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INSTRUMENTATION FOR ON LINE DETERMINATION OF VFA

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1 INTRODUCTION

Compartment II of the MELISSA Pilot Plant is dedicated to the consumption of the volatile fatty acids generated in the first compartment. For a reliable implementation of compartment II and the optimisation of the whole loop operation by the control software, it is necessary to have information on the type and concentration of volatile fatty acids (VFA) produced in the first compartment and its level of consumption by compartment II.

In order to implement on-line analysis of VFA concentration in such a process, different techniques have been considered in this technical note. This trade-off study has as a main goal the selection of the analysis instrumentation for monitoring the concentration of VFA taking into account the requirements of this particular application: frequency analysis required by the control and type of VFA present in the in/outflow of the compartment II. This analyser will be implemented in the Melissa pilot loop.

Compartment I (Liquefying compartment) pilot reactor is still under development in Ghent, Belgium. This compartment will also have on-line measurement of VFA concentration. For this reason this trade-off will be harmonised between both MELISSA partners (EPAS&UAB).

The different techniques taking into account in the trade-off are: IR (NIR; FTIR) and GC, which we have found the most interesting for our application. A tremendous number of possibilities is available in the market nowadays to cover such necessities.

2 GENERAL APPROACH TO IR &GC TECHNIQUES

2.1 Gas Chromatography

In a gas chromatograph the liquid or gas sample is injected by means of a micro syringe through a rubber septum and into a flash vaporiser port at the head of a chromatographic column that contains a liquid stationary phase adsorbed onto the surface of an inert solid. The

sample is transported through the column by a flow of inert carrier gas. The separation is due to the different retention rate of the compounds when they pass through the column. The effluent of the column goes to the detector, which emits a signal that is translated into a serial of peaks (chromatogram).

Position (retention time) of these peaks is used in qualitative determination and size (area or height) is related with concentration.

This Chromatographic technique gives the most powerful resolution of organic volatile compounds but has an important limitation: the thermal stability of these compounds.

2.2 Infrared Spectroscopy

Infrared Spectroscopy is a technique used to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities.

In an Infrared Spectrometer (described in figure 1) a source generates light across the spectrum of interest, a monochromater separates the source radiation into its different wavelengths. A slit selects the collection of wavelengths that shine through the sample at any given time. The sample absorbs light according to its chemical properties. A detector collects the radiation that passes through the sample and puts out an electrical signal, which is normally sent directly to an analogical recorder. A link between the monochromater and the recorder allows you to record energy (usually % Transmittance) as a function of frequency or wavelength. Depending on the IR radiation, we found three IR zones: NIR (Near IR) 12800-4000 cm, MIR (Medium IR) 4000-200 cm, FIR (Far IR) 200-10 cm.

There are several important limitations: First the monochromater/slit limits the amount of signal one can get at a particular resolution. To improve resolution you must narrow the slit and decrease sensitivity. Second there is no easy way to run multiple scans to build up signal

to noise ratios. Finally, the instrument must be repetitively calibrated, because the analogical connection between the monochromater position and the recording device is subject to misalignment and wear.

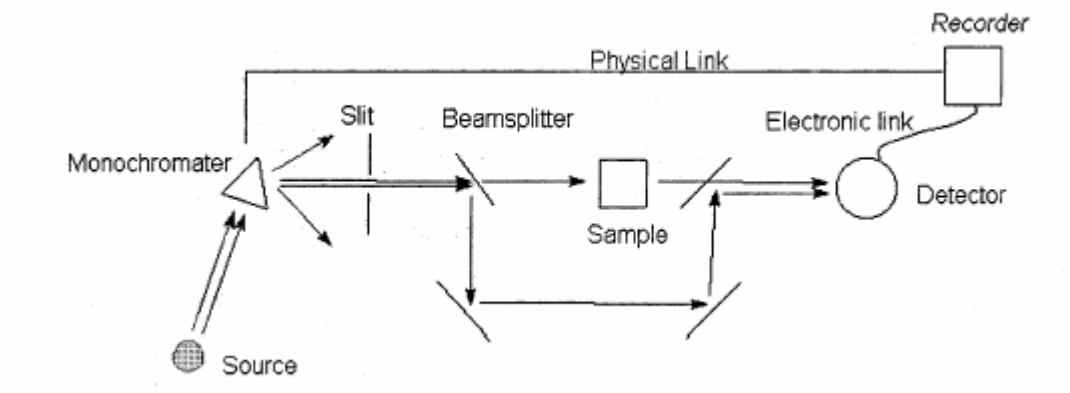

Figure 1 : Continuous wave spectrometer.

