Smart Sampling Enables a Fully Automated Workflow for Liquid Injection and Headspace GC and GC/MS

Douglas Doster[1], Roger Pearson[1], Ken Rice[1], Tom Flug[2], Brian Peat[2], Renzo Picenoni[2], Guenter Boehm[2] | [1]Aspen Research Corporation, Maple Grove, MN; [2]CTC Analytics, Zwingen, Switzerland

Overview:

Purpose:
- To demonstrate a fully automated workflow for both liquid injection and headspace for GC and GC/MS.
- Automatically optimize analysis conditions and derivatization parameters.
- Automate standard preparation and derivatization procedures.
- Reduce analysts time involved in the analysis.
- Compare manual versus automated preparation of standards.

Methods:
- Analysis of trace levels of diacetyl in ethanol by direct injection using both manual and automatic preparation of the standards.
- Headspace analysis of residual isopropanol in plastic parts using both manual and automatic preparation of the standards.
- Analysis of lactic acid content in polymeric material using both a manual and automatic derivatization procedure.
- PAL RTC robotic workstation for automated analysis and standard preparation.
- GC/MS analysis of extracts with an Agilent 5975C GC-MS

Results:
- Applying the automated workflow described above, the analyst's time to prepare samples and standards, and then optimize conditions was drastically reduced when compared to performing the experiments manually without any reduction in accuracy and reproducibility. At the same time the automated procedure enabled complete traceability of every step.

Introduction:

- The preparation of samples and standards is generally accepted as the most time consuming portion of the analysis in regard to the analyst's time. Automating the sample preparation and standard preparation drastically reduces the amount of time the analyst spends on the analysis.
- An important part of method optimization is the selection of the appropriate conditions. This normally requires a considerable amount of the analyst time. In practice, only a small amount of optimization work is actually done and most methods used rely on analyst experience.

- A new type of robotic sample handler allows for the automatic change of tools. This opens the possibility for the automated preparation of samples and standards as well as the optimization of key process parameters.

Methods:
- A novel PAL RTC robotic workstation was used to perform the preparation of samples and standards and injection into the GC/MS.
- PAL Sample Control Software v. 2.0.1.1 controlled the PAL RTC and data acquisition with the Agilent GC/MS instrument. GC/MS methods were written with Chemstation V.E.02.01.1177

Diacetyl in Ethanol:

- Working standard solutions in the range of 50µg/ml to 1000µg/ml were prepared in methanol both manually and automatically by a serial dilution from a 1000 µg/ml stock solution of diacetyl prepared in methanol.
- The samples were analyzed directly with no dilution.
- Diacetyl was quantified using the ion at 86 m/z and compared an external calibration curve.

GC-MS analysis was performed on an Agilent 5975C GC-MS

GC Method
- Initial temperature of 10°C,
- Ramped to 200°C at a rate of 10°C / minute
- Ramped to 280° at a rate of 40°C / minute,
- Held at 280°C for 5 minutes
- Carrier Gas helium flow rate 1.5 ml/min
- Split ratio of 50:1
- Injection volume was 1µl
- Injection Port 250°C
- Column used was an Agilent DB-5MS (30 m x 0.250 mm X 1µm).

MS parameters:
- SIM Mode 86 m/z
- Source Temperature 220°C
- Transfer Line 240°C

Isopropanol (IPA) in Plastic Parts:

- Working standard solutions in the range of 2.5 to 25 µg/µl were prepared in water both manually and automatically by a serial dilution from a 50 µg/µl stock solution prepared in water.
- One µl of each standard solution was used to make the headspace standards that ranged from 2.5 µg-50 µg both manually and automatically.
- The samples were analyzed directly by placing them in a 20 ml headspace vial.
- The total amount of IPA in the part was quantified by comparing them to the headspace standards prepared.

