Sub-ppt Atmospheric Measurements Using PTV-GC-FID and Real-Time Digital Signal Processing

Application Note No. 036

J.B McQuaid[1], A.C Lewis[1], K.D Bartle[1] and S.J Walton[2]

1 School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK;
jimm@chem.leeds.ac.uk, alyl@chem.leeds.ac.uk, keithb@chem.leeds.ac.uk

2 Thomas Swan & Co. Ltd., Crookhall, Consett, Co. Durham DH8 7ND, UK;
Steve.Walton@ps.com

Key Words: trace level atmospheric measurements; digital signal processing; signal to noise reduction

Summary

In order to make accurate measurements of atmospheric hydrocarbons such as the trace levels observed in the clean marine environment, the employment of numerous GC methods have been suggested. So called grab samples provide a very convenient method of acquiring such a sample and dismisses the need to transport what has always been considered as typical laboratory equipment. However the atmosphere is a constantly reacting body and any 'total air sample' will subsequently include the reactive species. A method has recently been developed to facilitate in-situ measurements of atmospheric hydrocarbons. Such an instrument has been deployed at Mace Head on the west coast of Ireland, a clean marine location frequently used for atmospheric studies. The concentrations monitored at such a site are at such a level as to necessitate manual analysis due to the constraints of currently available software. This work presents the application of a digital signal processing unit (DSP) to a trace level instrument and illustrates the advantages of such a coupling.

Introduction

Automated on-line trace level measurements in the atmosphere have become possible over the past ten years due to developments in large volume injection technology and the increased availability of non-cryogenic cooling devices using phenomena such as the Peltier effect. The analysis of hydrocarbon (HC) species in the atmosphere is a particularly challenging area where individual ambient concentrations as low as 1 ppt may be encountered in clean tropical marine air [1]. From measurements of hydrocarbon species taken in clean air it has been demonstrated that small but significant concentrations of some species remain constantly present. The presence of certain reactive alkene species even at levels below 5 ppt may have a significant impact on the oxidative capacity of the clean atmosphere. Whilst halogenated species have been routinely measured on-line at sub-ppt levels for several years [2], the analysis of HC species has been limited by the flame ionisation detector - the most popular detector for field measurements. The limiting parameter in using FID for trace determination is often the noise generated within the FID amplifier electronics rather than by the absolute detection limit of the FID itself.

Determinations at very low concentrations using automatic peak height or area integration prove difficult to perform with reliability due to a combination of poor signal to noise and transient detector spikes. By increasing data acquisition sampling rates coupled to the application of a digital signal processing algorithm, the electrometer output can be bandwidth limited to a frequency which allows peak information to be accurately represented whilst substantially reducing noise of higher frequencies. The roll off rate of a digital filter [3,4] is much greater than can be achieved using an analogue filter. A rejection of greater than 150 dB can be achieved with a pass band to stop band delta of a fraction of 1 Hz. The benefit of this is that chromatographic resolution and efficiency are not affected by the process, i.e. the peaks are not broadened.

The basic principle of digital signal processing DSP is to convert a dynamic analogue signal into discrete values by sampling at certain intervals, followed by the application of mathematical filter algorithms to remove any interference or noise that may be obscuring the desired signal. Once processed, the discrete signal may then be converted back to analogue if necessary [5].

Comparison of data from both systems demonstrates a large enhancement in minimum detectable amount and improved integration reliability. Use of a DSP unit has resulted in a lowering of detection limits to allow automated sub-ppt measurements to be performed. Comparison has also shown that raw FID output logged straight to PC leads to a consistent overestimation of peak height of the order of 25% at trace levels.