2.3 Fourier Transform Infrared Spectroscopy

In this IR technique we still have a source, a sample and a detector but now all the source energy is sent through an interferometer and onto a sample thus in every scan all source radiation gets to the sample (a schematic representation is presented in figure 2) . The sample absorbs all the different wavelengths characteristics of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector reports variation in energy versus time for all wavelengths simultaneously. A mathematical function called a Fourier Transform allows to convert intensity versus time spectrum to intensity versus frequency spectrum.

The advantages of FTIR are: First, all of the source energy gets to the sample, improving the inherent signal to noise ratio. Second, digitalisation and computer interface allows multiple scans to be collected, also improving the signal to noise ratio. Finally, the resolution is better and most of the computer programs allow subtract a reference spectrum, correct baseline, etc.

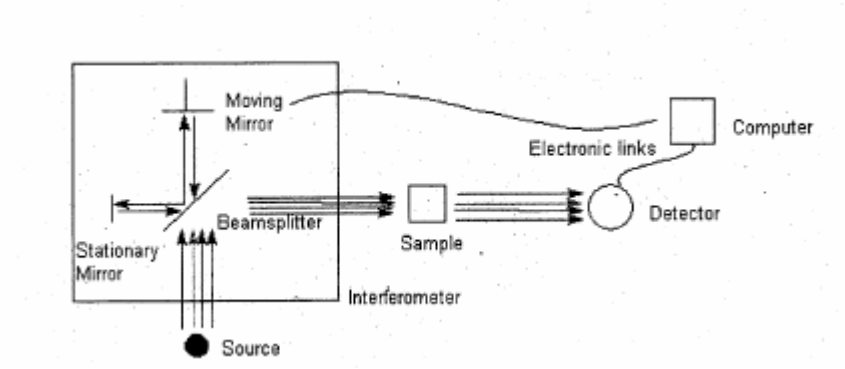

Figure 2 : Fourier Transform Infrared Spectrometer.

3 DETAILED COMPARISON BETWEEN IR & GC TECHNIQUES

3.1 IR (FTIR, NIR) main features

Advantages:

• Sampling of product for analysis is simple since flow is through an open cell.

• The spectroscopy is good at discriminating functional groups although not for quantitatively speciation.

• Scanning a wavelength range is very quick (response time 10-60s).

• With NIR Spectroscopy samples did not require dilution, because of the weak absorption peaks.

• It is capable of multicomponent analysis, but with an inherent cost of additional batch time for data updating.

• There are versions for sequential analysis to treat different streams of sample.

• Some IR analysers have cuvettes, which can be heated up to max 180ºC. This simplifies the gas preparation for many applications: measurements in which the condensing of the components would normally lead to a measurement component loss (like NH_3 and HCl in wet exhaust) are possible.

Disadvantages:

• If direct FTIR component analysis is used it generally relies on libraries to identify sets of peaks. These libraries must contain appropriate spectra for the blend being analysed.

• Calibration samples are still required to quantify the species being measured. Each instrument may have been calibrated using different sets of samples.

• With NIR Spectroscopy water absorption over the whole band generally did not detract from qualitative identification of foreign components.

• The IR analysers are designed for continuous measurement of up to 4 IR components, with high selectivity and measuring sensitivity.

• Very good filtration is required upstream in the sample conditioning.

3.2 GC main features

Advantages:

• Multistreaming and calibration using miniature selection ganged valves and parallel analysis streams built in the GC itself for a predefined design application is possible.

• Large number of functional groups able to be identified using latest detectors technology.

• GCs are very good at quantitative and qualitative analysis of different compounds.

• They are designed for continuous measurement of lots of components.