GC-MS analysis was performed on an Agilent 5975C GC-MS

GC/headspace Method
- Initial temperature of 40°C, held 5 minutes
- Ramped to 60°C at a rate of 10°C / minute
- Ramped to 150°C at a rate of 30°C / minute,
- Held at 150°C for 2 minutes
- Carrier Gas helium flow rate 1.0 ml/min
- Split Ratio 50:1
- Column used was an Agilent DB-5MS (30 m x 0.250 mm X 1µm).
- Injection volume was 1 ml
- Injection Port 250°C
- Tool Temperature 130°C
- Vial incubation 15minutes @ 80°C

MS parameters
- Scan Mode 29-350 m/z
- Source Temperature 220°C
- Transfer Line 240°C

Lactic Acid content in a Polymeric Material:

- Lactic content is determined by hydrolyzing the polymeric material with hydrochloric acid and converting it to the propyl derivative using isopropanol which is then extracted into trichloroethane.
- Working standard solutions in the range of 2000- 6000 ug/ul were prepared in water both manually and automatically by a serial dilution from a 20,000 ug/ul stock solution prepared in water.
- Both the sample and the standards were derivatized using HCL and IPA, @ 90°C for 3.5 hours and then extracted into trichloroethane. This procedure was done both manually and automatically.
- One ul of the trichloroethane layer was injected into the GC/MS

GC-MS analysis was performed on an Agilent 5975C GC-MS
- Initial temperature of 40°C, held 4 minutes
- Ramped to 65°C at a rate of 5°C / minute and held for 1 minute
- Ramped to 230°C at a rate of 40°C / minute,
- Held at 230°C for 2 minutes
- Carrier Gas helium flow rate 2.0 ml/min
- Split Ratio100:1
- Column used was an Agilent DB-FFAP (30 m x 0.32 mm X 0.25µm).
- Injection volume was 1 µl
- Injection Port 230°C

MS parameters
- SIM Mode 45 and 89 m/z
- Source Temperature 230°C
- Transfer Line 240°C

Results:

Diacetyl in Ethanol:

Figures 1 and 2 shows the standard curves for diacetyl when prepared manually and automatically by the PAL RTC. The manual preparation gave an R2 of 0.994 and the automatic preparation gave a R2 of 0.997. This demonstrates that the PAL RTC prepares standards with the same or better precision as a manual preparation in a significantly shorter time. Additionally more standards can be analyzed to improve accuracy with no additional analyst time involved.

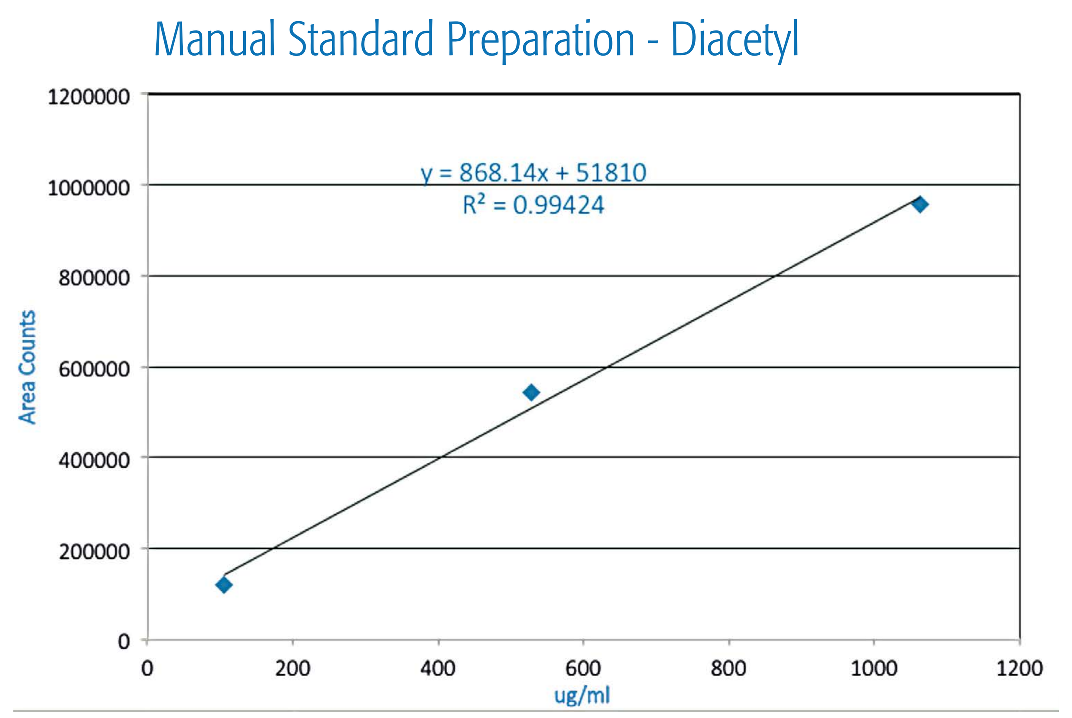

Figure 1: The standard curve for diacetyl prepared manually.

