APPLICATION NOTE

Prima PRO Process Mass Spectrometer

Controlling emissions by multi-component analysis of Volatile Organic Compounds (VOC)

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• Volatile Organic Compounds (VOC)

• Total Organic Carbon (TOC)

• Activated carbon adsorption

• Emissions control

• Magnetic Sector

• Secondary Electron Multiplier (SEM)

• Flame Ionization Detector (FID)

Introduction
To comply with local regulations, air containing VOCs generated by a large pharmaceutical site is fed to an activated carbon adsorption plant at a rate of 60,000 cubic meters/hour. The plant comprises three activated carbon beds; at any one time just one bed is being used, while the other two are being regenerated with steam. Activated carbon has small, low-volume pores that increase surface area; the surface area of one gram of activated carbon is more than 500 m^2, making it ideal for adsorbing VOCs. The plant is shown in schematic form in Figure 1.
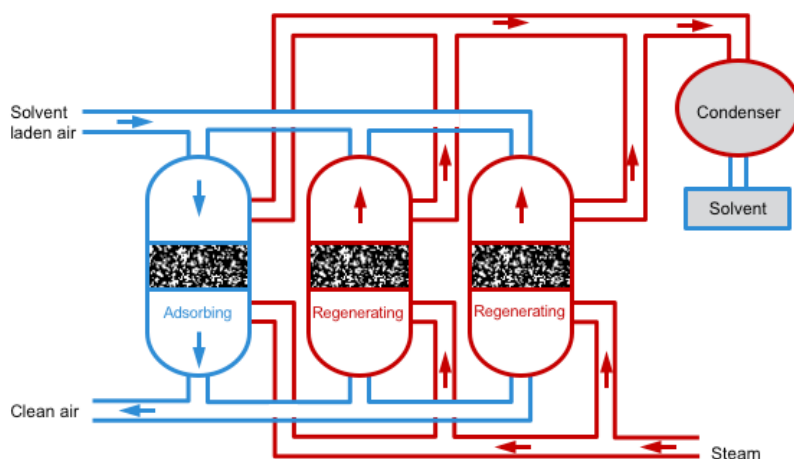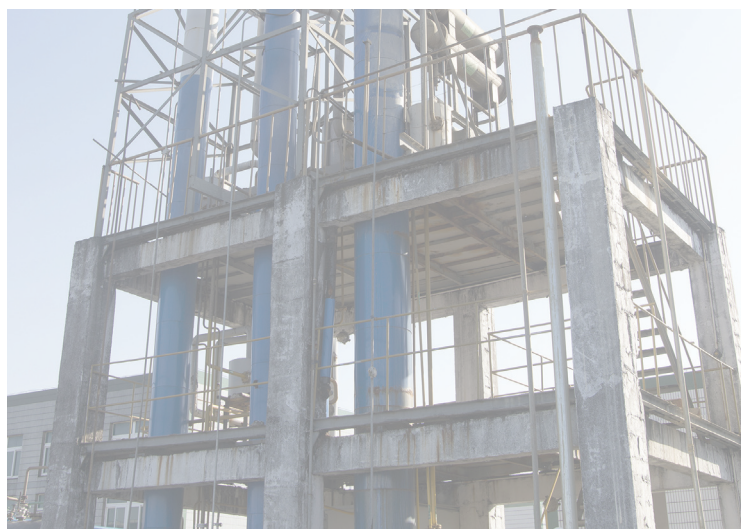

Figure 1 Schematic of activated carbon adsorption plant with three carbon beds

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Historically, the activated carbon adsorption plant operated by switching the plant air between beds approximately every 2.5 hours. This was the maximum rate, since it took around 5 hours to regenerate a bed for use again.

The adsorption plant inlet and outlet streams were monitored with Flame Ionization Detector (FID) analyzers; these only provide a reading of Total Organic Carbon (TOC), with no information on individual VOC concentrations. This online analysis was backed up by periodic laboratory analysis of average component concentrations with a Gas Chromatograph-Mass Spectrometer (GC-MS), using sample collection by adsorption trapping.

beds being switched prematurely, resulting in excess energy costs as steam was being used unnecessarily. They decided they needed a new gas analysis system with improved sensitivity and accuracy, providing the composition of each individual VOC. Real-time monitoring of individual component concentrations would enable the plant to predict when bed changeover was required, allowing more efficient steam use while still preventing over-limit emissions. They also needed the new gas analysis system to provide a continuous and complete log of all emissions at the site, providing evidence to regulating authorities that compliance with emission standards was being maintained.

