



Preface

When speaking about packaging evaluation, great emphasis is placed on so called FCMOs (Food-Contact Materials and Objects), with particular reference to characterization of hydrocarbons that may appear in food-packaging and, consequently in contained foods. Because of their potential toxicity, mineral oils content must be carefully monitored, especially in case of FCMOs based to varying degrees on recycled materials. Either the total amount of Mineral Oil (MO), and its characterization are important; this means being able to speciate aliphatic (MOSH) and aromatic (MOAH) fractions.

Although nowadays there is no ad hoc regulation, several authorities are putting efforts in order to harmonize analytical method to get homogeneous analytical data.

Among most relevant works, it is certainly to consider the one carried on at the Zurich Kantonal Labor (CH), that represents up to today the main road, either for a strictly analytical approach and for the attention given to the method automation I.

Starting from such work, SRA Instruments developed a comprehensive on-line system that meets the demand of reliability and automation.

Mineral Oil analysis in food & food packaging.

LC-GC on-line quantitation of aliphatic and aromatic fractions (MOSH/MOAH)

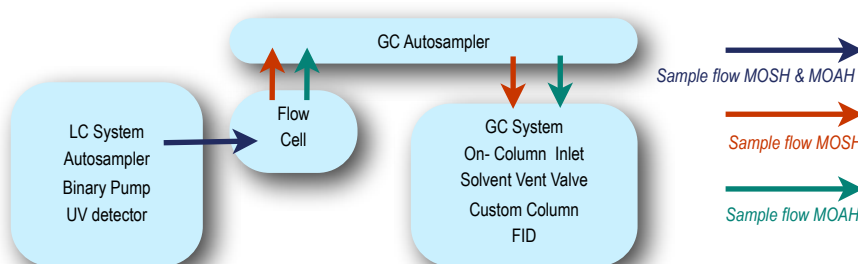
In order to meet labs needs, in terms of productivity, automation, and reliable results, SRA Instruments has developed an on-line analyzer which is able to manage within a unique sequence both separation and injection of hydrocarbon phases.



The analyzer consists of:

- LC preparation system equipped with binary pump, UV Detector and autosampler (Agilent Technologies)
- Flow Cell for LC elute (Gerstel)
- Multi purpose sampler (MPSxt) for withdrawal/storing/injecting/managing fractions coming from LC/Flow Cell (Gerstel)
- GC-FID equipped with LV-COC inlet (Agilent Technologies)

The sample is injected into LC, where MOSH/MOAH separation takes place. The LC effluent flows into the Flow Cell, where the MPS draws the fractions. Sampling can be extended to the whole amount (isokinetic), or can be restricted to its representative portion (split-dilution).



