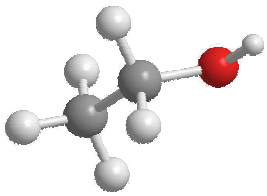
ANH28 - Evaluation of Purity & Contaminants

Application to food grade ethanol

Introduction

In industries where non-denatured alcohol is used for food products manufacturing (flavors and extracts, vinegar, food dyes, candy glazes, yeast, various sprays, animal-feed supplements, etc), quality is critical.
Food grade alcohol is assessed by organoleptic and analytical chemical methods to check it is neutral and free of foreign odors and tastes.
This application note proposes to evaluate food grade ethanol with a Fast Gas Chromatography Electronic Nose to verify its purity and sensory conformity.



Equipment

HERACLES Flash GC Electronic Nose

HERACLES Electronic Nose (Alpha MOS, France – Fig. 1) is based on ultra fast chromatography. It features 2 metal columns of different polarities (non polar RXT-5 and slightly polar RXT-1701, length = 10m, diameter = 180µm, *Restek*) in parallel and coupled to 2 Flame Ionization Detectors (FID). Two chromatograms are obtained simultaneously, allowing a sharper identification of the chemical compounds. It allows headspace or liquid injection modes.
The integrated solid adsorbent trap thermo-regulated by Peltier cooler (0-260°C) achieves an efficient pre-concentration of light volatiles and shows a great sensitivity (in the pg range).
With fast column heating rates (up to 600°C/min), results are delivered within seconds and the analysis cycle time is around 5 to 9 minutes.

Fig. 1: Ultra Fast GC based HERACLES Electronic Nose

The electronic nose is coupled to an autosampler (HS 100, CTC Analytics) to automate sampling and injection.
The instrument is operated through Alpha Soft software. In addition to classical chromatography functionalities, it provides chemometrics data processing tools such as sample fingerprint analysis and comparison, qualitative and quantitative models, quality control charts.

AroChembase: Kovats Index library for chemical & sensory characterization

HERACLES e-nose was additionally equipped with AroChembase module (Alpha MOS, France) that can be used within AlphaSoft E-Nose software. It consists of a library of chemical compounds with name, formula, CAS number, molecular weight, Kovats retention Index, sensory attributes and related bibliography. It allows pre-screening the chemical compounds and giving sensory features by directly clicking on the chromatograms' peaks.

Samples & Analytical Conditions

Four samples of pure ethanol used for spirits production (table 1) were analyzed with HERACLES Electronic Nose (table 2) in headspace injection mode. Sample R corresponds to reference quality (odorless ethanol), whereas among the 3 blind samples (U1, U2, U3), one in particular (U1) is recognized as having significant off-odors.
The analytical method was calibrated using an alkane mixture (n-pentane to n-hexadecane) in order to convert retention times in Kovats indices for further characterization of the molecules with AroChemBase module.

Table 1: pure ethanol samples

Sample Label	Ethanol content (% volume)
R (reference)	96.30
U1	96.11
U2	96.36
U3	96.01

Table 2: HERACLES e-nose analytical parameters

Parameters	Values
Sample volume	1 mL + 1mL of water
Vial volume	20 mL
Injected volume	2.5 mL
Incubation temperature	40°C
Incubation time	20 min
Columns temperature program	40°C (2s) to 280°C (8s) by 3°C/s
Acquisition duration	90 s

Chromatograms

The comparison of chromatograms shows slight differences of volatile profiles between odor-free samples and ethanol with off-odors (Figure 2). In the particularly odourous U1 sample (red chromatogram on Figure 2), the presence of several compounds is noticed, whereas the reference quality ethanol does not contain these compounds.

