Technical Note No AS147

Analysis of Formaldehyde from a Wax Candle Flame Using SIFT-MS

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Introduction

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is a real-time volatile organic compounds (VOCs) analyser. It uses controlled, soft ionisation techniques to rapidly quantify VOCs in gases, typically at detection limits of parts-per-trillion level (by volume; pptv). A previous application note (AS146) showed a small sample of the wide range of analyses that Syft Technologies' Voice 200*ultra* (see figure 1) can perform.

Figure 1: Syft Technologies' Voice 200*ultra* SIFT-MS instrument.

As with many small, polar molecules, formaldehyde analysis is a challenging task. Most chromatography techniques either give no response, poor detection limits or require trapping and derivatization prior to analysis. The inherent sensitivity of SIFT-MS to the small oxygenates offers a quick and easy alternative.

This application note will demonstrate the quantification of formaldehyde in the combustion products of lightly-scented wax candle by simply sampling with a syringe into a prefilled Tedlar bag.

Instrumentation

Syft Technologies' Voice 200*ultra* running LabSyft software (version 1.4.9)

Method

Voice 200*ultra* parameters:

Carrier gas – 99.999+% nitrogen
Heated inlet temperature – 120°C
Inlet flow (via restriction capillary) – 22 mL/min
Flow tube temperature – 110°C

As described in a previous application note (AS146), the accuracy of a SIFT-MS analysis can be improved by optimizing the reaction rates, *k*, for any of the analytes within the method. This is carried out by first analysing a known concentration and amending the library entry as appropriate. This was carried out using an 8.15 ppmv formaldehyde standard, prepared as described below. The following acquisition parameters were then used for the remainder of the analysis –

Reagent ions used – H_3O^+
Product ions used for quantitation – $H_2CO.H^+$ (31Da), $H_2CO.H^+.H_2O$ (49Da)
Reaction rate, *k* – H_3O^+ (2.37 x 10^{-9}), $H_3O^+.H_2O$ (5.0 x 10^{-12})
Dwell time – 200 msec
Length of analysis – 30 seconds

Based on the above analysis time and the zero-grade air used for the standards and sample preparation, the following LOD applied –

Formaldehyde concentration / ppbv	
Zero-air background	33.5
Limit of detection	1.13

All measured results are background subtracted prior to reporting.

Standard Preparation

Formaldehyde gas standards were prepared by injecting known quantities of a 1000 ppm aqueous solution of formaldehyde into a 1L Tedlar bag, prefilled with zero-grade air. The bag was gently heated to facilitate volatilisation and allowed to stand for 15 minutes prior to analysis. Three primary standards were prepared – 16.3 ppmv, 8.15 ppmv and 4.07 ppmv. All subsequent gas standards were prepared by serial dilutions of the primary standards in appropriately prefilled 1L Tedlar bags. The standards were analysed, using the method detailed above, via a needle on the end of the SIFT-MS heated inlet (see figure 2). When standards or samples were not being analysed, the instrument had a constant flow of zero-grade air passing through it.
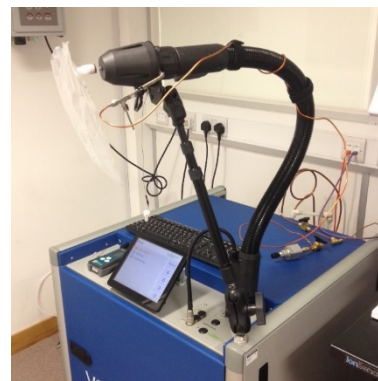

Figure 2: 1L Tedlar bag gas standard being sampled via the heated inlet of the Syft Voice 200*ultra*.

Sample Preparation

A lightly-scented wax candle was lit and allowed to burn for approximately 2 minutes to allow for stable generation of combustion products. Using a 50 mL syringe, the air close to the flame was sampled without allowing the syringe needle to come into contact with the flame. This was then injected into a prefilled 1L Tedlar bag and sampled in the same manner as the gas standards. Figure 3 shows the sampling process.

Figure 3: Sampling of combustion products from wax candle flame.

Results

Figure 4 and Table 1 (below) show the linearity results for the prepared formaldehyde gas standards. The linearity spanned three orders of magnitude and gave an R^2 value of 1.000. Concentrations lower than 16.1 ppbv were not prepared due to the difficulty of manually preparing low level standards by serial dilution in Tedlar bags and the relatively high level of formaldehyde in the air used for dilution.