• They have a very high dynamic range in which they can measure down to low ppm and up to 100% on the same analyser, depending on the detector.

• Using different injection methods, it is possible to analyse solid, liquid and gas samples.

Disadvantages:

• Physical separation of components requires specialised columns, sample valves accompanied by accurate timing sequences to actuate solenoid valves driving the sample valves to back flush, forward flush, inject… Each of these pieces of equipment is complex in its own right and needs specialists for any diagnostics. Also reparations such as sample valve overhauls are not trivial.(1)[1]

• The analyser is a batch analyser with an update time between 1 and 30 minutes depending on the application and it is also necessary take account of the sample transport time from the tapping point to the analysers. Most process applications and standard compliance applications can tolerate these lags but some can not afford this large analysis time. Every application needs to be checked, as do all extractive analyses.

• The response factors of the detectors are not the same for different compounds. That is to say, the detectors are not inherently absolute and require calibration against each component being measured.

• The output supplied for each individual component therefore needs separated treatment to ensure that it has been normalised correctly against a certified or trusted calibration standard.

• Very good filtration is required upstream in the sample conditioning.

• In order to minimize GC analyser injection mistakes it is necessary an internal standard, which sometimes is difficult to find.

4 TECHNOLOGY SELECTION CONCLUSIONS

Taking into account the requirements of the present trade-off (VFA composition and frequency of analysis), it can be concluded that:

Both techniques have the possibility of automatic sample devices, which will enable to obtain on-line samples of compartment II and of the interface between compartment I an II. These systems allow to automatically switch the measurement from one point to the other. The measurement devices in both techniques are able to supply the measured values to the control system, both analogically (4-20 mA) and digitally (RS 232, RS 485, Ethernet).

The problem arises with the necessity of a measurement system applicable to measure the liquid and gas phases, because VFA are volatile compounds and it is convenient to have a measurement both in the liquid and in the gas phase. In the case of IR gas analysers the possibility of heating the sample to 180 ºC for simplifying the gas preparation could be not enough for the application, because some VFA need higher temperature, and these spectrometers only quantify the components in the gas phase. To obtain information about the components in the liquid phase, it will be necessary an IR liquid analyser, which is not capable to analyse the components of the gas phase. It implies to use two equipments. GC analysers do not have this limitation, they can quantify the VFA in both the liquid and the gas phase that is in equilibrium with the liquid phase.

[1]Mark Thomson, Carl Robins, The future of gas Chromatographs as On lineProcess Analysers, www.measurementation.com.au/papers/icex98/Icex98.htm

Nevertheless, it should also stated that a rough estimation of the gas composition can be done using equilibrium data.

Finally, it will be considered the measurement, besides the VFA, of other compounds at the same time such as H2 or CH4. This specification is difficult to manage with an IR analyser, which is designed for continuous measurement of up to 4 IR components but not for a GC analyser that is designed for continuous measurement of several components with high selectivity, measuring sensitivity and accuracy.

5 SCREENING OF THE DIFFERENT EQUIPMENTS FOR GC

Once the analytical principle is decided, a set of different possibilities have been considered (Table 1).

Most of the equipments have the possibility to incorporate different number and type of detectors. Some of these are: Flame Ionisation Detector (FID), Thermal Conductivity Detector (TCD), Electron Capture Detector (ECD), Nitrogen Phosphor Detector (NPD), Flame Photometric Detector (FPD), Mass Spectrometry Detector (MSD), Photoionization Detector (PID), High Electrolytic Conductivity Detector (HECD). The type and number of detectors will be extremely important in the election of the equipment.