Experimental

An automated programmed temperature vaporisation injector-GC-FID system was used as the test chromatograph for the exercise. The instrument has been reported previously [6] however, it briefly comprises the following: A PTV (OPTIC 400, AI Cambridge Ltd., Cambridge, UK) injector liner is packed with activated charcoal adsorbent (160 mg) and capped at either end with glass wool. The liner is placed inside the PTV injector and a combination of two 6 port valves is used to route samples of air over the adsorbent trap for sample re concentration. Re-concentration of the sample (700 mL) was performed at -20 °C with a sample flow rate of 70 mL min^{-1}. Desorption is performed at 400 C directly onto a 50 m 0.53 mm id $_{Al2O3}$ PLOT column stabilised with Na_2SO_4 salt (Chrompack B.V, Netherlands) for temperature programmed GC (AI GC-94 AI Cambridge Ltd., Cambridge, UK) and flame ionisation detection. operating at 10 Hz sampling frequency.

A digital signal processing unit (ID/10, Thomas Swan Ltd., Consett, UK) was placed in parallel to the standard PC data capture package (EZChrom, Aston Scientific, Cambridge, UK) and the two resulting chromatograms compared.

Results

Using a standard concentrated mixture at ppb level (Air Products Special Gases, Crewe, UK) the resulting chromatograms were compared for 27 hydrocarbon compounds. Use of the DSP process in this instance produces a reduction in overall peak height between 2 and 5 % for most species. Little difference in integration accuracy was observed between the two methods with $R^2 = 0.9995$.

For clean air samples however the improvements in chromatogram signal to noise are very significant. ***Figure 1*** shows a portion of the resulting chromatogram obtained with and without signal processing.