Concentration of HCHO / ppbv	
Expected	Measured
16.1	23
31.5	35
53.5	54
81.9	76
206	204
413	425
819	829
1620	1610
4070	4060
8150	8120
16300	16200
R^2	1.000
Linearity equation	$y = 0.994x + 6.026$

Table 1: Linearity results for prepared formaldehyde gas standards.
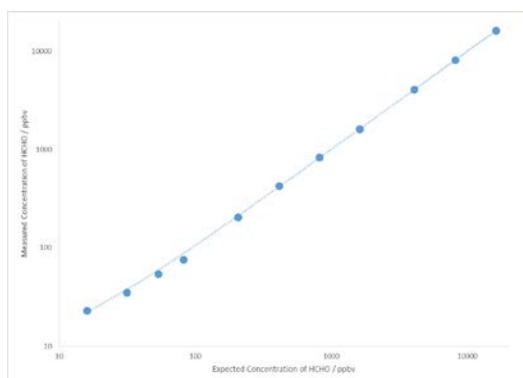

Figure 4: Linearity plot for prepared formaldehyde gas standards.

It can be seen from the slope of the regression line (m = 0.994) that there is a very good agreement between the measured and expected concentrations.

It should be noted that it is not necessary to run a set of calibration standards prior to analysis – SIFT-MS is inherently quantitative. Once there is confidence in the accuracy of the measurements being made, the instrument should not need to be recalibrated again.

Figure 5 shows plots for the concentration measurements of the three primary standards that were prepared from the aqueous formaldehyde solution. As all subsequent gas standards were derived from these, it important that these are accurate and the measured concentrations were as expected.
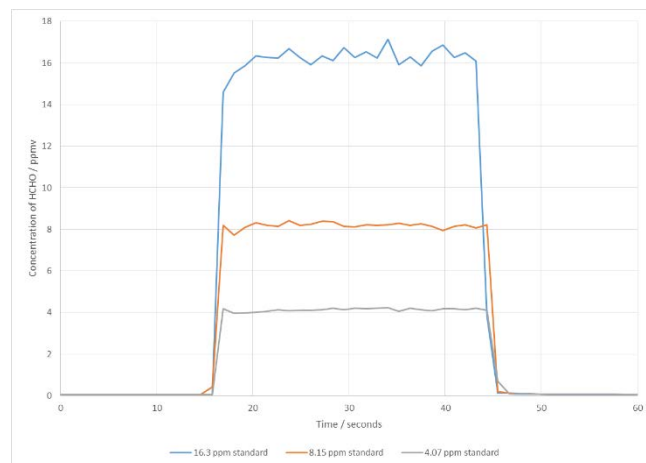

Figure 5: Plot of primary standard concentrations.

With three primary gas standards available for the subsequent serial dilution, it was possible to make lower concentration standards in more than one way. For example, the ~400 ppbv standard could be prepared either as a 1:20 dilution of the 8.15 ppmv standard or a 1:10 dilution of the 4.07 ppmv standard. Figure 6 shows the results from both of these preparation routes. It can be seen that there is very good agreement between the standards, which suggests that the serial dilution method will give accurate, lower level gas standards.
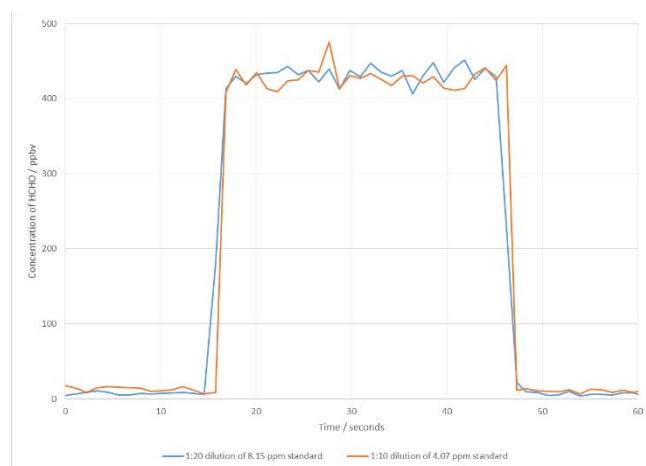

Figure 6: Plot of ~400 ppbv standard prepared via two different dilutions.

The precision of the measurement made by the instrument was assessed by repeat analyses of the prepared gas standards. Figure 7 and Table 2 show the results for the 206 ppbv gas standard. It can be seen that there is good agreement between all measurements.