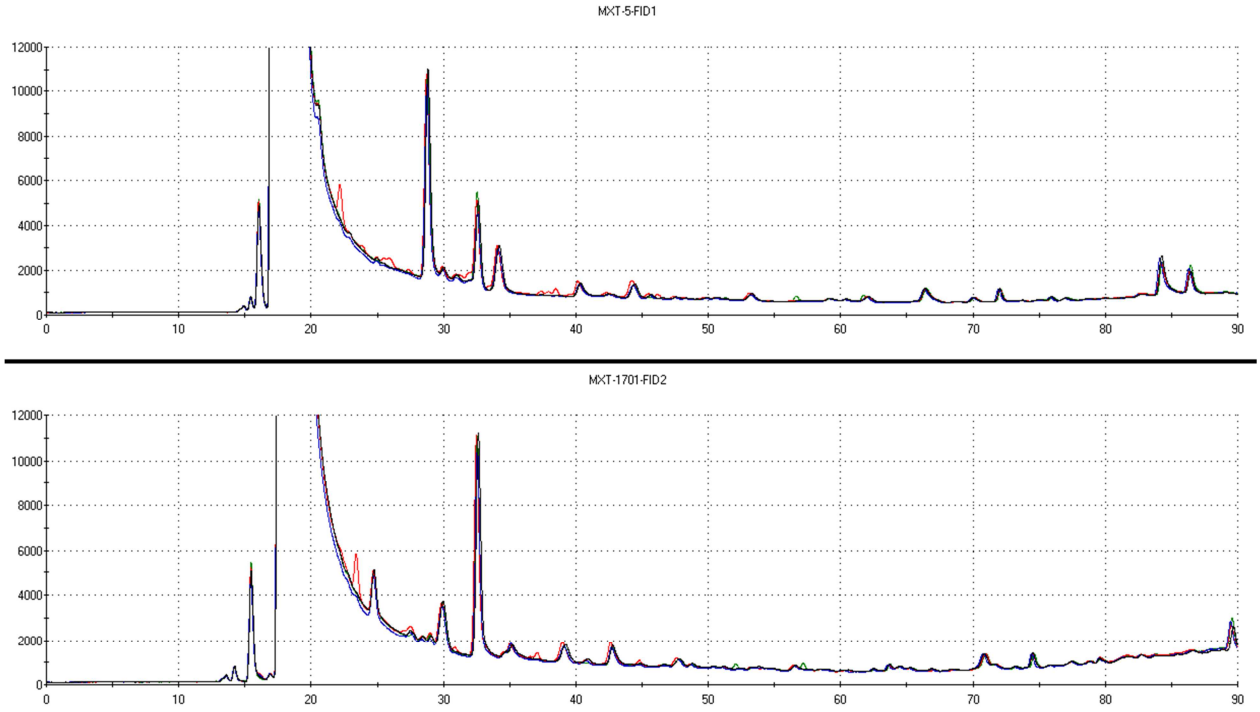


Fig. 2: Superimposed chromatograms of ethanol samples on MXT-5 and MXT-1701 columns of HERACLES

Odor map

An odor map based on Principal Components Analysis (Figure 3) applied to HERACLES measurements, was generated by taking into account the most discriminant volatile compounds. The four ethanol samples are clearly differentiated based on their volatile profile. However, samples U2 and U3 are very close, therefore very similar in terms of odor profile.

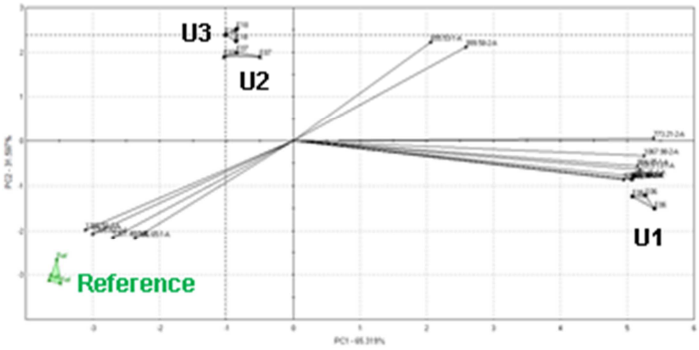


Fig. 3: Odour map (PCA) of ethanol samples obtained from the most discriminant volatile compounds

Characterization of volatile compounds

The nature of the most discriminant volatile compounds involved in the odor differences was investigated using Kovats indices and the AroChemBase database (Table 3).

Table 3. Main volatile compounds identified in the headspace of ethanol samples using AroChemBase

RT MXT-5 (s)	RT MXT-1701 (s)	K MXT-5	K MXT-1701	Possible matching compound	Corresponding odor attribute	Presence in sample
22.1	23.4	603	701	Butan-2-ol	Ethereal	U1
25	27.5	656	775	Butan-1-ol	Cheese, fermented	U1
27.3	29	701	800	Pentan-2-ol	Fruity, green, plastic	U1
38.5	32.1	883	936	Isoamylacetate	Banana, fresh	U1
45.5	40.7	999	997	n-decane 1,3-dichlorobenzene	Alkane	U1
46.2	44.8	1011	1069	2-ethyl 6-methyl pyrazine		U1
42.3	40.7	946	997	Propylbenzene		U1
56.5	52.7	1201	1202	n-dodecane		R
61.7	57.2	1301	1301	n-tridecane		R