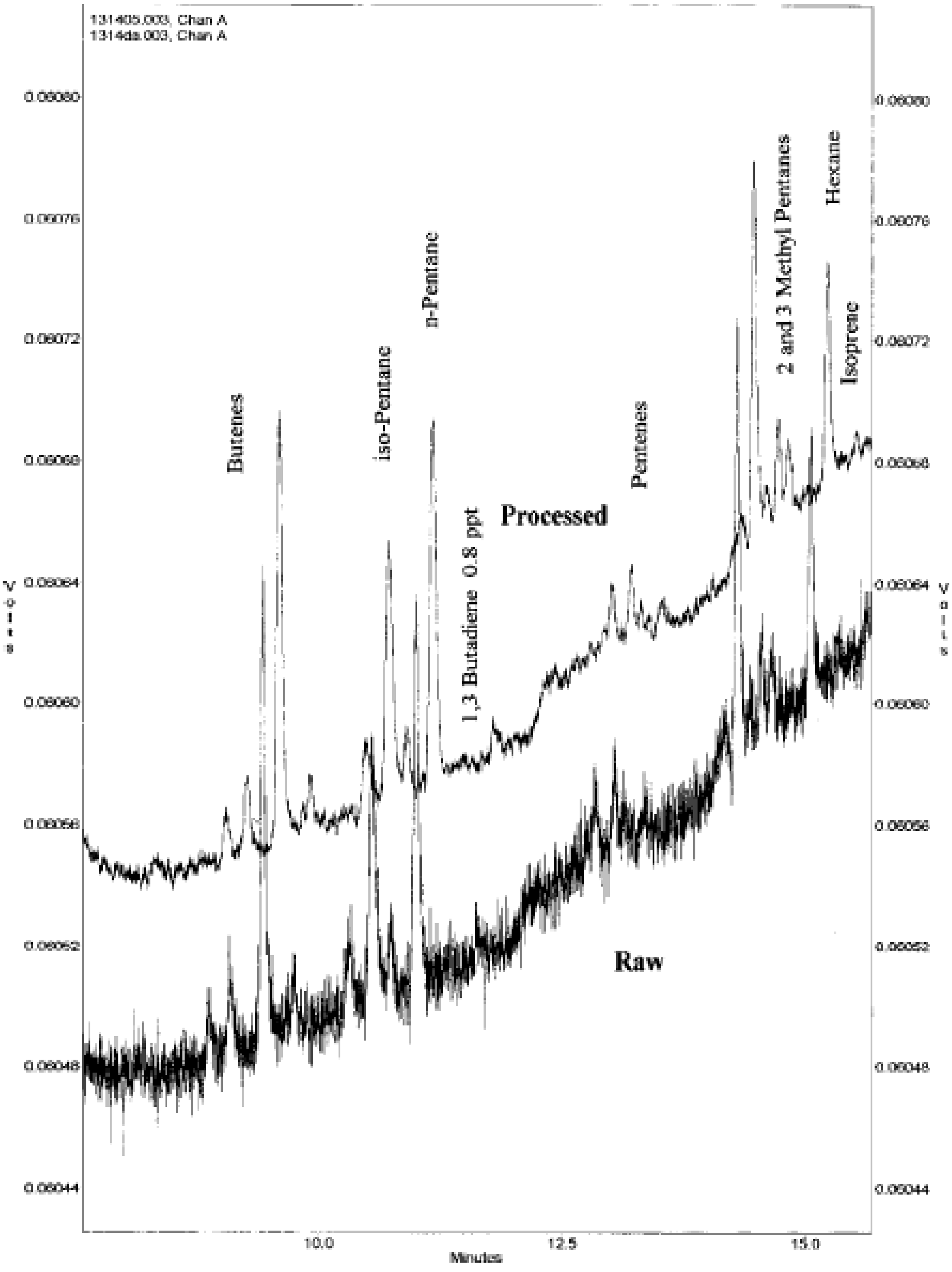
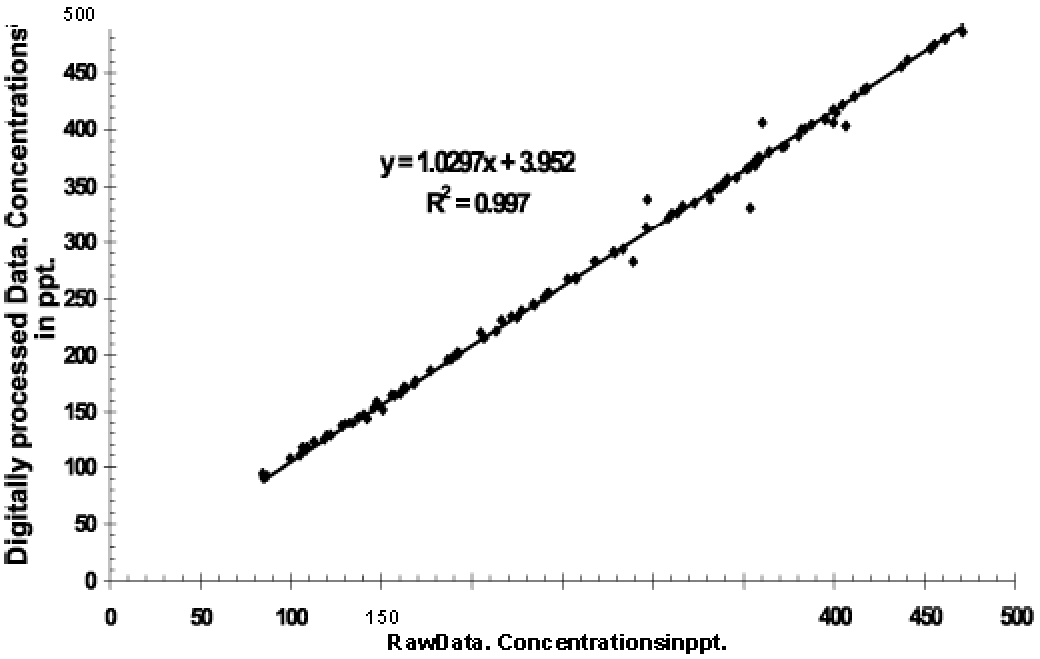


Figure 1: Raw and processed data for C_4 - C_6 species in clean marine air.

Low concentration species where S/N is 2:1 in the raw chromatogram result in a processed signal chromatogram with S/N of 6:1 or better. Whilst ideally a standard mixture of gases at the low ppt level would be used to test the reliability of each approach, technically cylinders of these concentrations are currently impossible to manufacture. As an alternative a period of stable very clean air flow (measured at Mace Head Atmospheric Observatory, Galway, Eire) is used to assess the variance in integration produced by each method.