Improving process control by implementing Process Mass Spectrometry

Plant management were concerned that switching beds on a simple time basis was potentially inefficient, with

Examples of VOC results

Example MS data from the time when the operation of the activated carbon plant was based on switching beds at fixed time intervals are shown in Figures 2 to 5.
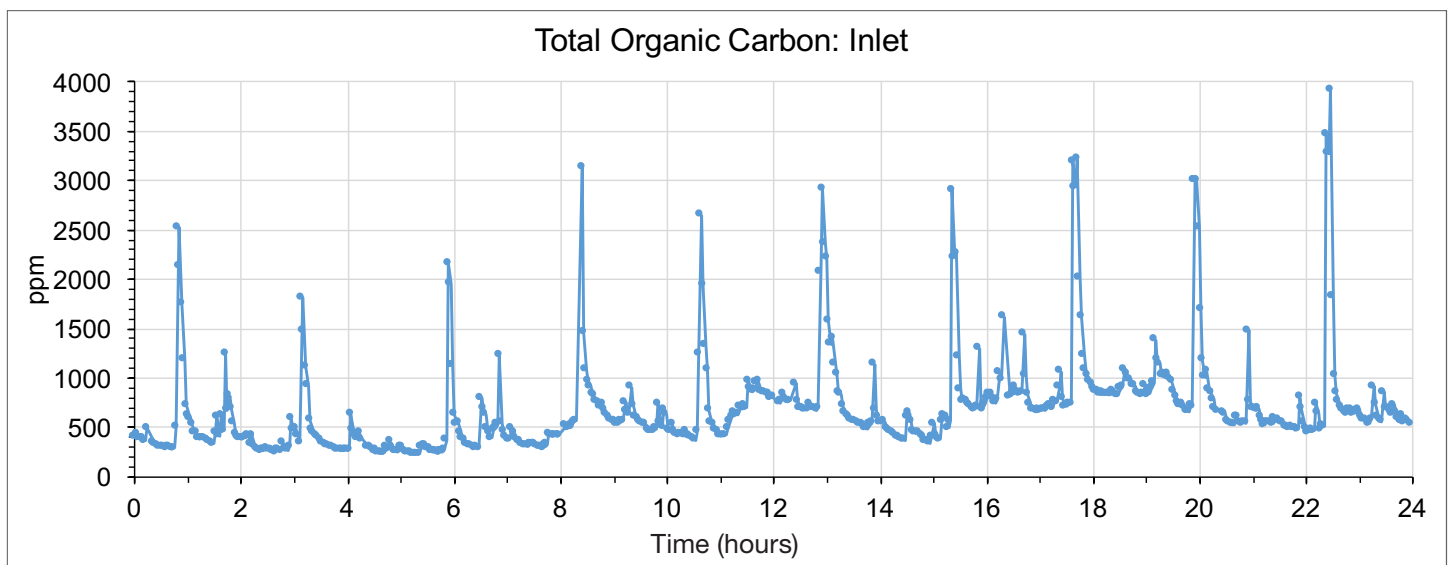

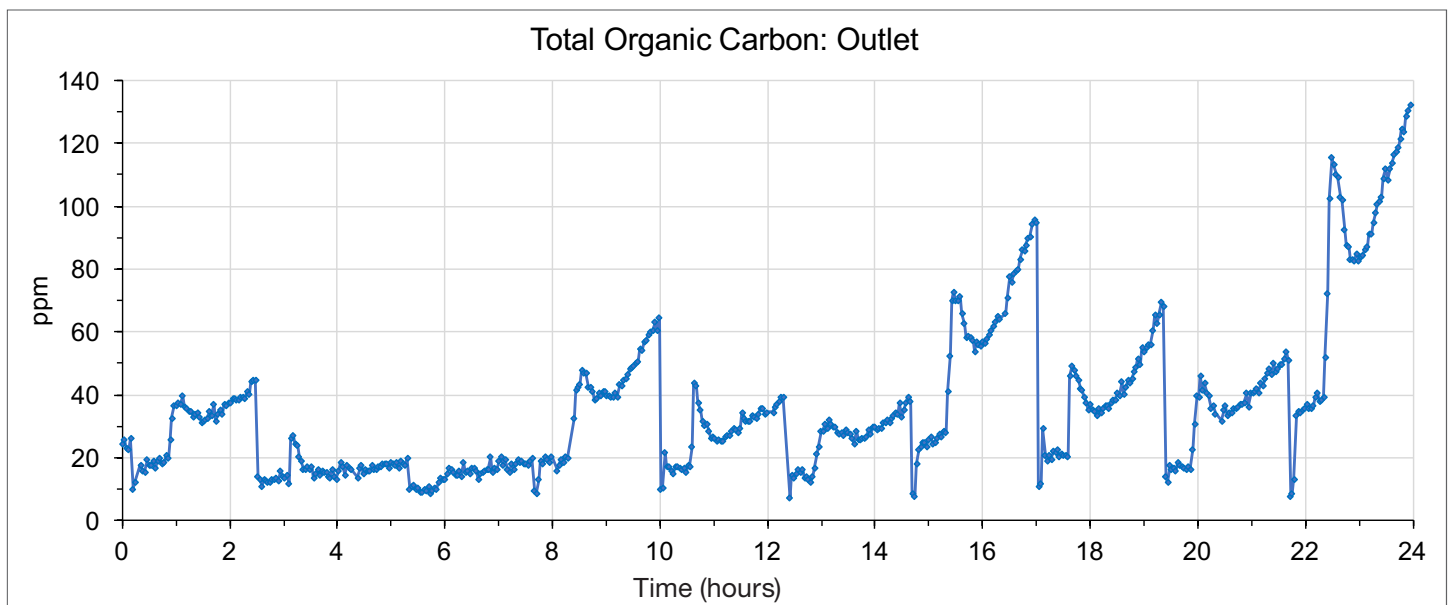**Figure 2 Inlet stream Total Organic Carbon**