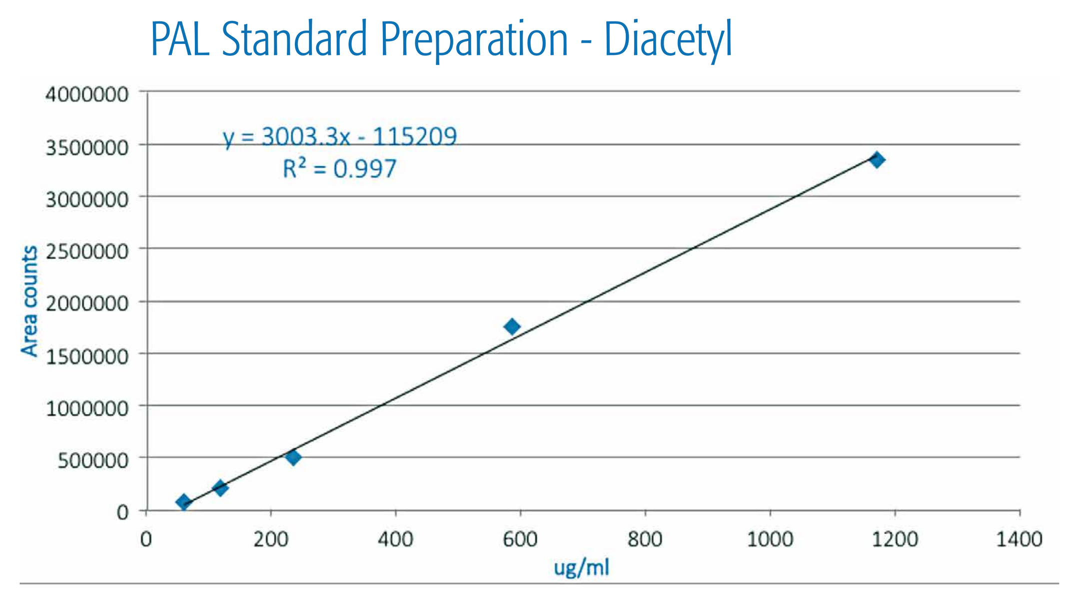

Figure 2: The standard curve prepared for diacetyl by the PAL RTC automatically.

Isopropanol (IPA) in Plastic Parts:

Figures 3 and 4 show the standard curves for IPA when the headspace standards were prepared manually and automatically by the PAL RTC. The manual preparation gave an R2 of 0.998 and the PAL RTC automatic preparation gave a R2 of 0.998. This demonstrates that the PAL RTC is capable of preparing the liquid standards and then using these liquid standards prepare the headspace standards with the same linearity as a manual preparation with significant less amount of analyst time involved.