Table 1-Characteristics of five different equipments

	Agilent	ABB	Siemens	Konik	Shimadzu
Data Evaluation Software	Chemstation Software	Vistanet	Windows, EZChrom	Konikkrom 32	GC solution
Maintenance Requirements	Every 6 months recommended	8 years	Unknown	Unknown	Once a year
Measuring Range	Detector dependent	Detector dependent	Detector dependent	Detector dependent	Detector dependent
Detection Limits	Detector and sample dependent	Detector and sample dependent	Detector and sample dependent	Detector and sample dependent	Detector and sample dependent
Precision	RSD¡Ü 2%	RSD¡Ü 1%	RSD¡Ü 1%	Unknown	RSD¡Ü 2 -5%
Multiple sampling points	Yes	Yes	Yes	Yes	Yes
Measuring frequency	2-12inj/hour Application dependent	5-8inj/hour Application dependent	Application dependent	Every 10-15 min	2-12inj/hour Application dependent
Autocalibration	Yes	Yes	Yes	Yes	Yes
Detectors	FID,TCD,ECD, NPD, FPD,MSD	FID,TCD,FPD	FID,TCD,FPD, ECD, HECD,PID	FID,TCD,ECD, NPD,FPD,HECD, PID,MSD	FID,TCD,ECD, NPR, FPD
Detectors number	Up to two simultaneous	Up to two simultaneous	Up to two simultaneous	Up to two simultaneous	Up to two simultaneous
Dilution Cell and tape filtration	Yes	Yes	Yes	Yes	Yes
Oven Operating Temperature	4 - 450 ºC	30 – 180 ºC	-50 – 450 ºC	-90 – 490 ºC	90 – 450 ºC
Injectors number	Up to two simultaneous	Up to five simultaneous	Up to two simultaneous	Up to two simultaneous	Up to four simultaneous

Volatiles Inlet	Yes	Yes	Yes	Yes	Yes
Oven rate	Up to 120 ºC/min	Up to 120 ºC/min	Up to 25 ºC/min	0,1 – 40 ºC/min	Up to 100 ºC/min
Solvent vapor exit	Yes	Yes	Yes	Unknown	Yes
Programmable T vaporizer	Yes	Yes	Yes	Yes	Yes
Dimensions (cm)	80*60*200	496*34*117,5	Unknown	40*64*55	51,5*43,7*52,0
Cost (euros)	40000 extras dependent	42 - 48000 extras dependent	40000 extras dependent	30 - 50000 extras dependent	40000
Delivery time	20 days	Unknown	5 months	8 – 10 weeks	Unknown
Reference Services (Spain)	Agilent (Barcelona)	ABB (Madrid)	Siemens (Madrid)	Konik (Barcelona)	Izasa (Barcelona)
Number of programming steps	6	Unknown	Unknown	5 (Up to 15 on demand)	5 (Cooling step is avalaible)
Columns	Capillary	Packed, Capillary	Capillary	Capillary, Packed, Semicapillary	Capillary, Packed, Semicapillary
Comments	Cleaning of non volatile components after each injection	Low flexibility.	Additional devices: methanizer and Oxygen Specific Detector	It is not necessary cleaning of non volatile components after each injection	Cleaning of non-volatiles components after each injection

If we consider the information in table 1, we can conclude that Shimadzu equipment is the most versatile because it allows the configuration of up to four simultaneous injectors, and

of course four simultaneous acquisition channels. It means that we can have information of more than one sample point at the same time.

Another important characteristic is the use of an adaptor which enables the use of capillary, semicapillary and packed columns. This is very useful if we decide in the futur to use this equipment for other applications (not only for fatty acid analysis) .

Finally, this equipment has been widely used by EPAS (Ghent, Belgium) for this application.

6 DETECTOR CHARACTERISTICS AND SELECTION

In order to make a selection of detector that is useful for the application, we have to consider on one hand our sample composition and what do we want to quantify, and on another hand depending on the detector selected, characteristics such as detection and quantification limits, sensibility and linearity will vary (Table 2).

We have to quantify the volatile fatty acids of an ammonium rich aqueous flow, thus we can discard N, P, S, Cl selective detectors (NPD, HECD and FPD), PID because it is only applicable to ionisable compounds and ECD because it is destroyed by water. Final selection should be done among FID,TCD and MSD detectors.

Detectors that are proportional to concentration are usually more used to identify than to quantify. They need an extreme control of experimental parameter because detector response depends on flow rate of carrier gas, and it is necessary to multiply peak areas by flow rate of carrier gas. Mass proportional detectors are usually more used to quantify because peak areas are direct related with mass and detector response do not depend on carrier gas flow rate.

Water and ammonia are not detected by FID, thus they will not be interferences in our VFA determination.