Figure 3 Outlet stream Total Organic Carbon

Figure 2 shows the variable and sometimes high TOC level in the carbon adsorption plant inlet stream, while Figure 3 shows a much lower TOC level in the outlet stream, typically reduced by a factor of 20, where there is a regular accumulation effect between bed switches every 2.5 hours.
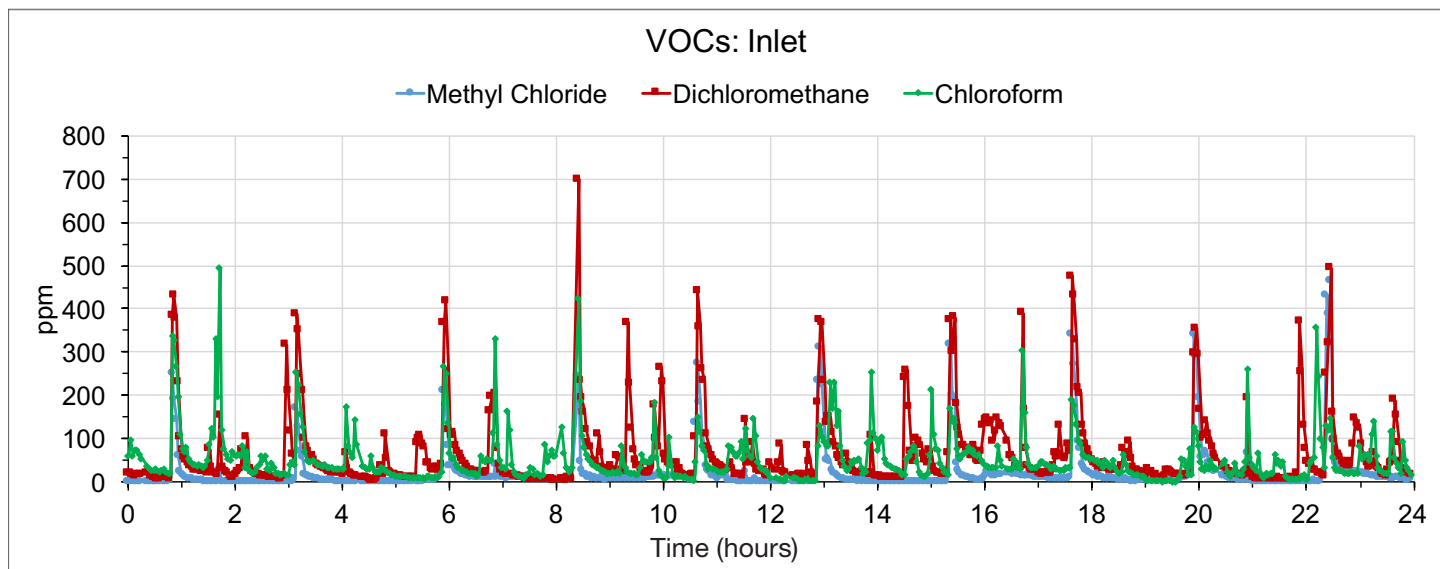