Results are compared over a period of 6 days continuous sampling at 1 sample per hour for a moderate concentration species (propane) between 80 and 500 ppt in the atmosphere and a low concentration species (1,3 butadiene) present at concentrations between 2 and 20ppt. ***Figure 2*** shows the comparison of values obtained from both raw and processed chromatograms for propane in the moderate concentration range where S/N is 7 or better in the raw chromatogram. $_{R2}$ (for n=125) values approach unity with a slope of approximately 1.

500



150 **400** **450** **500**

RawData. Concentrationsinppt.

Figure 2: Comparison of Propane determinations over a 6 day period in clean air (n=125)

Figure 3 shows the comparison of values obtained from processed and raw chromatograms for 1,3 butadiene at trace level concentrations where S/N is between 2 and 5. The plot shows a good correlation between smoothed and raw signal (R^2= 0.88) however with a slope of 0.75 over the concentration 2-20 ppt range, demonstrating an over estimated peak height integration in the raw data when S/N levels are between 2 and 5. For the processed chromatogram 6 runs required manual peak integration compared to 23 manual reprocesses for the raw/ signal.

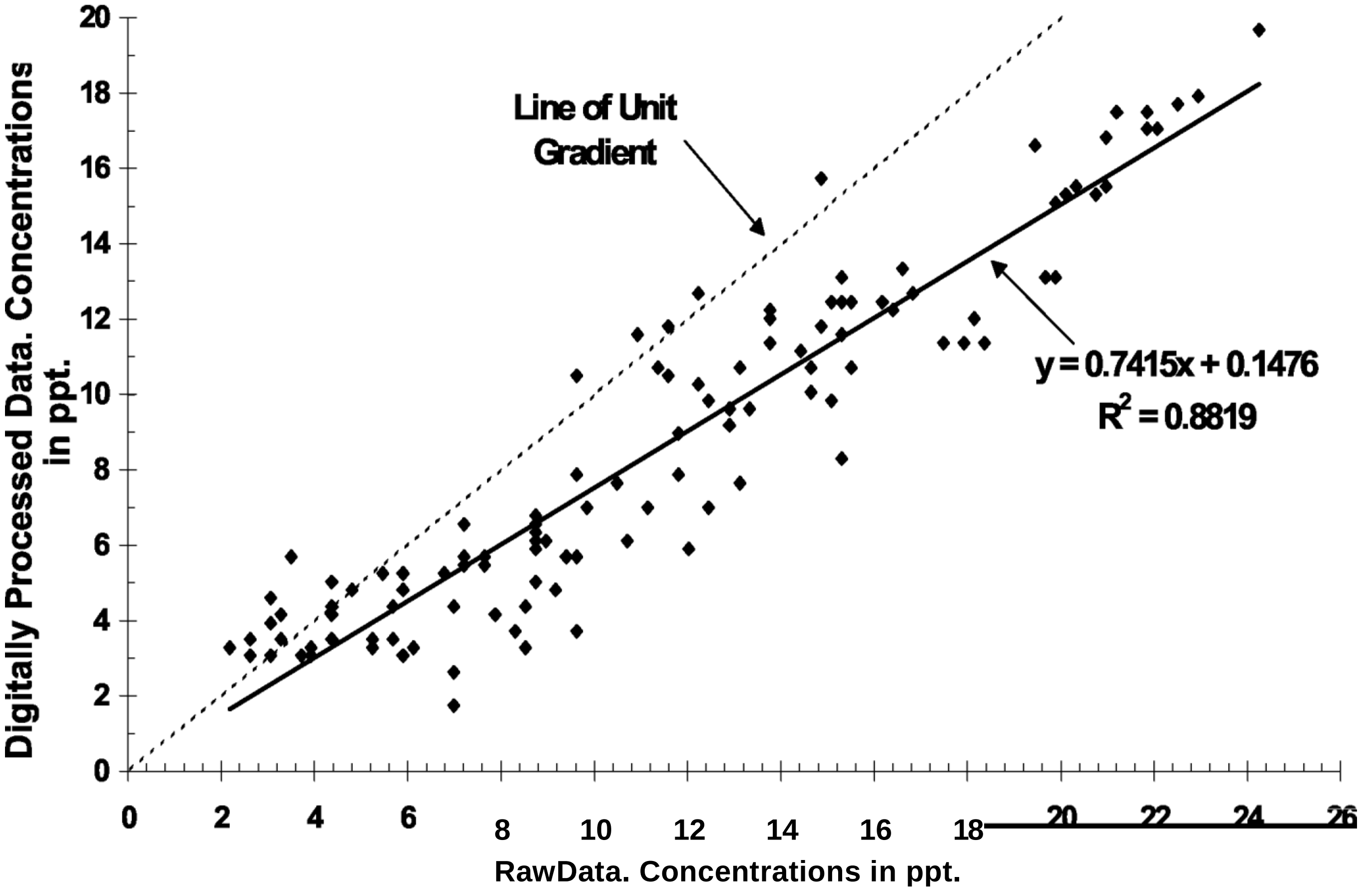


Figure 3: Comparison of 1,3-Butadiene determinations over a 6 day period in clean air (n=125)

Conclusions

Using a digital signal processing of FID electrometer output can improve minimum detectable amount by a factor of 6 - 10. Using an unprocessed data system a detection limit of 3-5 ppt is established (for a C_6 hydrocarbon species in a 1 L air sample). Using the processed output however, the detection limit is improved to around 0.5 - 0.8 ppt for the same species and sample volume. The reduction in amplifier noise significantly improves the reliability of peak integration by a factor of 4 for S/N levels between 2 and 5.

