Application Note: 10131

Ultra Fast GC Analysis of Pure Petroleum Products through Nanovolumes Injection

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Key Words

- TRACE GC Ultra
- Nanovolume Injection
- Plunger-in-needle Syringe
- Pure Petroleum Products
- Ultra Fast GC

TRACE GC Ultra™ with AS3000 Autosampler.

Introduction

The injection of sample volumes as small as 10-20 nanoliters is extremely valuable whenever very concentrated samples have to be analyzed, since the main constituents easily overload the capillary column even at the highest achievable split ratios. Column overloading results in peak broadening with the consequent deterioration of the separation power. This aspect is even more critical with narrow bore columns, characterized by limited sample capacity, typically used in Fast and Ultra Fast GC. Dilution with a solvent is generally not desired because it requires an additional sample preparation step, and some of the components of interest may be hindered by the large solvent peak.

Injection of very small volumes may also be desirable for diluted samples when a splitless injection has to be performed in combination with Fast GC. In fact, a classical 1 µL splitless injection is hardly compatible with narrow bore columns since it requires a long splitless period to complete the transfer at the low flow rates used.

Additionally, the large amount of solvent will easily produce peak deformation due to the flooding effect.

This application note demonstrates how the analyst can automatically control the injection of nanovolumes in a precise and accurate way, through the use of a special plunger-in-needle syringe, combined with an upper-tapered liner using the cold needle injection technique. Further details are reported in a former application note [5-6]. This technique is applied to the analysis of pure petroleum products in Ultra Fast mode.

Plunger-in-Needle Syringe Type

Ordinary GC syringes of 5-10 µL are not suitable for injecting sample volumes smaller than 0.1 µL since they cannot provide enough volume accuracy. The use of plunger-in-needle syringes (Figure 1) allows an accurate measurement of volumes ten times smaller than ordinary syringes, although their conventional use, when used in conjunction with a hot inlet, has serious shortcomings. The problems are mainly related to premature evaporation of the sample during needle insertion in the inlet, evaporation of sample from the annular space between the internal needle wall and the plunger, and sample discrimination due to distillation inside the needle [1]. These drawbacks essentially come from the classical use of a split-splitless injection where the sample is introduced through the syringe needle to the place where it will evaporate (hot needle technique).

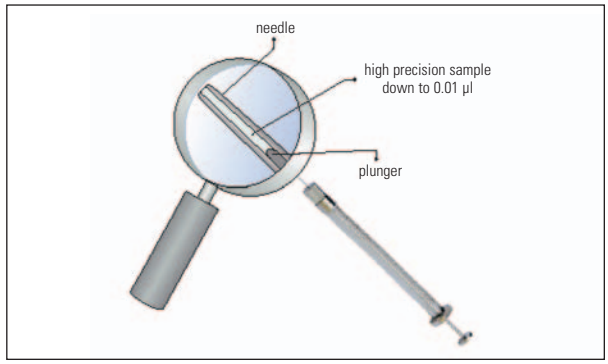

Figure 1: Plunger-in-needle syringe schematic diagram. The plunger is extended to the tip of the needle (zero needle volume) and when liquid is pulled up, it fills only a part of the needle with no glass contact.

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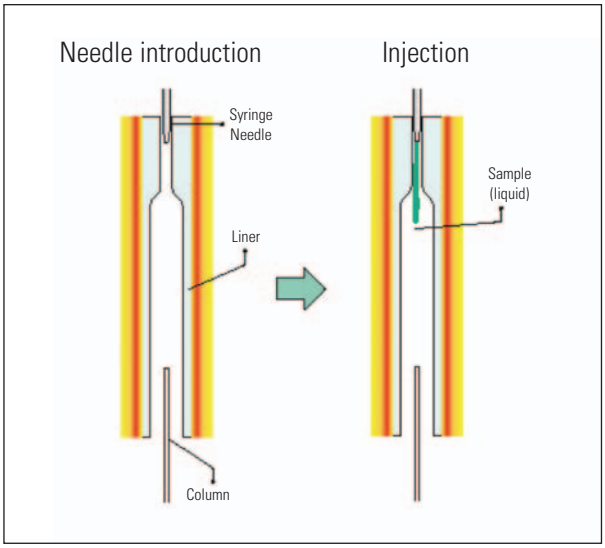

Figure 2: Cold Needle Injection Technique into hot inlets.

In this application, plunger-in-needle syringes have been used in combination with a hot inlet exploiting the liquid band formation technique (cold needle, see next section) [2] which allows the liquid sample to be "shot" into the vaporization chamber without significant evaporation from the needle (Figure 2). Sample volumes as low as 10-20 nL have been injected with high accuracy and precision.

Injection Techniques Into Hot Inlets

By means of visual experiments, it has been demonstrated that two mechanisms are involved in sample injection inside a hot injector [2]: thermospray and liquid band formation. Depending on the injection mode, one of these two mechanisms will predominate strongly influencing the sample evaporation process and the sample transfer to the separation column. Namely, a hot empty needle injection mode will provide a thermospray while a cold needle will provide a liquid band formation.

These two injection modes can be automatically achieved through the Thermo Scientific AS3000 Autosampler by selecting "standard mode" or "minimum mode", with respect to the needle penetration depth in the inlet [3]. Achieving independent mechanisms of vaporization is the key to obtaining good data accuracy and repeatability.