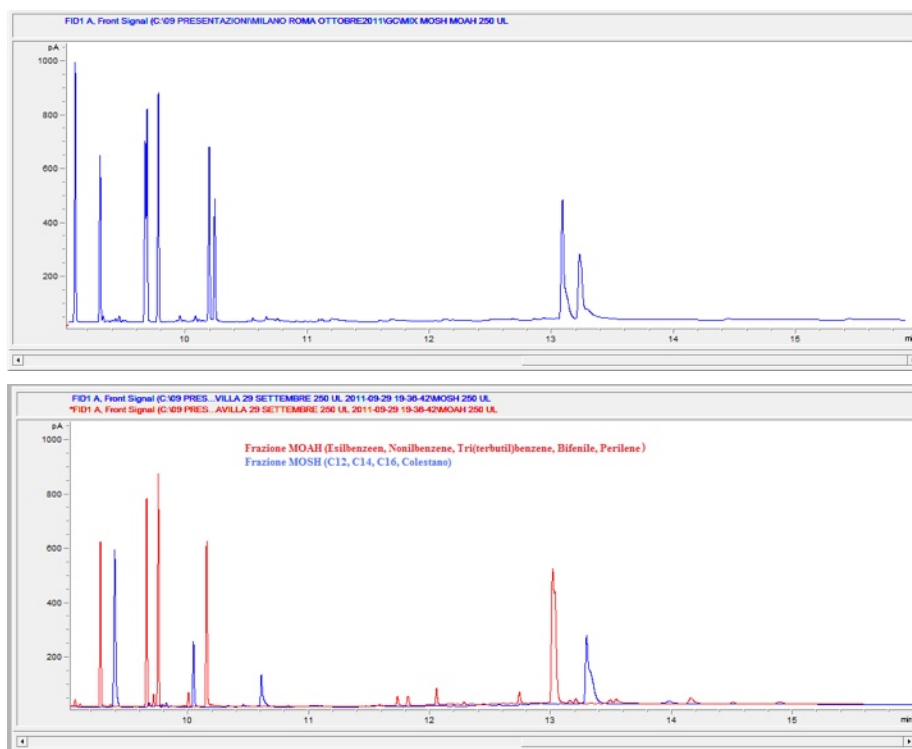
Experimentals

In order to evaluate system efficiency, according to the reference work (Grob et al.), a mix of aliphatic and aromatic hydrocarbons has been considered:

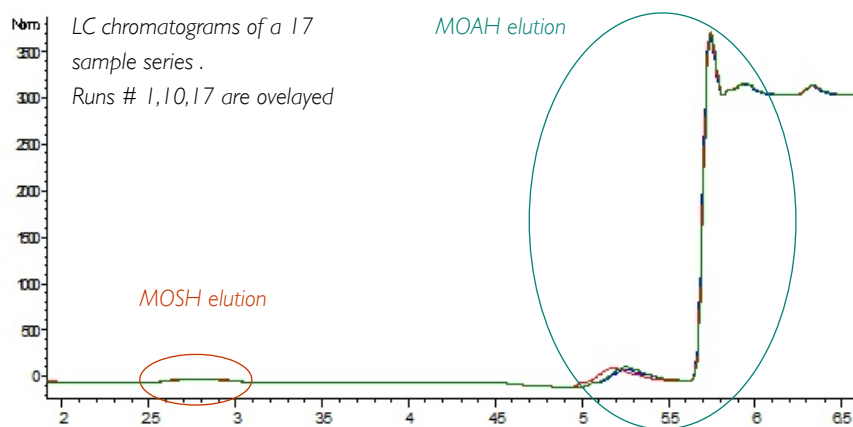
MOSH: dodecane, tetradecane, hexadecane, colestane

MOAH: 1,3,5 tri-terbutylbenzen, hexylbenzen, phenylnonane, biphenyl, perilene

An hexane solution containing all nine analytes was injected into LC; the separated fractions were then automatically injected into GC-FID. Obtained results are shown alongside. It is clear how separation is definitely satisfactory.



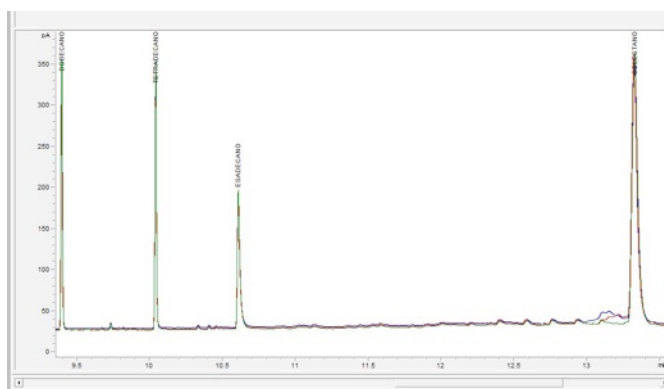
LC chromatograms of a 17 sample series .
Runs # 1,10,17 are overlayed



Even LC robustness is verified, as can be seen in the picture nearby.

Then, the robustness of the whole system has been investigated. Indeed, LC repeatability is a mandatory but not sufficient condition in order to ensure the reliability of the entire process. The same behavior must be observed with regards to GC separation.

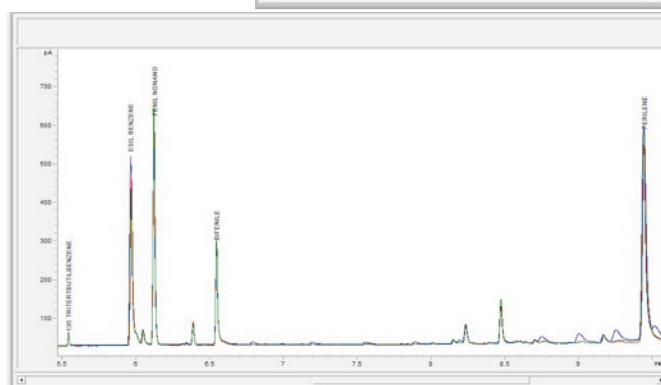
Even this aspect is satisfied, as shown by the two pictures alongside.