Figure 4 Three individual VOCs in the inlet stream
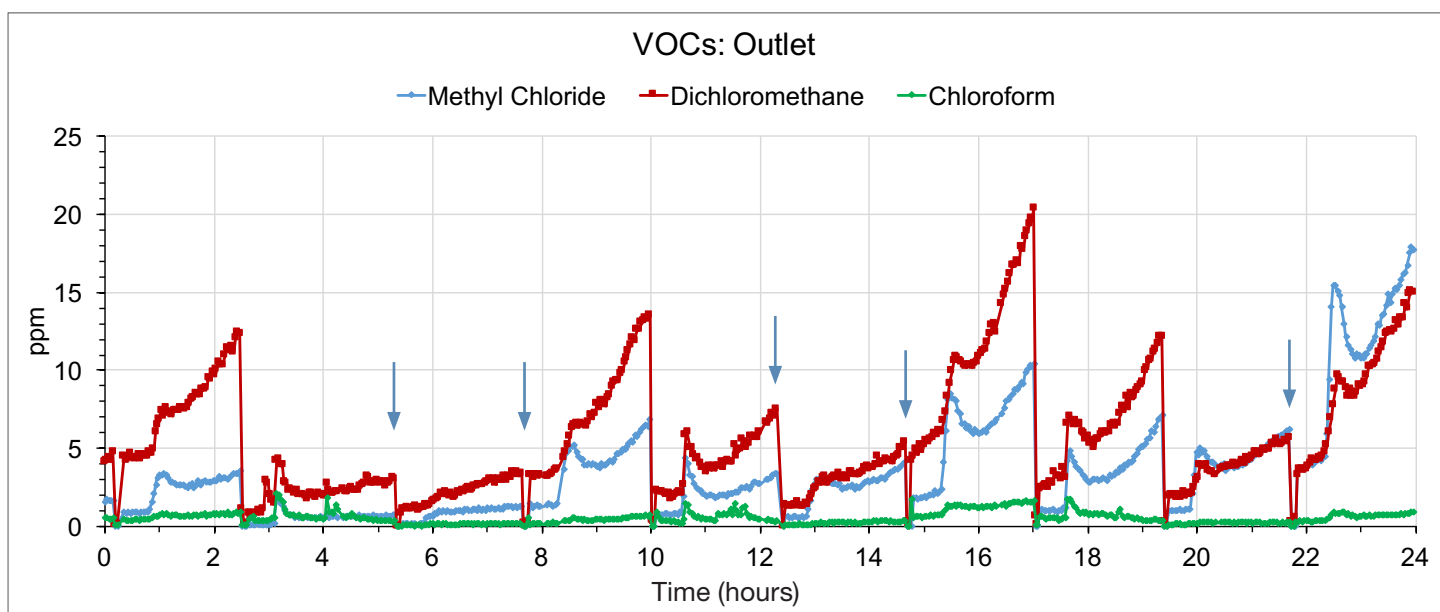

Figure 5 Three individual VOCs in the outlet stream, showing unnecessary bed switching

Figure 4 shows three of the major inlet VOCs, methyl chloride, dichloromethane and chloroform. Figure 5 shows these same three VOCs in the outlet. Of all the VOCs, the chlorides and methyl bromide have the lowest acceptable emission standards. It can be seen from Figures 3 and 5 that on five occasions the bed was switched unnecessarily, when the outlet VOC levels were relatively low. These five unnecessary bed switches out of a total of ten bed switches over the 24 hour period equates to consuming 70% more steam for bed regeneration than is necessary. This was the primary reason for installing the process mass spectrometer: to control the bed switching process to conserve energy and reduce the plant running costs.

TOC and individual VOC results for inlet and outlet are summarized in Table 1, showing the mean inlet TOC level of 692 ppm reduced to 36 ppm in the outlet.

Table 1 24 hours' inlet and outlet stream data from VOC adsorption plant

Component	Inlet mean	Inlet max.	Inlet min.	Outlet mean	Outlet max.	Outlet min.
Methanol	5.1	17.5	0.0	6.0	10.5	0.0
Ethanol	5.3	36.0	0.0	0.1	2.4	0.0
Methyl Chloride	20.7	463.9	0.0	3.5	17.9	0.0
Acetone	77.6	407.6	0.0	0.0	2.7	0.0
2-Propanol	11.9	30.4	5.2	0.8	1.6	0.0
Methyl Ethyl Ketone	27.4	167.1	3.1	1.1	4.8	0.0
Tetrahydrofuran	0.0	0.6	0.0	0.0	0.0	0.0
Dichloromethane	65.0	700.1	4.0	5.4	20.4	0.0
Toluene	3.9	51.3	1.0	0.0	0.1	0.0
Methyl Bromide	0.0	0.5	0.0	0.0	0.0	0.0
1,2 Dichloroethane	0.0	0.0	0.0	0.0	0.0	0.0
Methyl Isobutyl Ketone	22.0	349.9	0.7	2.3	11.8	0.0
Chloroform	52.9	495.4	2.2	0.5	2.1	0.0
TOC	**692.00**	**3914.4**	**232.0**	**36.3**	**132.3**	**7.3**

Comparison of MS and FID

Previously the site had used Flame Ionization Detector systems to monitor TOC levels. However the FID's response is extremely dependent on the species being measured, with halide and oxygen containing species giving a very different response from hydrocarbons [1], so that errors of 50% relative are possible. Calibration of an FID analyzer for this application is also problematic, because the component make up of the process gas is so variable. Using a FID to control bed switching therefore runs the risk of exceeding emission standards for individual or groups of components. Thermo Scientific™ Prima PRO's accurate multi-component analysis has allowed the site to control bed switching without exceeding emission standards.

Online process MS results were also compared with laboratory results using sample collection by adsorption trapping, followed by Gas Chromatograph-Mass Spectrometer analysis. Good agreement was obtained, which served as a final consistency check.