A constant overestimation of peak height was observed in integration of raw FID signal at low concentration levels. This over estimation arises from incorrect assignment of baseline by the integration software to the bottom of the baseline noise, this is removed by use of the DSP. For automated instruments operating under these types of atmospheric conditions this intrinsic error in integration has important implications on both system accuracy and resulting atmospheric model calculations based upon them. In applications such as the one presented a very wide dynamic detector range is not required. In this situation digital amplification of the processed signal may be used to eliminate noise induced at the data capture input stage, however the direct integration of digitally processed data direct to data capture software will ultimately produce the most significant improvements.

The Authors are aware that some manufacturers are using DSP techniques within their detectors. For this exercise, it was not possible to perform a direct comparison of the DSP unit used here with the digital filtering provided in other commercial detectors. Other studies with both GC and LC detectors have indicated that a minimum increase in signal to noise ratio of 5:1 can be achieved in addition any improvement that commercial detectors can provide [7].

Acknowledgments

The authors would like to express their thanks to Thomas Swan Co. for the kind loan of the ID/10 DSP unit and Dr. G. Ferrier for the supply of calibration mixtures. The inter comparison exercise was performed as part of the 1997 OXICOA experiment (UK NERC ACSOE thematic programme) for which funding is acknowledged.

This work has recently been accepted as a short communication in the Journal of High Resolution Chromatography.

References

[1] A.C Lewis, J.B McQuaid, D.H Heard, M.J Pilling and P.W Seakins. *J. Chem. Soc. Faraday Trans.* **1997,** 93, 2921

[2] P.G. Simmonds, R.G Derwent, A. McCulloch, S. O'Doherty, A. Gaudy. *Atmos. Environ.* **1996,** 30, 4041.

[3] A.V. Oppenheim, and R.W. Schafer, in *Digital Signal Processing.* **1975.,** Prentice Hall Inc. Englewood Cliffs, NJ, USA.

[4] A. Antoniou,. in *Digital Filters: Analysis, Design and Applications,* 2nd ed. **1993.,** McGraw-Hill Inc. New York. USA.

[5] K.D Jackson, S.J Walton, D Campbell. *J. Automatic Chemistry.* **1997,** 19, 145-152

[6] A.C Lewis, J.B McQuaid, P.W Seakins, M.J Pilling, K.D Bartle P Ridgeon. *J. High Res. Chrom.* **1996,** 19, 686.

[7] Thomas Swan, Consett, UK. Internal Report **1997**