Run no.	Average Measured Concentration / ppbv	%RSD of Measurement
1	195.9	5.2
2	210.7	4.5
3	203.0	4.1
4	204.8	4.2
Average Concentration	203.6	
%RSD	2.6	

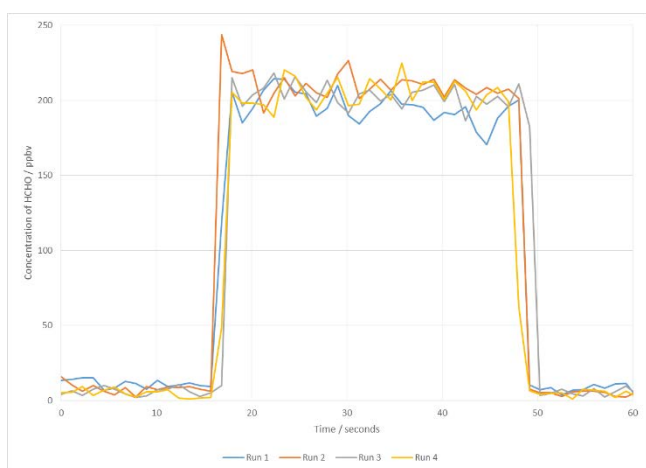**Table 2: Repeat measurement of a 206 ppbv gas standard.**

Figure 7: Plot of repeat measurements of a 206 ppbv gas standard.

The lowest concentration gas standard prepared was at 16.1 ppbv. Whilst the instrument can achieve lower limits of detections (see Method section) for this measurement time, generating low level standards via serial dilution in Tedlar bags can be problematic. Figure 8 shows the results from this gas standard measurement.
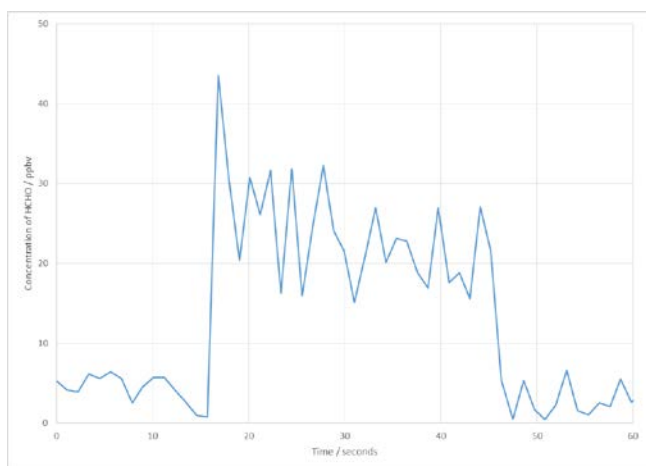

Figure 8: Plot of 16.1 ppbv gas standard measurement.

The concentration of formaldehyde in the combustion products from the wax candle was measured by injecting 50 mL of sampled air into a prefilled 1L Tedlar bag, giving a dilution of 1:20. Figure 9 and Table 3 show the results obtained from three repeat measurements of this sample.

Run no.	Average Measured Concentration / ppbv	%RSD of Measurement
1	235.2	4.8
2	234.6	5.8
3	233.7	3.6
Average Concentration	234.5	
%RSD	0.28	

Table 3: Results from measurement of formaldehyde concentration in the combustion products of a wax candle flame.
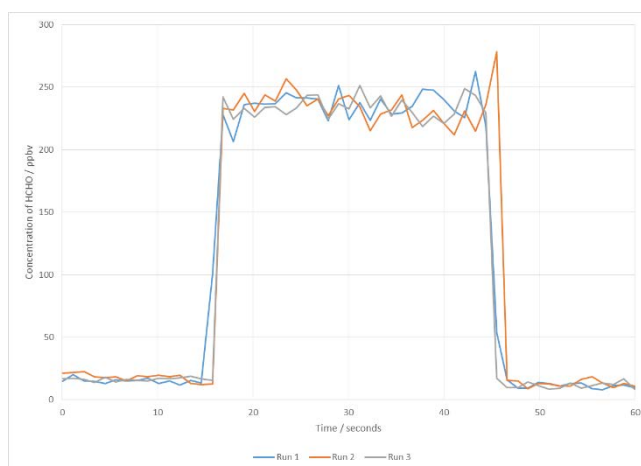

Figure 9: Plot of formaldehyde concentration in the combustion products of a wax candle flame.

Based on a dilution of 1:20 and converting from ppbv to mg/m^3 of air, the amount of formaldehyde degassed from this candle sample was found to be 6.4 mg/m^3.

Discussion

This application note has shown how SIFT-MS can make straightforward measurements of formaldehyde concentration around a burning candle flame. Accurate results can be obtained from only a few seconds of measurement time and over a wide concentration range without the need to trap, preconcentrate or other more complicated sampling techniques. Anatune have previously demonstrated HCHO determination by automated deviatisation and detection by HPLC (Note no. AS109).