Advantages of Prima PRO Process MS

At the heart of the Prima PRO is a magnetic sector analyzer which offers unrivalled precision and accuracy compared with other mass spectrometers. Thermo Fisher Scientific manufactures both quadrupole and magnetic sector mass spectrometers; over thirty years of industrial experience have shown the magnetic sector based analyzer offers the best performance for industrial online gas analysis.

Key advantages of magnetic sector analyzers include improved precision, accuracy, long intervals between calibrations and resistance to contamination. Typically, analytical precision is between 2 and 10 times better than a quadrupole analyzer, depending on the gases analyzed and complexity of the mixture.

Neutral gas atoms and molecules are first converted into positively charged ions in the Prima PRO ion source. This is an enclosed type for high sensitivity, minimum background interference and maximum contamination resistance. It is a high-energy (1000 eV) analyzer that offers extremely rugged performance in the presence of gases and vapors that have the potential for contaminating the internal vacuum components. Prima PRO has a proven track record of monitoring high percent level concentrations of organic compounds without experiencing drift or contamination.

Ions are then accelerated through a flight tube, where they are separated by their mass to charge ratios in a magnetic field of variable strength. Since the magnetic sector mass spectrometer produces a focused ion beam at the detector, the peak shape obtained is 'flat-topped' and uniform response is observed over a finite mass width. As the height of the peak is directly proportional to the number of ions striking the detector it is also directly proportional to the concentration of the component being measured. As long as the measurement is taken anywhere on the peak's flat top, high precision analysis will be observed.

The system has a dual Faraday/Secondary Electron Multiplier (SEM) detector, with the Faraday detector used to measure percentage level major air components (nitrogen, oxygen and argon) and the SEM detector used to measure the ppm level components (carbon dioxide and VOCs). The relative response of the SEM detector compared to the Faraday detector is measured using the $^{16}O^{18}O$ mass 34 peak present at 800 ppm in air, which can be measured with high accuracy on both detectors.

Selectivity

Table 2 shows the relative sensitivities and mass spectral fragmentation patterns of the VOCs of interest, obtained after calibration. The VOC molecules generate a significant amount of spectral overlap; it is therefore extremely important that the fragment peaks are measured with high precision. There is an additional complication for measurements at mass 31, caused by the presence of a very large peak at mass 32 from the percentage levels of oxygen in the plant air. The intensity of the oxygen tail at mass 31 compared with the intensity of the oxygen molecular peak at mass 32 is 0.02%. So when the oxygen concentration is around 20%, this means the signal at mass 31 is equivalent to around 40 ppm. During calibration this interference is recorded and used to correct subsequent measurements of mass 31. With Prima PRO's magnetic sector instrument the measurement is very reproducible; on a quadrupole MS this interference level is much greater and also variable, resulting in excessive uncertainty in low level measurements of mass 31. Low level signals effectively tend to get 'buried' in the noise from the oxygen peak.

Table 2 Prima PRO VOC analysis set-up

Component	Relative Sensitivity	Fragmentation Patterns																		
		28	31	32	33	40	44	45	46	50	57	58	62	71	72	83	86	92.2	96	100
Nitrogen	1	100																		
Oxygen	0.85			100																
Argon	1.57					100														
Carbon dioxide	1.28						100	1.2	0.4											
Methanol	0.63		100					0.3	0.2	0.1	0.2	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0
Ethanol	1.01		100					38.2	19.4	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methyl chloride	0.87		7.1					1.2	0.7	100	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acetone	0.40		11.4					1.4	0.3	0.2	3.2	100	0.0	0.1	0.1	0.8	0.1	0.1	0.2	0.0
2-Propanol	1.61		8.7					100	2.5	0.1	0.4	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methyl ethyl ketone	0.36		13.3					12.5	0.5	2.3	34.5	2.3	0.0	4.5	100	0.2	0.1	0.1	0.0	0.0
Tetrahydrofuran	0.35		16.8					6.9	0.4	0.7	0.7	0.7	0.0	88.3	100	0.1	0.0	0.1	0.0	0.0
Dichloromethane	0.33		10.5					4.7	0.6	9.7	0.3	0.4	0.0	0.1	0.4	5.1	100	0.1	0.0	0.0
Toluene	1.41		2.8					9.4	6.3	5.6	0.1	0.1	3.9	0.0	0.0	0.1	1.0	100	0.0	0.0
Methyl bromide	0.45		8.3					17.6	10.1	0.6	0.3	0.2	0.1	0.0	0.1	0.2	0.1	4.9	100	0.0
1,2 Dichloroethane	0.39		8.8					1.0	0.2	2.4	0.4	0.3	100	0.0	0.1	0.3	0.0	0.0	0.5	16.4
Methyl isobutyl ketone	0.82		5.1					1.7	0.1	0.8	45.2	100	0.1	0.4	1.4	1.0	1.6	0.1	0.3	29.7
Chloroform	0.79		4.4					0.4	0.1	4.5	0.2	0.2	0.0	0.0	0.4	100	1.3	0.0	0.0	0.0