Table 2- Characteristics of different detectors

	FID	TCD	MSD
Type	Response is proportional to Mass	Response is proportional to Conc.	Response is proportional to Mass
Carrier gas	He, N_2, H_2	H_2, He	He
Linearity	10^7	10^5	10^3
Limit of Quantification	20 to 100 pg	1 to 10 ng	< 1 pg
Selectivity	No selective	No selective	Specific

7 INJECTION METHODS

Injection technique depends on the physical state of the sample (liquid, solid or gas), the range of solute concentrations and chromatographic conditions such as column, detector, and stationary phase composition and flow rate.

7.1 Head Space

This technique is used to detect volatile compounds of solid or liquid samples, analysing the vapour phase that is in equilibrium with the sample in a closed recipient. It is specially used to analyse volatile compounds in samples difficult to analyse for conventional GC.

a) diluted samples where the matrix will shape the desired compounds, damage the column or need too large analysis times.

b) inorganic compounds or high molecular weight polymers which can not be dissolved or volatilised under normal conditions.

c) heterogeneous samples such as blood, urine and residual waters that need special treatment before to be analysed by GC.

d) samples in which we are only interested in volatile compounds.

In all these cases Head Space allows to introduce the components practically free of matrix, avoiding the possible matrix interactions with the GC system. This technique has some advantages: when vapour is injected the peak of the solvent is smaller than when liquid is injected, it is not necessary any previous treatment of the sample and the column is not damaged by non volatile compounds. We can consider some disadvantages, for example, for quantitative analysis, it is required an accurate calibration, which sometimes is difficult to obtain. The components must have a high vapour pressure.

There are two different experimental ways for doing Head Space: the static and the dynamic method (see figure 3):

In the static method the sample is introduced in a glass flask, which is closed with a rubber septum. This flask is heated with care (from 40ºC to 190ºC) since there is equilibrium between the sample and the gas phase, which is named Head Space. The gas is introduced to the chromatographic system with a syringe or a pneumatic system.

The dynamic method is similar to the static method but it has a continuous flow of gas on the sample that drags the volatile compounds. With this method sensitivity since 10 ppb is allowed, depending on the compound volatility. It is effective for intermediate volatile compounds, because we can loose very volatile compounds if we do not fit purge time.

The static method is difficult to apply in an on-line GC system, because it implies a special chamber to vaporize the sample and, of course, an additional time of analysis. Depending on the frequency of analysis required, this additional time could be a problem.

The dynamic method could be interesting, but may be some compounds such as acetic acid would be lost.

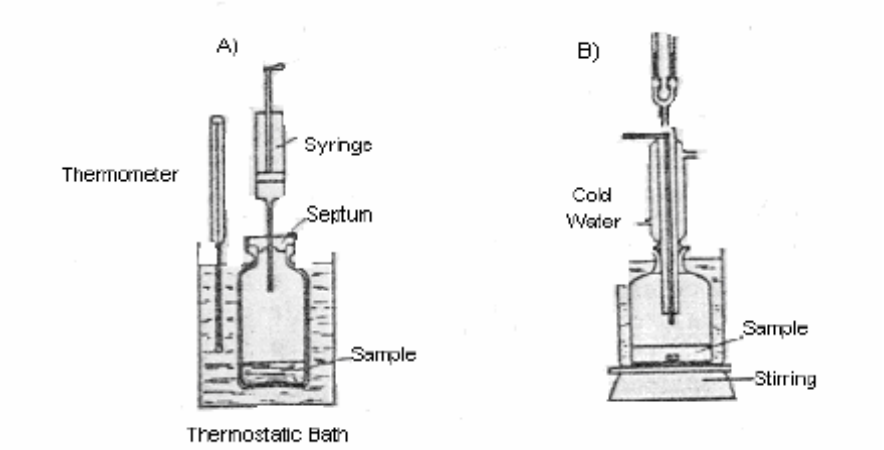

Figure 3: A) Static Head space B) Dynamic Head space

7.2 Injection methods for capillary columns: split

In this technique the volume of sample (0.1-2 µL) is introduced in a vaporizer injector. This sample is transformed into vapour and mixed with carrier gas flow. Then it is divided in two different parts, the greatest part is wasted and the smallest one pass through the column. Usual split ratios are from 1:20 to 1:200. It is a technique for major components, because the quantity of sample that is introduced on the column is small, and the use of highly volatile solvents should be avoided whenever possible.