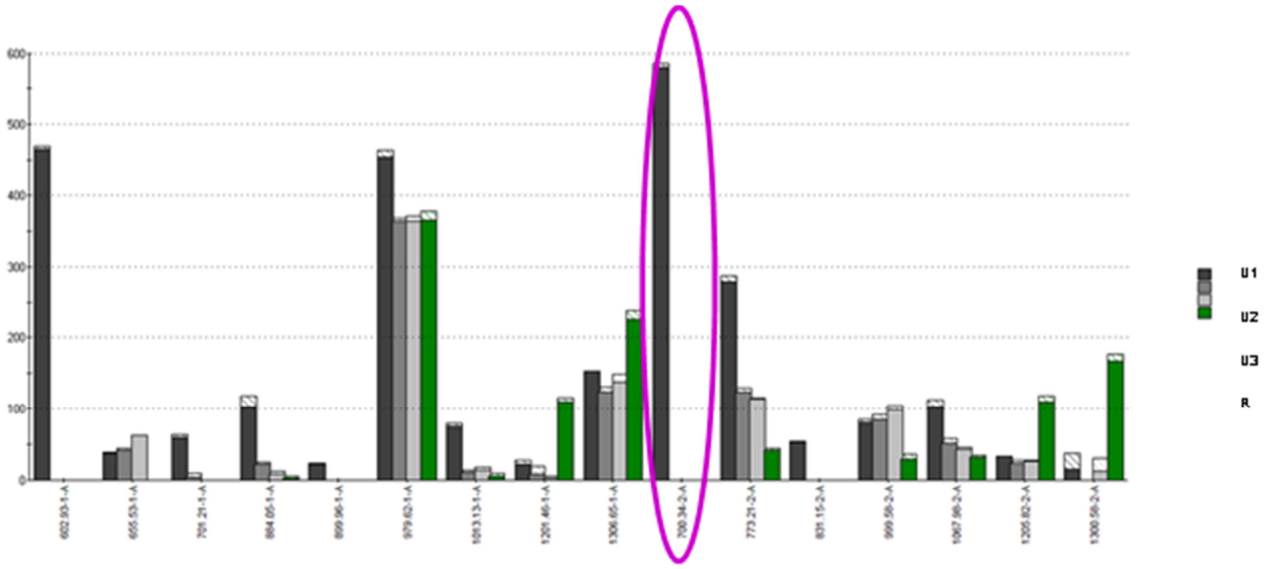


Figure 4. Concentration (peak area) of the main volatile compounds in ethanol

The proportion of the main volatile compounds in the different samples is compared on Figure 4. One compound in particular is found with an important proportion in U1 sample (circled in purple on Figure 4). It is identified as butan-2-ol (Kovats Index of 603 on MXT-5 column and 701 on MXT-1701 column).

Quality Control

A quality control model based on Statistical Quality Control processing was established with sample R as the reference quality (Figure 5). On this quality control model, the three batches U1, U2 and U3 are projected out of the conformity area (green band), indicating that they do not comply with the desired quality of ethanol, especially sample U1 which is the furthest from the conformity zone.

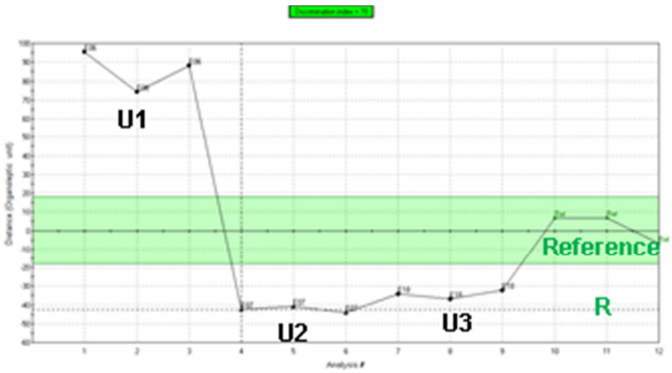


Fig. 5: Quality Control Card of pure ethanol used for spirits manufacturing

Conclusion

In this study, HERACLES electronic nose was used to rapidly determine the purity and sensory quality of food grade ethanol.

The instrument can detect low amounts of contaminants or traces of denaturants that may be responsible of unwanted off-odors.

Thanks to its high sensitivity of detection, the analyzer can also differentiate samples that can seem acceptable upon human testing whereas they may show a different volatile profile.