Figure 6 shows the logarithmic mass spectrum around mass 31 for air on the Prima PRO, Figure 7 shows the logarithmic spectrum for air containing around 400 ppm ethanol. The magnetic sector analyzer's flat-topped peaks are clearly shown in these figures.
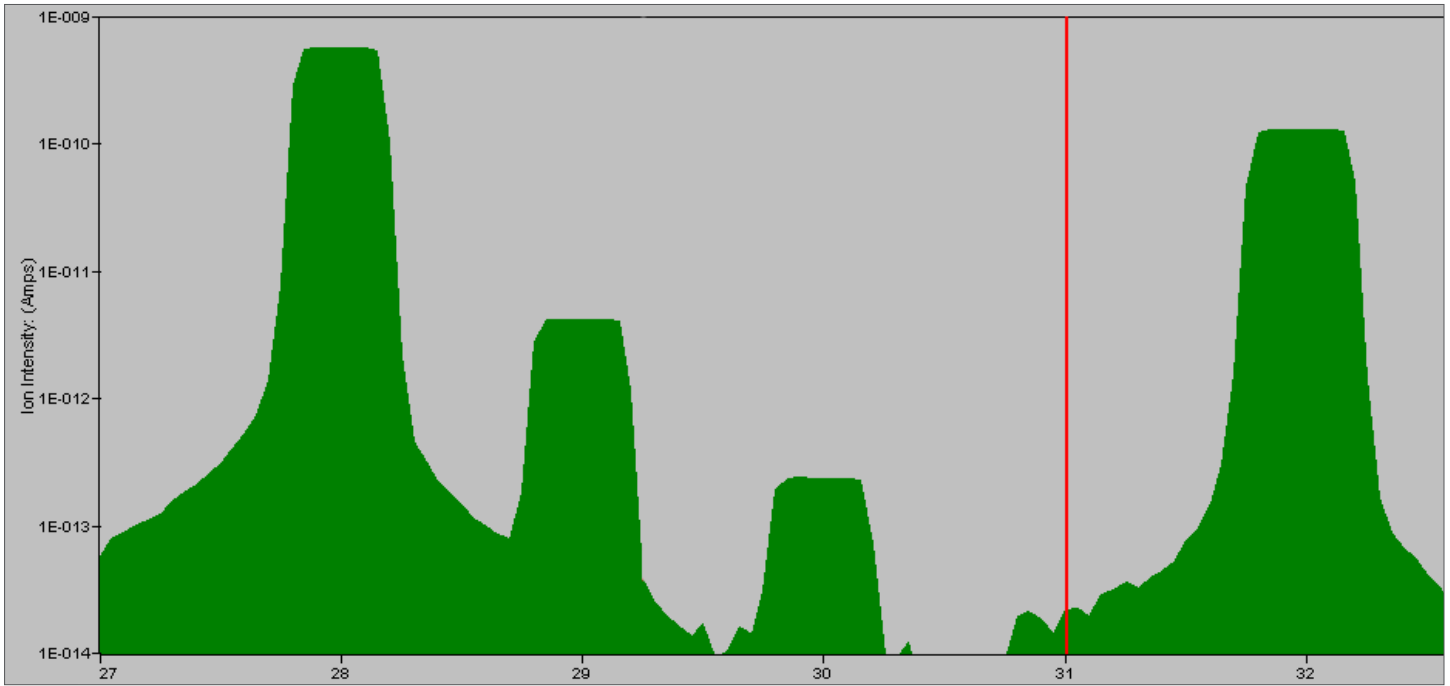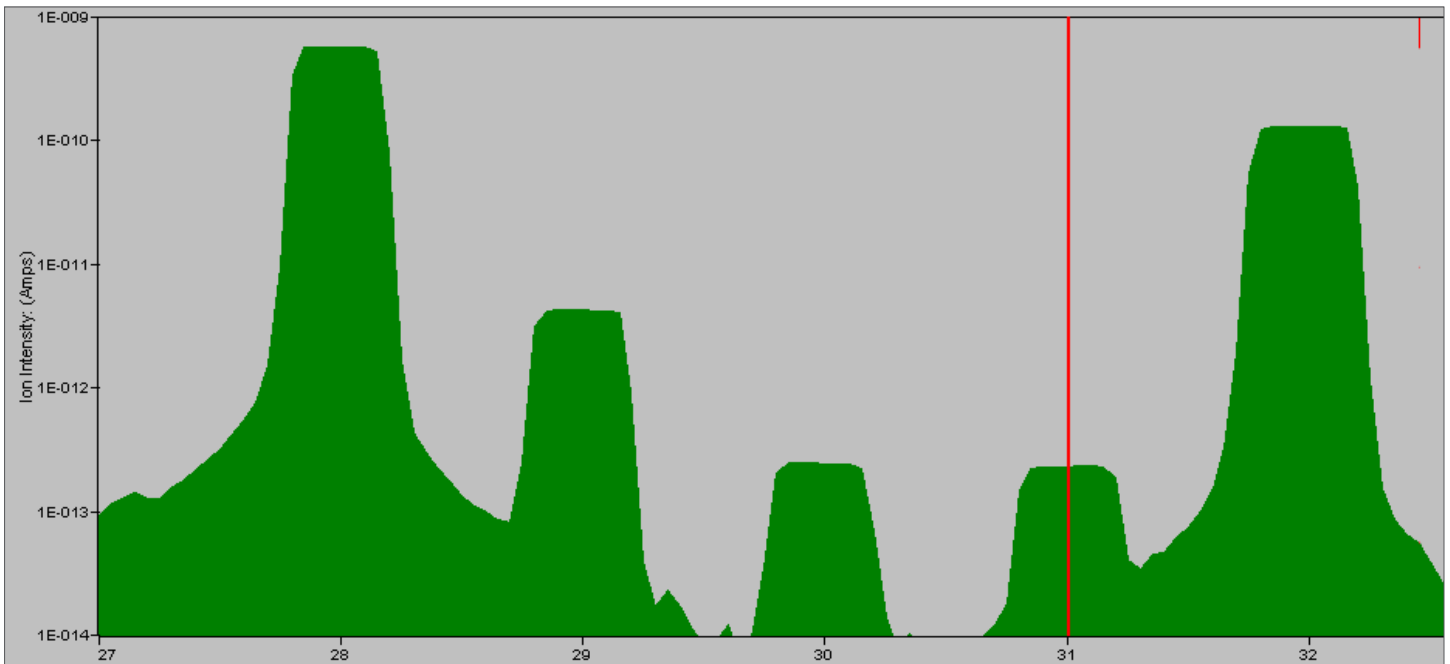