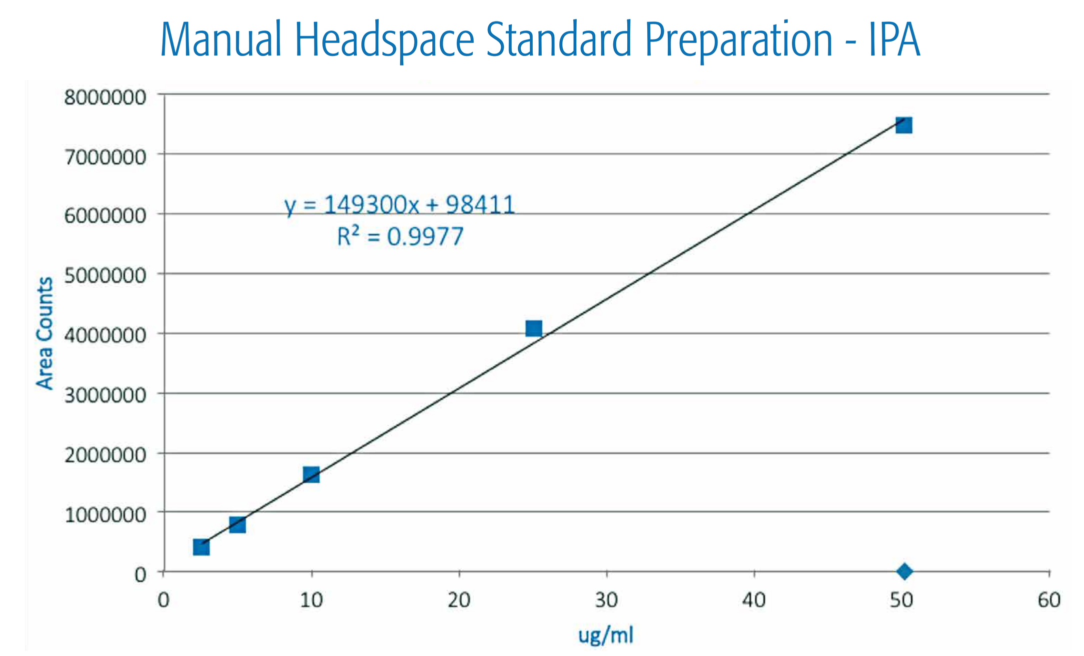

Figure 3: The standard curve for IPA headspace standards prepared manually.

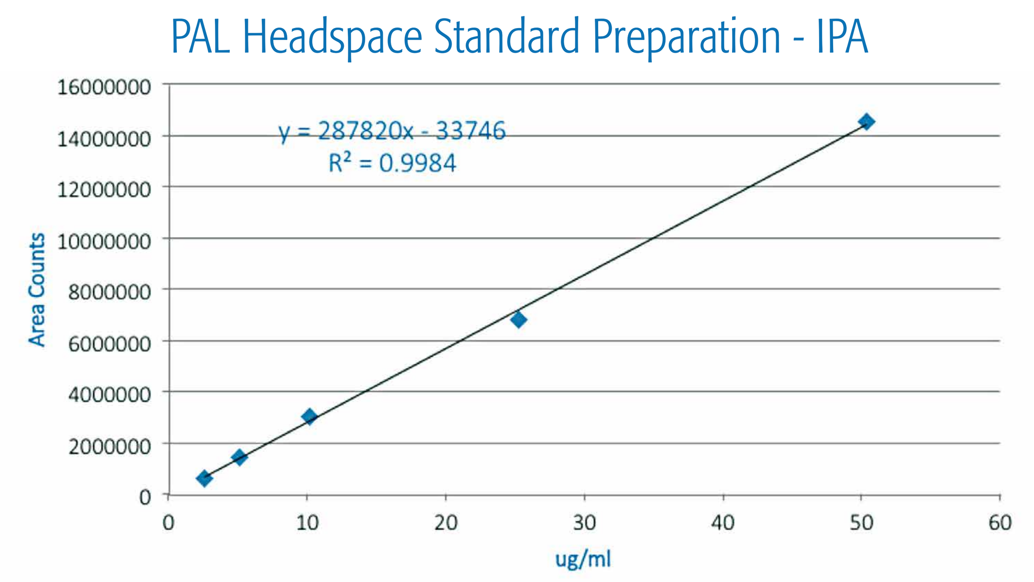

Figure 4: The standard curve for IPA headspace standards prepared by the PAL RTC automatically.

Lactic Acid content in Polymeric Material:

Figures 5 and 6 show the standard curves for lactic acid when the standards were prepared manually and automatically by the PAL. The manual preparation gave an R2 of 0.990 and the PAL RTC automatic preparation gave a R2 of 0. 996. This demonstrates that the PAL prepares the liquid standards and then derivatizes them to prepare a calibration curve with the same linearity as a manual preparation with a dramatic decrease in the analyst's time involved from 4 hours per sample to 15 minutes per sample.