For quantification either standard addition or internal standard method is preferred but the external standard method in which absolute peak areas are compared can be used. Reproducibility will be enhanced by not varying the injected volume.

7.3 Injection methods for capillary columns: splitless

It is a preconcentration technique for diluted samples such as traces analysis, and for samples containing labile compounds or compounds that are eluted very near to the solvent. The volume of sample (1-2 µL) is injected in the vaporizer injector, vaporized and introduced on the column (a schematic representation is presented in figure 4).

For quantification, both standard addition and internal standard can be applied. Reproducibility will be enhanced by not varying the injected volume.

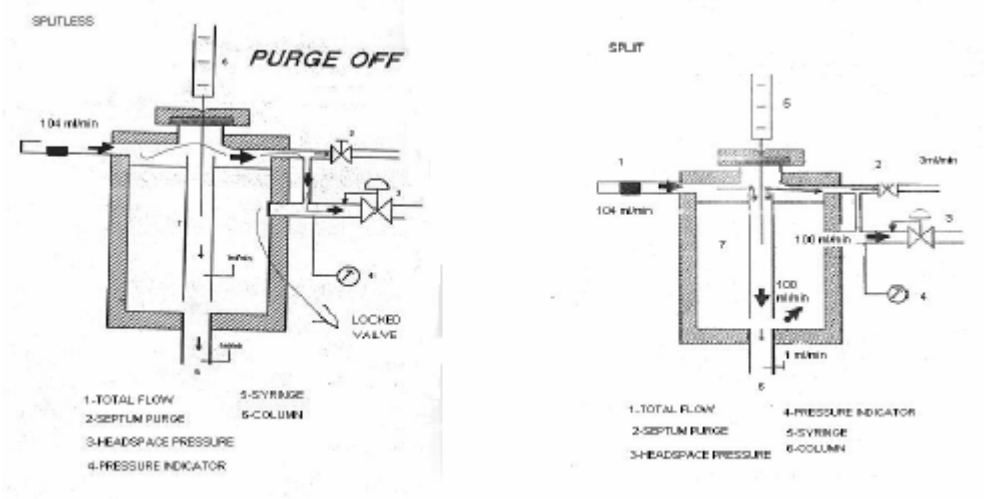

Figure 4: Splitless and split injection method

7.4 Injection methods for capillary columns: on column.

The most relevant difference with the split and splitless techniques is the fact that the liquid sample is introduced directly on the column. There is not a previous vaporizer chamber.

To introduce the sample on the column, special syringes are required, with a small needle diameter, which permit the direct introduction of the sample on the column. The column temperature has to be lower than boiling point of the solvent, to avoid the sudden vaporization of the solvent in the needle. The injection zone is cooled by fresh air and has to be fast and continuous. After that temperature rises sharply up to working temperature.

For quantification, both the internal and the external standard methods can be applied. This system gives accurate quantitative results and is perfect for low volatile samples and for mixtures of wide volatility range compounds, because of its small discrimination due to volatility of compounds. This system avoids the decomposition of labile compounds, but it requires very clean samples.

All these injections methods for capillary columns could be employed to detect our VFA mix. We have to choose the most adapted method from experimental information.

8 EXAMPLES OF VFA ANALYSIS

There are different possibilities of VFA analysis: different columns, injection methods, carrier gases, oven temperatures, etc. Some examples of analytical methods for detecting fatty acids are presented in figures 5 and 6.