Figure 6 Spectrum of air

Figure 7 Spectrum of air with 400 ppm ethanol

The potential effects of cross interference can be tested by analyzing each VOC calibration gas sequentially. Typical results obtained by running each calibration gas in turn for 3 minutes are shown in Table 3.

The results from this test are generally extremely accurate, with no significant interferences and no interferences for the more harmful compounds such as the chlorides and methyl bromide, which have the lowest

Table 3 Calibration gas checks for accuracy and cross-interference

Calibration gas	Recorded mean result for calibrated VOC	Other VOCs recorded above 0.2 ppm
Methanol at 97.2 ppm in N_2	96.7 ppm	
Ethanol at 105.5 ppm in N_2	105.0 ppm	0.7 ppm Methanol, 0.2 ppm 2-Propanol
Methyl Chloride at 100.0 ppm in N_2	99.5 ppm	0.3 ppm Methanol
Acetone at 98.1 ppm in N_2	98.0 ppm	0.6 ppm Methanol
2-Propanol at 92.2 ppm in N_2	92.2 ppm	0.7 ppm Methanol
Methyl Ethyl Ketone at 97.1 ppm in N_2	97.4 ppm	0.4 ppm Methanol, 0.4 ppm Methyl Ethyl Ketone
Tetrahydrofuran at 99.4 ppm in N_2	99.8 ppm	0.4 ppm Methanol, 0.3 ppm Acetone
Dichloromethane at 103.5 ppm in N_2	104.7 ppm	0.2 ppm Methanol
Toluene at 99.0 ppm in N_2	99.7 ppm	0.3 ppm Methanol
Methyl Bromide at 99.9 ppm in N_2	99.9 ppm	0.5 ppm Methanol
1,2 Dichloroethane at 100.4 ppm in N_2	99.9 ppm	0.2 ppm Methanol
Methyl Isobutyl Ketone at 104.1 ppm in N_2	105.5 ppm	0.7 ppm Methanol, 0.2 ppm Methyl Ethyl Ketone
Chloroform at 98.2 ppm in N_2	99.3 ppm	0.6 ppm 2-Propanol
Air	78.09% N_2, 20.94% O_2, 0.930% Ar, 389 ppm CO_2	

acceptable emission standards. For example, the emission limit for methanol is twenty times higher than that of dichloromethane.

Stability

The stability of the system can be checked by the daily analysis of one of the calibration gases. A typical stability check on a cylinder containing 100 ppm of 1, 2 dichloroethane over 14 days without re-calibration is shown in Figure 8.