In "standard mode" the needle is programmed to fully enter the injector for a preset dwell time, typically 3-5 seconds. Adequate heating of the needle is obtained, and a thermospray formation is achieved. In "minimum mode" the needle is programmed to enter the inlet for a limited depth with no dwell time. Heating of the needle is avoided, and a liquid band formation is achieved. In this way, lack of reproducibility due to mixed vaporization modes is eliminated

Experimental

Reagents

A standard ASTM D3710 mix has been used to verify injections of very volatile compounds (C3, C4). An undiluted sample of unleaded gasoline has been analyzed to show the benefits of the nanovolume injections involving real petroleum samples.

Instrumentation

Analyses are performed in Ultra Fast GC mode using a Thermo Scientific TRACE GC Ultra™ equipped with a Split/Splitless injector (SSL) and a Digital Pressure and Flow Controller, as well as a Fast FID detector. The GC is also equipped with an Ultra Fast Module (UFM).

The UFM consists of a metal cage containing the fused silica column combined with a heating element and a temperature sensor to ensure direct resistive heating of the capillary column. The UFM module is housed inside the GC oven (Figure 3) and is capable of heating rates up to 1200 °C/min, and also provides fast cooling times, taking about one minute to get back to 50 °C from 350 °C (compared to about 4 minutes in conventional mode) [4].

Figure 3: UFM column module housed in the TRACE GC Ultra oven.

The detector features a 6 ms time constant and acquisition frequencies up to 300 Hz. Such a high speed is, in fact, a compulsory requirement for the correct acquisition (15-20 points/peak) of the extremely narrow peaks (approx. 100 ms $PW_{1/2}h$) typical for this type of chromatography.

The column module, connected to the split-splitless injector and the FID detector as a removable accessory, is completely and directly controlled by the instrument local user interface and electronics. The same GC unit can be used in conventional mode after quick removal of the module.

Split injections from 20 nL (0.02 µL) are performed with a AS3000 Autosampler using a 0.5 µL plunger-in-needle syringe. A minimum penetration depth in the injector (cold needle mode) is set, and 0.3 µL of air are automatically withdrawn after the sample to ensure that the part of needle inserted into the injector is empty. A 3 mm i.d. upper-tapered empty liner with an 8 mm long and 1 mm wide restriction at the top is installed. The SSL injector is set to 225 °C and the FID to 320 °C. Helium carrier gas is supplied at 0.5 mL/min in constant flow mode and split ratio is set to 1:1000. Column temperature is programmed from 40 °C (6 sec) to 300 °C (6 sec) at 180 °C/min.

Results and Discussion

Ultra Fast GC Analysis of Petroleum Products

Nanovolume injection is a very useful tool for the analysis of pure petroleum products, especially in combination with Ultra Fast GC, which implies the use of narrow bore columns having a limited sample capacity.

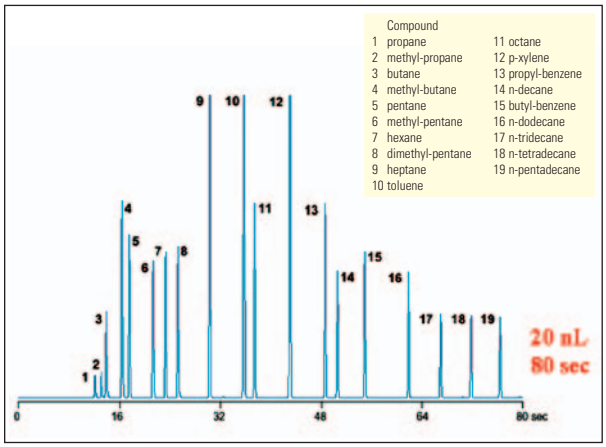

Figure 4: D3710 standard mix chromatogram achieved in Ultra Fast mode (20 nL injection).

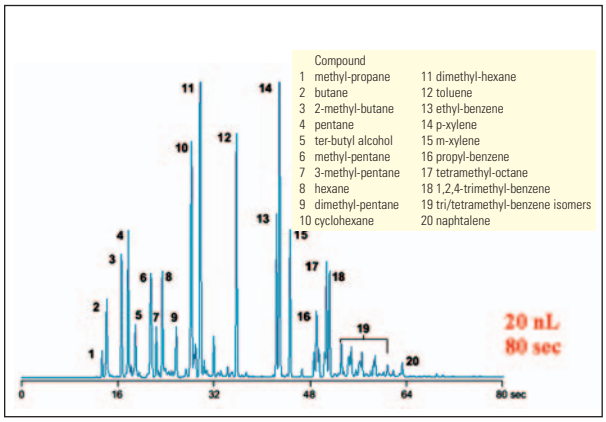

Figure 5: Undiluted unleaded gasoline chromatogram achieved in Ultra Fast mode (20 nL injection).

Figure 4 shows an 80-second analysis of 20 nL of the light hydrocarbons ASTM D3710 standard mix: even very low-boiling compounds, as propane and butane, are transferred at sub-microliter volumes, exhibiting perfect peak shapes. This allows correct identification and quantification of very volatile petroleum fractions, as in the undiluted unleaded gasoline sample reported in Figure 5.

Conclusions

Optimization of the injection method, on the basis of the mechanism of vaporization inside a hot SSL injector, allows reduction of the injection volume to the sub microliter range using a standard autosampler. The key elements are the use of a low capacity syringe (0.5 µL) with in-needle-plunger (zero volume needle), combined with an upper-tapered liner and with the cold needle injection technique. Injections in the range of 10-50 nL with split ratio around 1:1000 allow for the analysis of pure samples without overloading the column, also in the case of narrow bore columns as used in Fast and Ultra Fast GC.

Pure petroleum products can be characterized by Ultra Fast GC in about 1.3 minutes without need of dilution, significantly simplifying the sample prep and permitting the detection of any volatile components.

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Acknowledgement

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AN10131_E 09/07C