Application Note No. 040

Applications of PTV Injectors for Problem Solving in the Petrohemical Industry Part 2:- In-Liner Derivatisation for the Analysis of Organic Acid Mixtures.

Key Words:
In-Liner Derivatisation
succinic acid
levulinic acid
silyl ethers

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Summary
The analysis of mixed acid streams plays an important role in the control of production processes for acetic acid and the determination of dicarboxylic and keto-acids, such as succinic (butane-dioic acid) and levulinic acids (4-oxypentanoic acid), can present particular problems to the analyst. As a result derivatisation methods have been employed to achieve satisfactory results in terms of sensitivity and chromatographic resolution in capillary GC. These derivatisation methods however are time consuming and expensive when dealing with a large number of samples. This paper describes the development of a fast and effective technique for quantifying levulinic and succinic acid in process streams for acetic acid production using in-liner derivatisation to silyl ethers in a PTV injector equipped capillary gas chromatograph.
The PTV in-liner derivatisation technique gives efficient conversion to silyl ether derivatives with good precision, minimal sample preparation and low sample volume and reagent consumption and results in a circa 5 fold decrease in analysis time.

1 Introduction

The analysis of mixed acid streams plays an important role in the control of production processes for acetic acid and the determination of dicarboxylic and keto- acids, such as succinic (butane-dioic acid) and levulinic acids (4-oxypentanoic acid), can present particular problems to the analyst. In process streams at high temperatures these components are fully soluble but at ambient temperatures they can crystallise out resulting in multiphase samples. GC methods using conventional injection techniques therefore require dilution in a solvent to obtain a representative sample with trace level components being close to, or below the detection limit. In addition peak tailing of major acid components can cause further significant problems in conventional GC analysis. As a result of this derivatisation methods such as methylation [1] have been developed to enable concentrated liquid and solid samples to be analysed without excessive dilution while achieving satisfactory chromatography.
However, these derivatisation methods are manually intensive, time consuming, and often require a solvent extraction step and therefore a technique capable of analysing sample solutions directly would be of significant benefit. For example, one method employed converts short chain carboxylic acids to their methyl ester derivatives using a mixture of boron trifluride BF_3 and methanol [2].

Although this provides a successful derivatisation of carboxylic acids to form methylesters for GC analysis it cannot be employed directly as BF_3 and the reaction by-products are potentially damaging to capillary columns and GC instrumentation. Capillary electrophoresis (CE) [3] has been shown to be capable of acceptable sensitivity with minimal sample preparation although this has not yet been widely accepted as a routine analytical tool for bulk chemical process control. This paper describes an alternative approach by using the features available in a commercial Programmable Temperature Vaporisation (PTV) injector [4] to develop an in-liner derivatisation of carboxylic acids to a substrate which is then more easily analysed by gas chromatography which is routinely employed in process control regimes.
PTV injectors are particularly suited to in-liner derivatisation due to the flexibility of control over parameters such as injection volume [5] , carrier gas flow and liner temperature [6]. In addition commercially available injectors can readily be retrofitted to existing GC equipment at relatively low cost.

2 Experimental

2.1 Instrumentation

An Optic 200 PTV injector was installed on a Chrompack CP9001 GC with FID detection. Data collection and analysis was performed using a VG Multichrom data system. The PTV injector was fitted with a liner packed with Supelcoport. The PTV and GC conditions are summarised below:

Optic PTV Program:	
Injection mode:	Split
Initial temperature:	45°C
Ramp rate:	16°C/Sec
Final Temperature:	250°C
Desorption time:	2 minutes
Desorption pressure:	0 Bar
Transfer pressure:	0.7 Bar
Transfer time:	0.3 minutes
Initial pressure:	0.55 Bar
Final pressure:	0.65 Bar

G.C. Conditions:	
Column:-CPSIL8 25m X 0.53mm i.d, df.5µm	
Detector temperature:	270°C
Initial Temperature:	45°C
Final Temperature:	250°C
Ramp Rate:	10°C/min
Detector Range:	2

Conditions on the PTV injector were optimised such that the reactants were injected into the liner under stopped flow conditions at 45°C. The injector was then ramped at 16°C/second to 250°C and held there for 2 minutes under stopped flow conditions to allow the derivatisation reaction to proceed. The derivatised products were then transferred onto the GC column using a pressure pulse technique.

2.2 Materials

Process stream samples containing succinic acid and levulinic acid were obtained from BP Chemicals process plants. The derivatising reagent Bis(trimethylsilyl)trifluroacetamide (BSTFA) was purchased from Supelco, and was chosen as it gives bi-products compatable with capillary G.C. columns and equipment unlike other silating agents such as dimethyldichlorosilane (DMDCS). Levulinic acid (98%) and the succinic acid (99%) for standard preparation were purchased from Sigma.