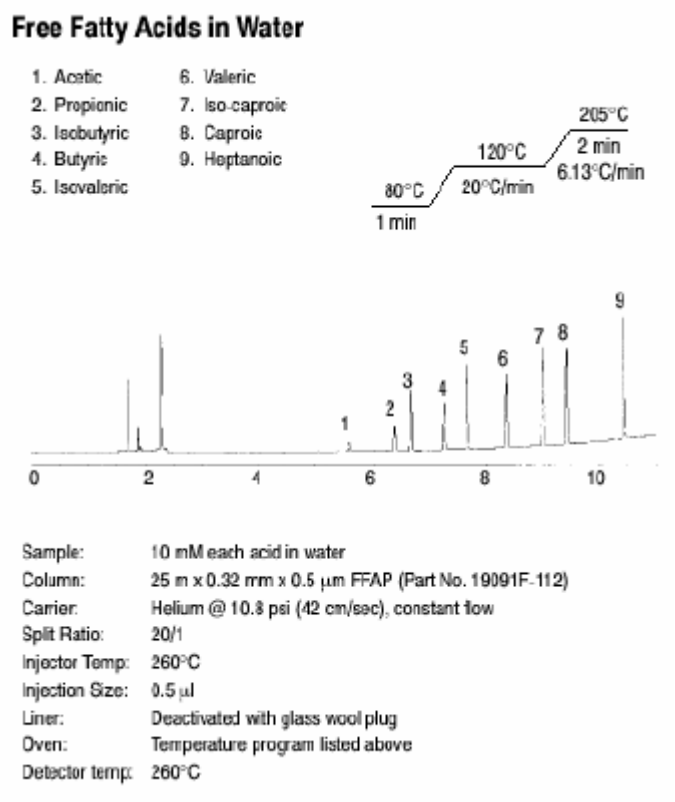

Figure 5: Example of GC method for free fatty acids quantification in an aqueous solution. The instrument is a HP6890.

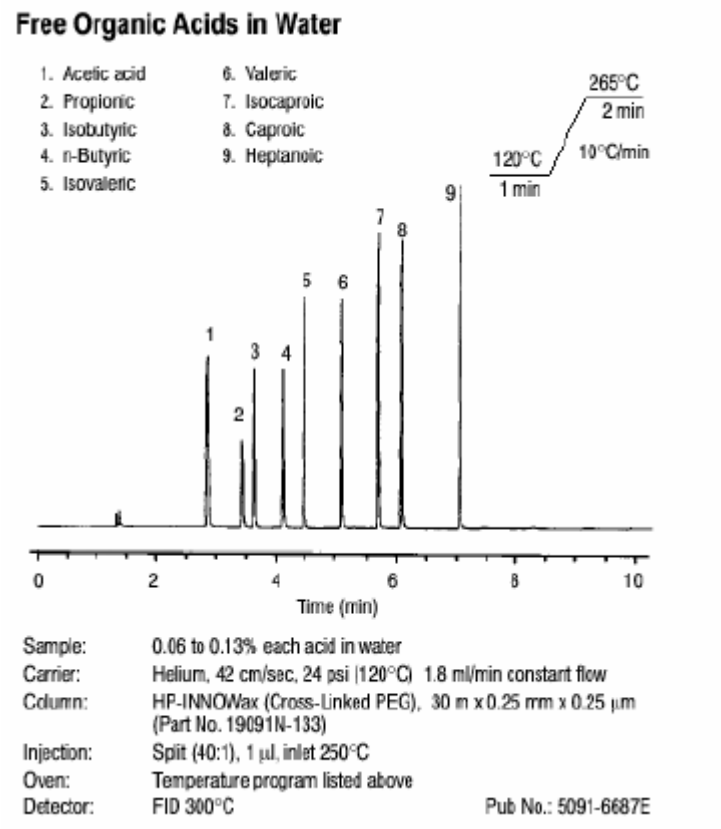

Figure 6: Example of GC method for free organic acids quantification in an aqueous solution. The instrument is a HP6890.

9 OTHER CONSIDERATIONS AND FINAL COMMENTS

In this technical note we have made a comparison between different analytical techniques and we have concluded that GC would be the most interesting for our particular application.

As a main result of this trade-off as well as due to the harmonization required with other MELISSA partners, the final proposal submitted to ESA for approval is a Shimadzu gas chromatograph. Latest issues of this trade mark allow to carry out the analysis using a fast

chromatography technique, which allows to reduce the analysis time considerably. This and other minor aspects should be decided with the purchaser and after some small tests. These selections will impact the final price of the equipment.

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