The day-to-day and longer term accuracy is typically ± 5% at the 100 ppm level. Over the short term (one hour), the reproducibility at 100 ppm is typically ± 1%. Longer term fluctuations are mainly due to changes in the SEM gain. These effects could be reduced if the results were normalized relative to a SEM peak representative of air, such as the $^{16}O^{18}O$ mass 34 peak; however it is more informative to see the additional analysis of the major air components nitrogen, oxygen and argon. These indicate that analysis results are correct - one of the problems with trace environmental analysis is that it is not always obvious that the results are 'real'. Including air components in the analysis serves as a consistency check.
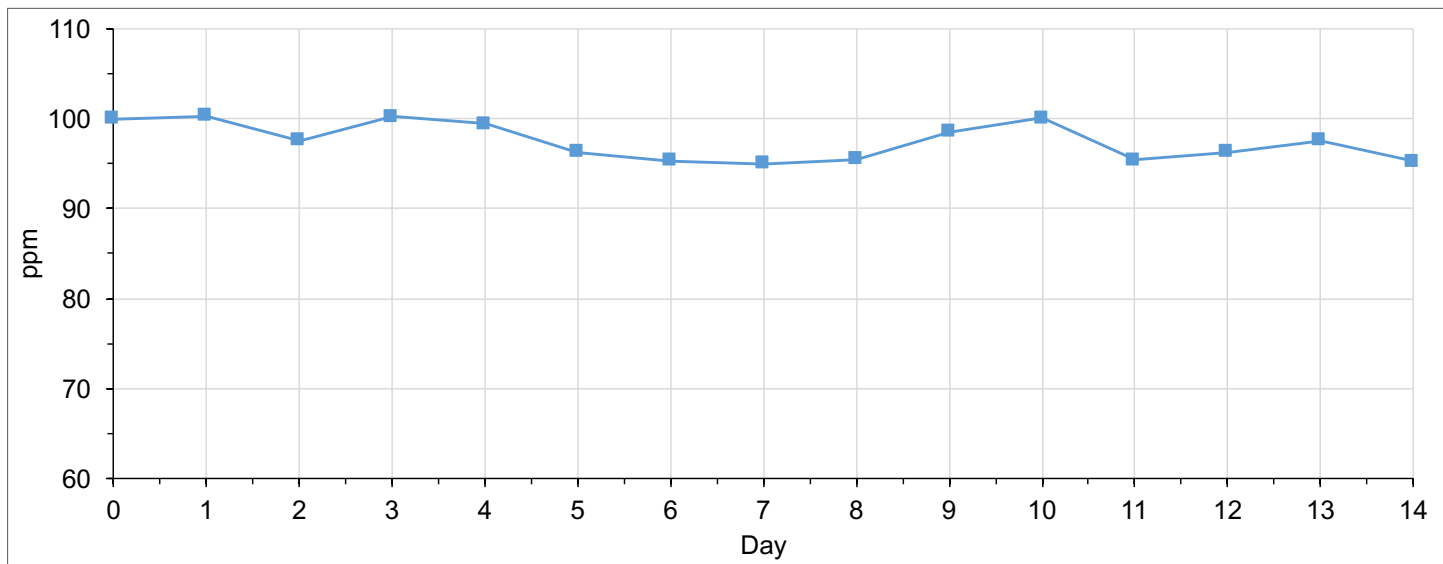
Figure 8 Stability check analysis of 1, 2 dichloroethane over 14 days without recalibration

Communication with Plant Control System

Analysis results of the inlet and outlet streams for each component can be transmitted from the Prima PRO to the plant control system by serial protocols such as Modbus or OPC, or by analog outputs. Digital outputs are available for stream identification, hardware faults, analyzer status (analyzing, standby or calibration) and component high concentration alarms.

In normal operation, Prima PRO is set to run a calibration check daily at a set time. If the analysis of one of the calibration gases is outside a certain tolerance (for example 5%), the instrument is automatically re-calibrated in respect of the SEM gain. If the check analysis is outside a wider tolerance (for example 10%), the instrument performs an automatic re-calibration of sensitivities and fragmentation patterns for all components. A digital signal tells the plant control system when the Prima PRO is performing a calibration.

Real-time monitoring of individual component concentrations can alert plant operation departments to limit the usage of a particular solvent or solvents.

Conclusions

• Prima PRO provides fast, accurate multi-component VOC analysis of inlet and outlet streams

• TOC analysis by Prima PRO has been shown to be more accurate than by FID, because of the variation in concentration levels of different VOC species

• Prima PRO's multi-component analysis means that emission sources can be identified and traced to source

• Component alarms can be used as warnings to limit individual solvent usage, preventing over-limit emissions

• On a multi-bed carbon adsorption plant, bed switch-over is controlled by Prima PRO's analysis of emissions, leading to a considerable reduction in steam usage and plant running costs

• Prima PRO generates a continuous and complete log of all emissions, providing evidence to regulating authorities that compliance with emission standards was being maintained

Reference

1. Analytical Instrumentation, editors R.E. Sherman and L. Rhodes, *Instrument Society of America*, 627-629 (1996)

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