2.3 Preparation of Standards and Samples

Standard solutions were prepared by dissolving the appropriate amount of pure substances in THF to cover the analyte concentration ranges of interest in samples and calibration plots constructed. The applicability of the method was then examined using four process samples, one for succinic acid content, the other three for levulinic acid. The samples were diluted in THF prior to analysis.

2.4 Sample Analysis

An 850µL aliquot of sample in THF was pipetted into a standard auto-sampler vial and 350µL of BSTFA reagent added. The vial was crimp capped then a 1µL sample injected into the PTV injector.
3 Results and Discussion The existing derivatisation method employed in the laboratory used methylation prior to GC analysis of the methyl esters. Therefore the initial work programme studied in-liner methylation of levulinic and succinic acid using Trimethyaniliniumhydroxide (TMAH) [7], TMAH was used since it was claimed to be particularly suited to in liner derivatisation. Unfortunately initial results showed poor reproducibility and incomplete derivatisation of the acids and therefore an alternative derivatisation reaction using the more reactive silating agent BSTFA was chosen. This reaction replaces active hydrogen with tetramethylsilyl, $Si(CH_3)_3$ to produce silyl ethers. Initially an internal calibration method was devised to minimise the effects of random error in sample injection volume. The internal standard chosen was pimelic acid (heptane dioic acid) which had been employed in the conventional methylation derivatisation. Structures of succinic, levulinic and pimelic acid can be seen in Figure 1.

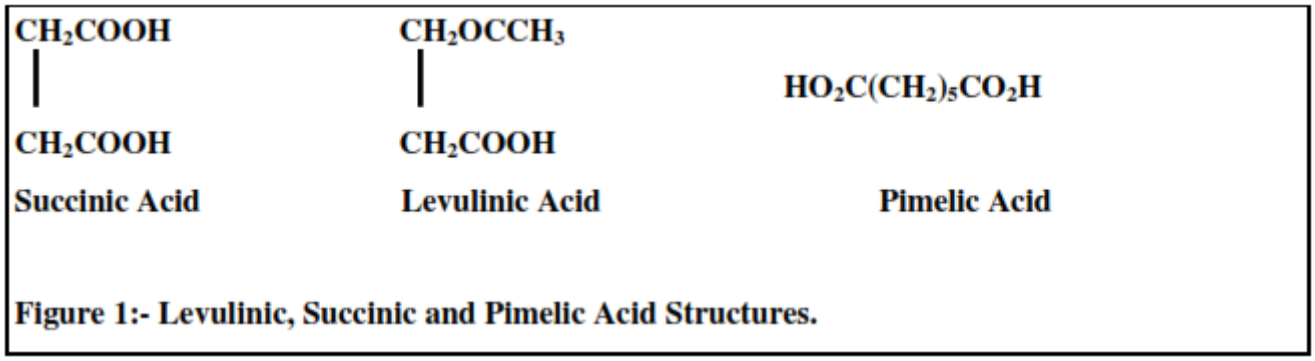

Figure 1:- Levulinic, Succinic and Pimelic Acid Structures.

The internal standard method gave very poor reproducibility possibly due to inconsistent derivatisation and therefore an external standard calibration method was investigated which gave much better performance. Typical chromatograms of the silyl ether derivatives of succinic and levulinic acid is shown in Figure 2. and the retention times for levulinic, succinic acid and their corresponding silyl ethers are listed in Table 1.

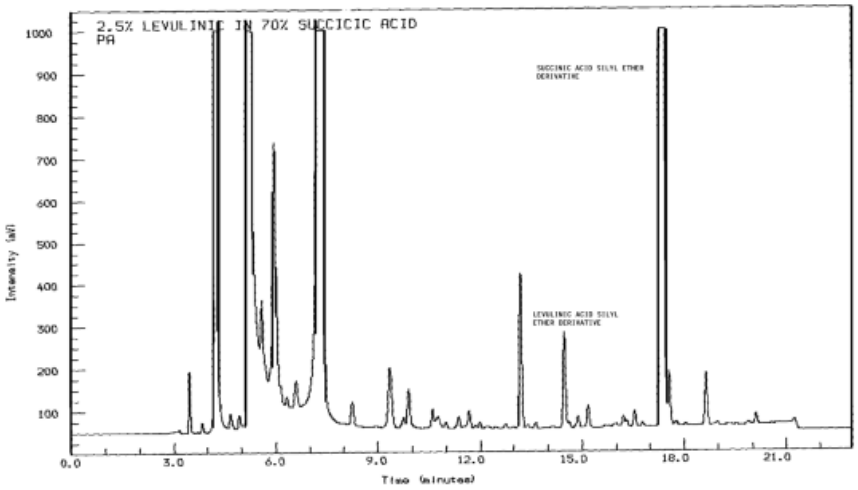

Figure 2:- A typical chromatogram from a sample containing Levulinic and Succinic Acid which has been derivatised to their silyl ethers.