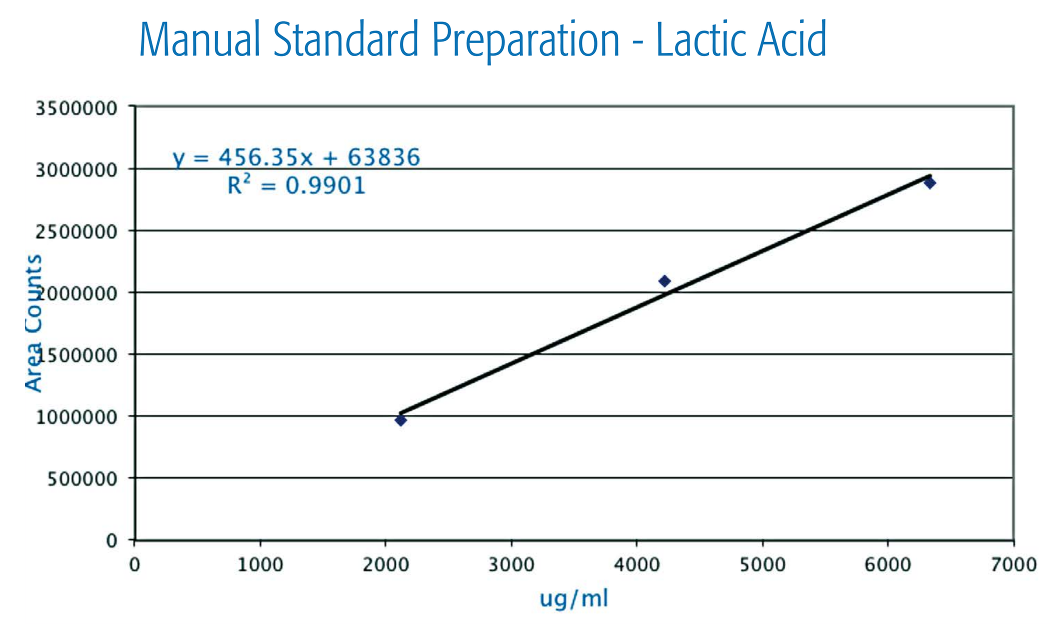

Figure 5: The standard curve for Lactic acid standards prepared manually.

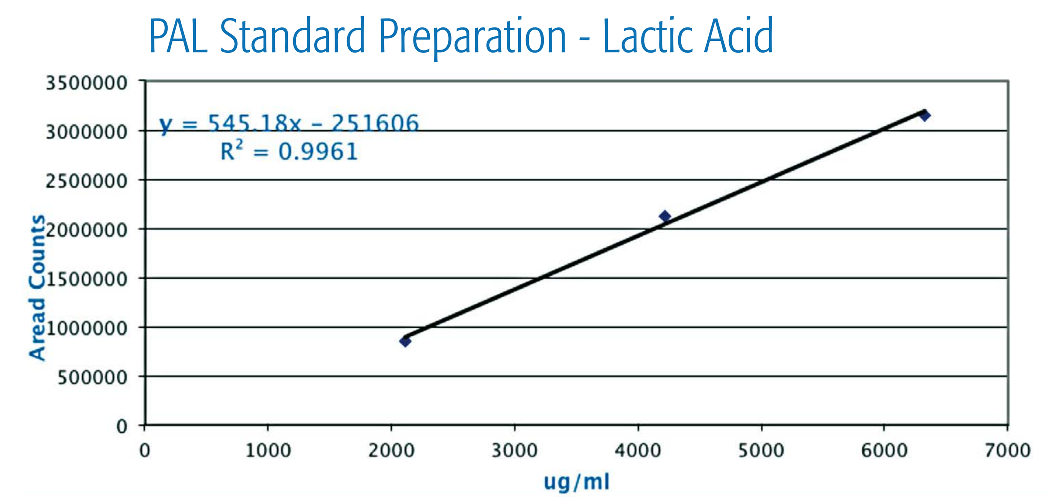

Figure 6: The standard curve for lactic acid standards prepared by the PAL RTC automatically.

Conclusions:

- A workflow has been described enabling the automated preparation of standards and samples for the GC/MS analysis.
- It was demonstrated the automated preparations were equivalent or better compared to the manual preparation with a dramatically reduction the analyst's time involved.
- Applying the automated workflow described above increases sample throughput while reducing the analyst's time involved from hours per sample to minutes per sample.
- Future work will enable the PAL RTC to determine if a sample is out of range, then dilute the sample or inject a larger volume and re-run it automatically. The ability to perform this automatic adjustment of the concentration level in the sample will increase the productivity of this system further.