MOSH
(LC)GC chromatograms
of a 20 samples series
Runs # 1,11,20 are
overlayed

Excellent repeatability of the process is then guaranteed, with respect to all aspects, that is:

- LC separation
- Flow cell sampling
- 100 µl GC injection in LV-COC mode (see below)
- GC-FID acquisition



MOAH
(LC)GC chromatograms
of a 20 samples series
Runs # 1,11,20 are
overlayed

Sensitivity

The current approach is to consider acceptable LOQs of hundreds ppb level. Such limit is hardly reachable by injection of standard extract volumes (few μl), even if a concentration step of final extract itself is carried on.

A different approach has been therefore adopted: the system has been configured to allow to inject up to 250 μl (in Solvent Vent mode), keeping however low discrimination by mean of COC inlet.

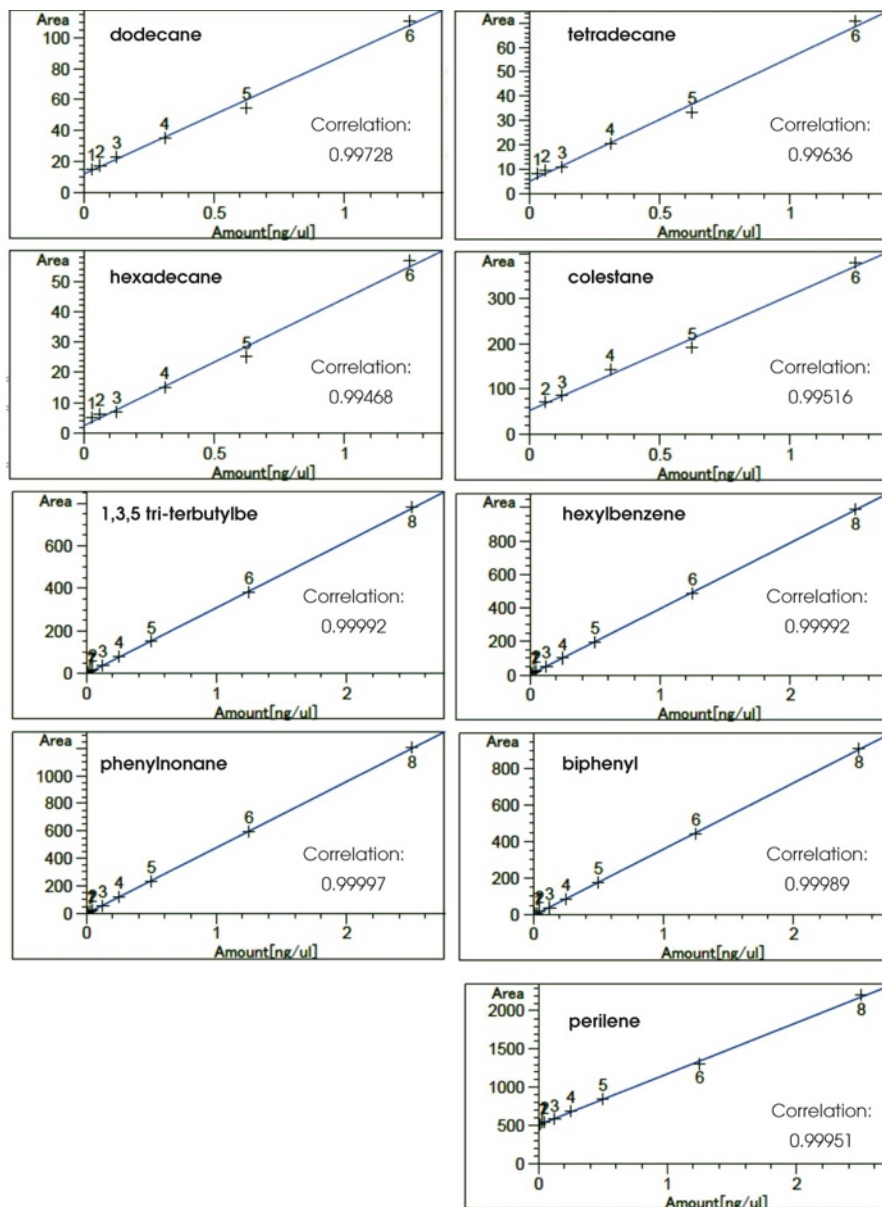
In such condition is possible to reach the required sensitivity for each single analyte, as shown by calibration curves reported alongside.



