sample under examination. The procedure proposed provides for the direct injection of the alcoholic solution into the gas chromatographic system, after the correct dilution. A calibration curve has been prepared by employing aqueous solutions of ethanol. A straight line has been obtained in the range from 0 to 800 mg/L ethanol content.

INTRODUCTION

This study shows an application of HRGC (high resolution gas chromatography) to evaluate the analytical determination of ethanol in spirits and in beer. The method suggested requires a short time of instrumental analysis (2 minutes) for the determination. This procedure is proposed as an alternative to the Italian and international official methods of analysis (1,2), both providing for the determination of ethanol content in spirits after collection by distillation from the sample under examination. One of the official A.O.A.C. methods for the determination of alcohol content in wine provides for direct sample injection into the gas chromatographic system after the addition of suitable internal standard (3). This method is not applicable to the samples with high ethanol content. This paper is an improvement on a work, reported in literature (4), in which the grounds of the introduction of the gas chromatographic analysis for the ethanol content in spirits, as an alternative to the method based on the distillation of the sample, are well explained.
We suggest to utilize a widebore column, with 100% methyl silicone as a stationary phase, in place of a packed column and to eliminate the internal standard, n-propanol, because manual injection results are satisfyingly reproducible, so that two injections of the sample give an average value sufficiently accurate.

MATERIALS AND METHODS

Standards

Ethyl alcohol min. 99,9% (v/v) analytical grade (Fluka, Buchs, Switzerland); ultrapure water produced by Milli-Q Plus system (Millipore Corporation, Bedford, MA, USA).

Apparatus and gas chromatographic conditions

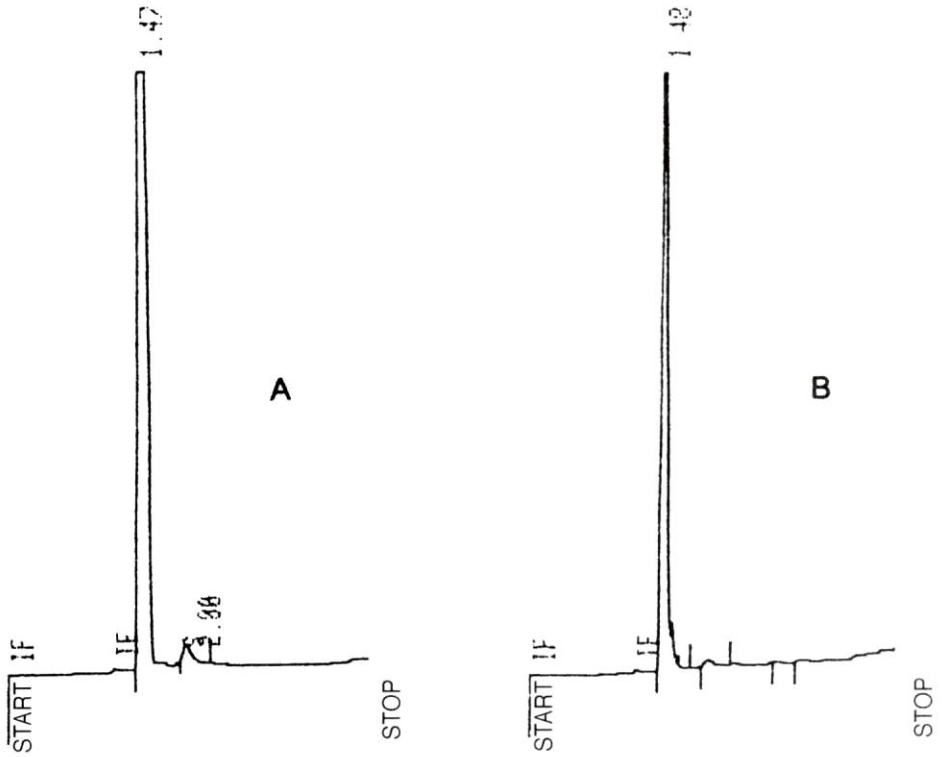
GC analysis was carried out using a DANI mod. 86.10 HT instrument, equipped with a 30 m x 0,545 mm i.d. polymide capillary column coated with a 5 µ thick DB-1 film (Megabore, J & W Scientific, Falsam, CA, USA).
Sample was introduced by a P.T.V. injector. P.T.V. temperature ranged from 125°C to 180°C for 1 min. with gradient of 400°C/min.
F.I.D. temperature was 200°C and column temperature ranged from 100°C to 130 with gradient of 20°C/min. Carrier gas (helium) flow rate was 5.0 mL/min; Split 1:100; Split valve was closed in starting step and opened one minute later.
GC traces and quantitative data were obtained using an HP 3390A (Palo Alto, CA, USA) electronic integrator.

Injection technique and quantitative determination

The alcoholic aqueous solution was injected into the gaschromatograph by "total technique": the split valve was held closed during the temperature program. The quantitative determination of ethanol was performed by using a calibration curve obtained by injecting two times the same standard and reporting the average value.