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The calibration for determining succinic acid over the range 50 to 100 percent w/w is shown in Figure 3 and is linear over this range with a regression coefficient of 0.9993.

Component	Retention Time (Minutes)
Levulinic Acid	12.4
Succinic Acid	13.1
Levulinic OTMS	14.5
Succinic OTMS	17.3

Table 1:- Retention times of main components

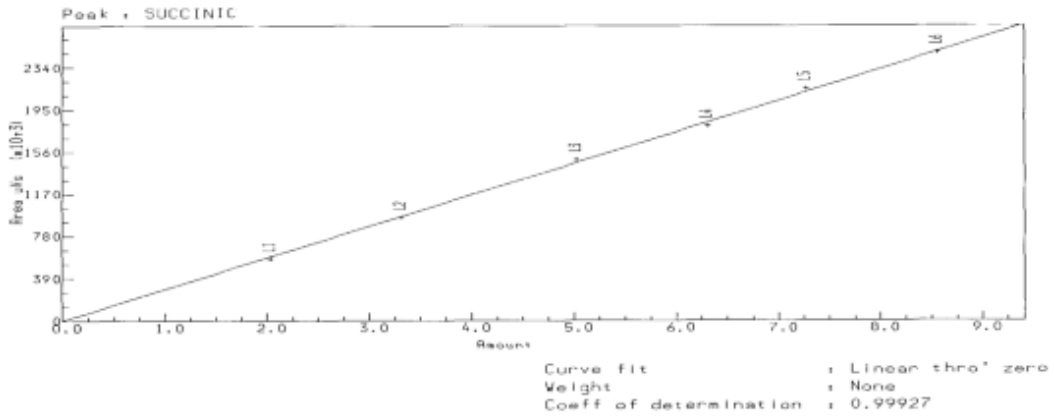

Figure 3 :- Calibration plot for Succinic acid by in-liner derivatisation.

The succinic acid content of a typical sample was quantified using in in-liner derivatisation to the silyl ether, six replicate analysis were made including full sample preparation in each case. The individual results obtained are detailed in Table 2 and a mean of 78.8% + 1.0% (95% confidence) was obtained from the data.

Analysis Number	% wt Succinic Acid
1	79.9
2	78.7
3	79.7
4	78.2
5	78.7
6	77.3

Table 2: - Repeat Analysis of Succininc acid content by in-liner silyl ether derivatisation.

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However, the main challenge of the work was to be able to determine low percent levels of levulinic acid in high percentage levels of succinic acid.

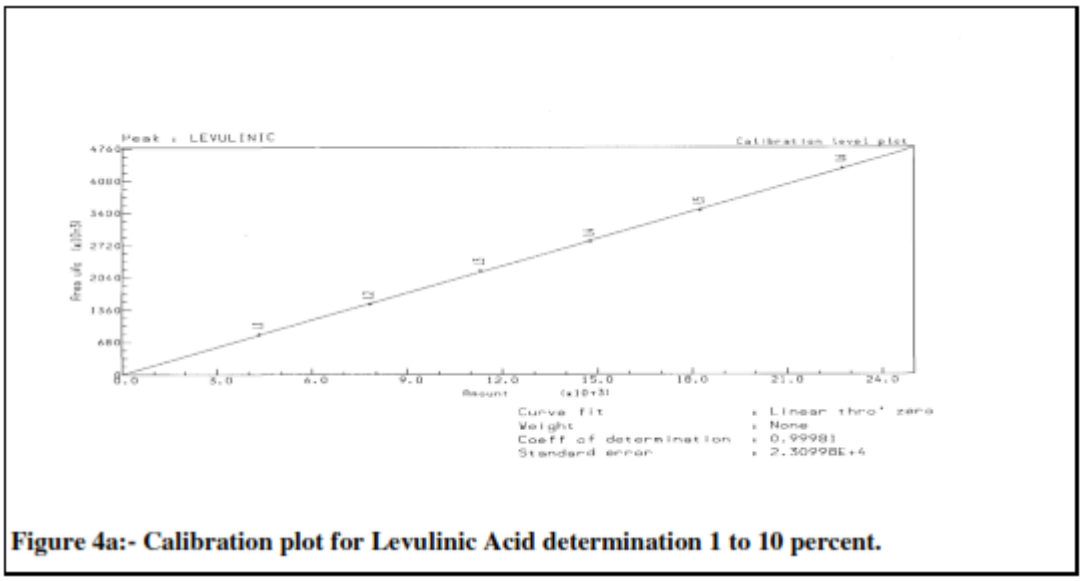

Figure 4a:- Calibration plot for Levulinic Acid determination 1 to 10 percent.