Calibration curves

The following curves were obtained by spiking 10 g sample (durum wheat pasta), at several ppb level (MOSH: 50 to 1250 $\mu\text{g/kg}$; MOAH: 50 to 2500 $\mu\text{g/kg}$).

Samples were then extracted with n-hexane (10 ml): ultrasonic bath for 24 hours. An aliquot, without any further manipulation, was injected into the LC-GC system.



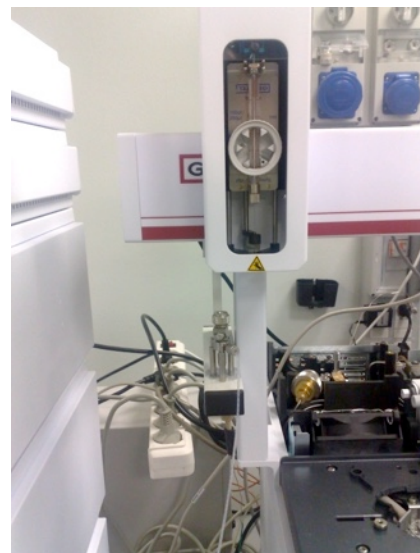
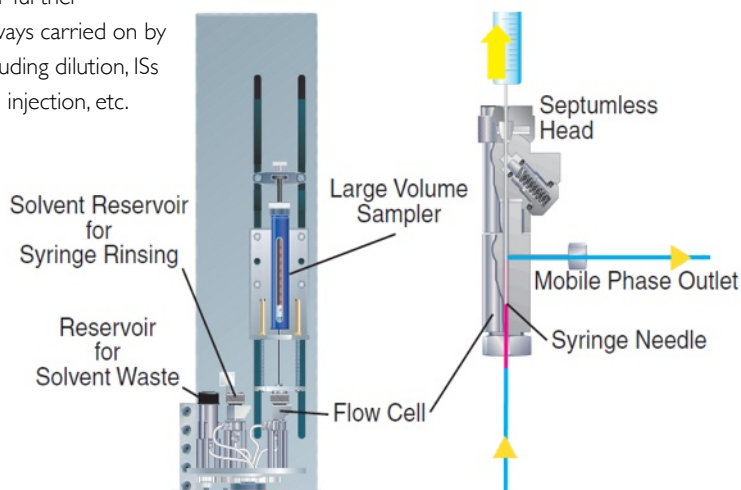
¹Bibliography

¹Cfr.: "Aromatic Hydrocarbons of Mineral Oil Origin in Foods: Method for Determining the Total Concentration and First Results", Maurus Bledermann, Katell Fiselier and Koni Grob, JAF 2009, 57, 8711-8721

LC-GC is based on two dedicated features: Flow Cell (Gerstel), and Coupling System (SRA Instruments)

Flow Cell (FC)

The LC eluate flows seamless into the FC; the autosampler collects each fraction and injects into GC. Alternatively, fractions can be stored in vials for further manipulation, always carried on by autosampler, including dilution, ISs addition, delayed injection, etc.



SRA LC-GC Coupling System

Completely developed by SRA Instruments, such device consists of an interfacing module and a dedicated software

Any I/O signal coming from LC, GC and autosampler is managed by such device, which converts every signal in operative instructions.

By means of an evolved triggering UV signal algorithm, the dedicate software allows to detect time by time the MOSH/MOAH exit, avoiding wrong sampling due to matrix interference.

Conclusion

A complete on-line MOSH/MOAH analyzer has been developed and tested by SRA Instrumentas, but not only.

Both FC and coupling system are extremely versatile; on the other hand, the whole system is based on a modular configuration.

This allows to plan different uses of the analyzer, even involving only GC and/or LC and/or FC/MPS.