Calibration curve preparation

Weigh about 1 g of pure ethanol in a 100 mL volumetric flask and add water up to the mark. Transfer 1, 2, 3 and 4 mL of this solution in four 50 mL volumetric flasks and add water up to the marks. In this way you obtain solutions with concentrations of about 200, 400, 600 and 800 mg/L.
Inject 1 µL of each standard solution accurately into GC. Evaluate the calibration graph of ethanol area versus ethanol content.



Gas chromatogram of spirit (dil. 1:1000) (A) - Gas chromatogram of beer (dil. 1:100) (B).

Spirits analysis

Transfer 1 mL of analysing spirit in a 100 mL volumetric flask and add water up to the mark. Then, transfer 10 mL of this solution in a 100 mL volumetric flask and add water up to the mark. Inject 1 µL of this solution accurately into GC. Evaluate ethanol concentration by calibration curve.

Calculation:
Ethanol (% vol.)= $C_e/(10*D_e)$
where:
C_e = ethanol concentration (mg/L)
D_e = ethanol density (g/mL).

Beer analysis

De-gas 10 mL of beer in examination by vigorous shaking for 1 minute in a test tube. Transfer 1 mL of analysing beer in a 100 mL volumetric flask and add water up to the mark. Inject 1 µL of this solution accurately in to the GC. Evaluate ethanol concentration by calibration curve.

Calculation:
Ethanol (% vol.) = $C_e/(100*D_e)$

where:
C_e = ethanol concentration (mg/L)
D_e = ethanol density (g/mL).

RESULTS AND DISCUSSION

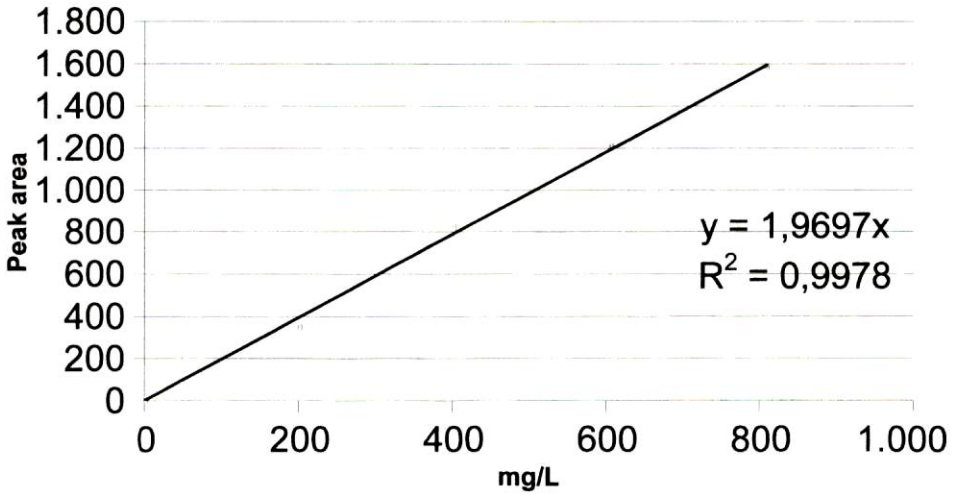
Figure 1 shows the chromatograms: (A) spirit; (B) beer. Total injection makes useless the addition of internal standard and so the gas chromatographic analysis becomes like HPLC analysis in terms of reproducibility. The precision of the injection has been contained under 2% (maximum deviation from the average value on five injections).

Figure 2 shows the calibration curve obtained. Each standard has been injected into GC two times and the average of the areas was reported graphically. Experimental points were interpolated by a straight line, resulting from linear regression, with a correlation coefficient of 0.998.
Two samples of spirits and one of beer, all commercial products, have been examined in order to verify the accuracy of the HRGC method in comparison with the official method (1).

Table 1 shows the results obtained by the official method, by means of three determinations and by gas chromatographic procedure by means of ten determinations, on commercial samples.
Results obtained by the HRGC method on commercial samples have been lower than those obtained by the official meth-

Table 1 - Comparison between the results obtained by the official method and by HRGC method.

Sample	Label claim	Official method	HRGC method
Spirit 1	42	42,50±0,03	41,7±0,4
Spirit 2	40	40,40±0,03	39,7±0,4
Beer	4,7	4,80±0,08	4,67±0,07



Calibration curve for ethanol.

od. Differences in results lie in the fact that, during preliminary distillation of sample provided by the official method an enrichment of collected alcoholic solution with other volatile components (e.g. methanol, esters, etc.) (4) is inevit-able.
On the contrary, the HRGC method determines only the ethanol content and then all interferences are eliminated.
The lifetime of column was not shortened for the injection of more than one hundred samples of spirits and beers, since the samples are diluted about a thousand and a hundred times respectively.

CONCLUSIONS

The method suggested, for the determination of ethanol content in spirits and beer, reduces to a minimum the preparing operations of sample and eliminates the internal standard keeping, at the same time, high precision and accuracy.
Our procedure also offers more advantages if it is compared with official methods: it is more rapid and simple; it eliminates the possible interferences of other volatile components; it allows the use of a smaller volume of sample for the determination; it allows analysis of samples of spirits with a high ethanol content.

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