The calibration plots for levulinic acid in the ranges 1 to 10 percent and 0 to 1% w/w are shown in Figures 4a and 4b respectively and in both cases correlation coefficients better than 0.9998 were achieved.

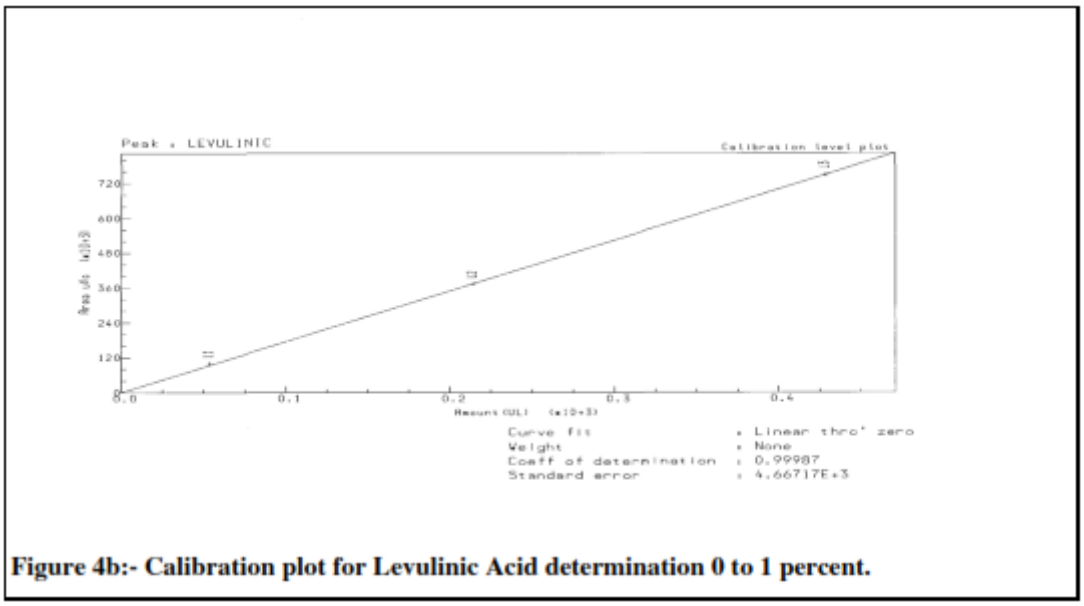

Figure 4b:- Calibration plot for Levulinic Acid determination 0 to 1 percent.

These calibrations were then employed to measure levulinic acid in 3 samples covering the range of interest. Each sample was analysed 7 times and the results obtained are listed in Table 3. The results demonstrate the effectiveness of the in-liner derivatisation of levulinic and succinic acid to their silyl ethers for GC analysis. It gives improved component separation and peak resolution with excellent precision. The method is also much quicker and less labour intensive with a run time for each analysis of approximately 35 minutes compared to the existing off line methylation analysis time of approximately three hours.

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Analysis No.	Sample 1(% w/w)	Sample 2 (% w/w)	Sample 3 (% w/w)
1	8.1	2.9	0.27
2	8.7	3.1	0.30
3	8.6	2.7	0.25
4	8.3	2.8	0.25
5	8.4	2.7	0.27
6	8.5	2.5	0.30
7	8.1	2.5	0.25
Mean	**8.4 %± 0.2**	**2.7 %± 0.2**	**0.27% ± 0.02**

Table 3: - Repeat Analysis of Levulinic acid content of 3 different samples by in-liner silyl ether derivatisation.

In-liner silyation has been demonstrated to be very simple, saving on labour and reagent costs and is capable of determining levulinic acid down to at least 0.25% ± 0.02% (95%) in a matrix of succinic acid which was sufficient for the purposes of this work.

4 Conclusions

A fast and effective technique for quantifying levulinic and succinic acid in process streams for acetic acid production has been developed using in-liner derivatisation to silyl ethers in a PTV injector equipped capillary gas chromatograph. The PTV in-liner derivatisation technique gives efficient conversion to silyl ether derivatives with good precision, minimal sample preparation and low sample volume and reagent consumption. It results in a 5 fold decrease in analysis time thereby giving a faster turnaround and significant reduction in analytical costs.

References

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