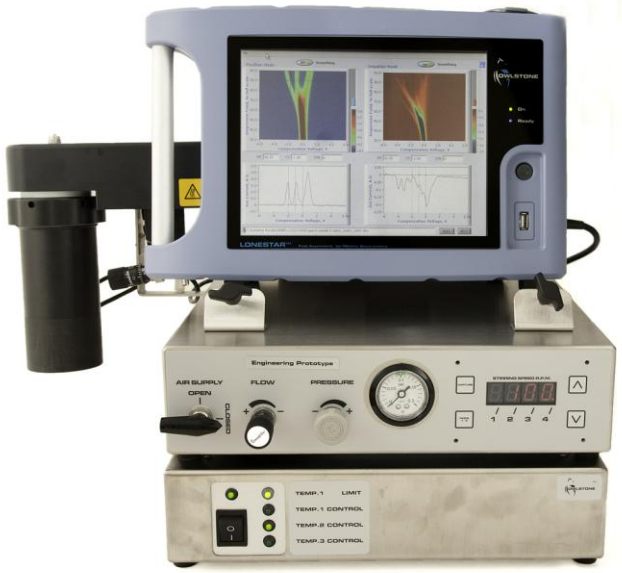
Quantification of Methanol in Crude Oil Using a LONESTAR™ Portable Analyzer

Standard Operating Procedure



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Introduction

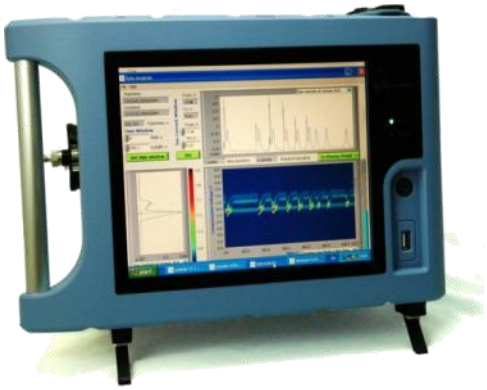
The presence of certain contaminants in crude oil can cause expensive problems at downstream processing plants. Species such as methanol and triazine can impact refinery water treatment facilities and cause corrosion and fouling in downstream equipment. The Lonestar crude oil analyzer is a versatile new instrument that can be used by non-specialist personnel to detect and quantify a wide range of possible crude contaminants.

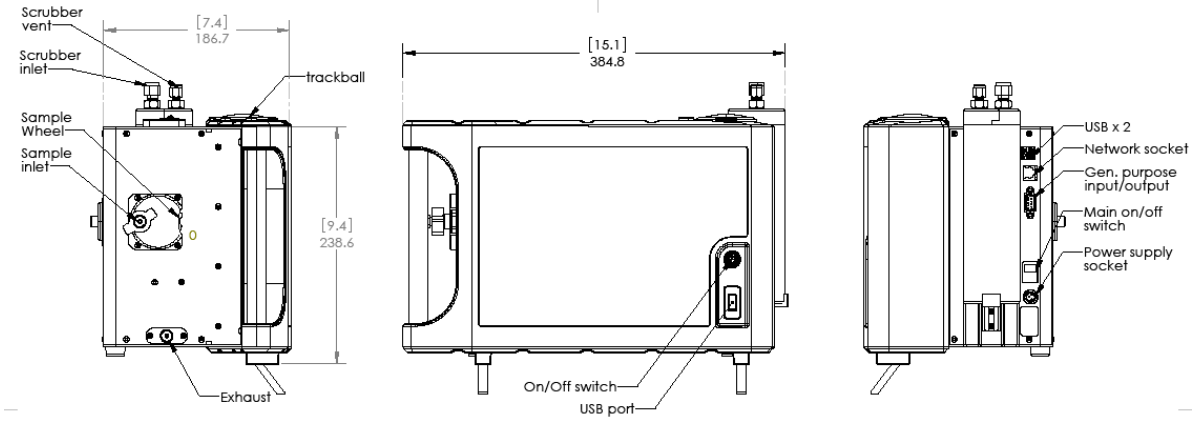
Utilising Owlstone's proprietary Field Asymmetric Ion Mobility Spectrometry (FAIMS) technology (see Appendix A), Lonestar can be used at-line to analyze crude oil samples, ensuring the quality of crude before it reaches the refinery. A major advantage of the Lonestar system is that no special sample preparation is necessary other than weighing a small quantity of crude into a sample holder. The crude analysis itself takes only 7 minutes after which Lonestar provides a simple concentration value (in ppm) of the contaminant in question. Lonestar can also be easily configured to provide a warning if the measured concentration is outside of pre-designated limits.

This document details the procedure used to detect the methanol content of a crude oil sample.

The LONESTAR™ Portable Analyzer

The LONESTAR is an analytically powerful, portable chemical analyzer that can be operated by non-specialists. Incorporating Owlstone's proprietary FAIMS technology (see Appendix A), the instrument combines high sensitivity and selectivity. New methods can be developed using Owlstone's EasySpec software, making the LONESTAR suitable for a broad range of applications in the oil industry.





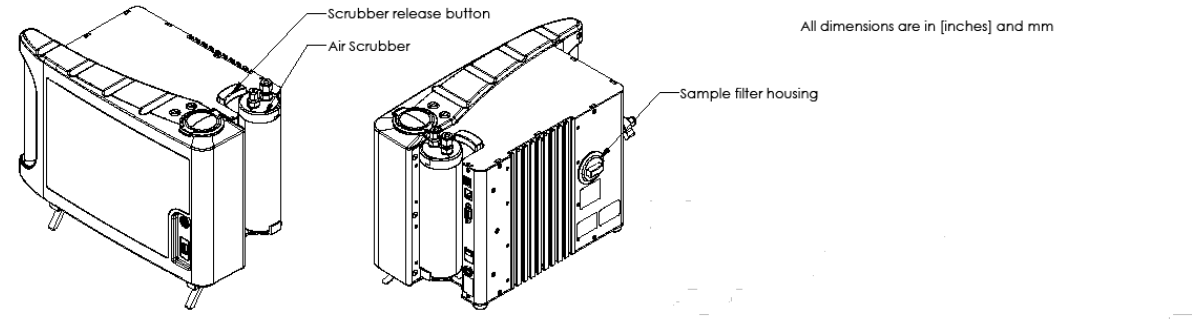


Figure 1 LONESTAR connection figures

Lonestar Method for Methanol detection in a Crude oil matrix

Principles

A 10g of sample of crude oil is weighed out into a sampling bottle accurately using an analytical balance. The sample is then loaded into a pre-calibrated Lonestar system which continually flushes the headspace with clean dry air. Within the sampling module of the Lonestar the air flow is split and then diluted by another factor of 1 in 2000. The purpose of this is to reduce the background signal from the crude oil matrix, allowing a clearer methanol response to be seen.. As the headspace replenishment rate is temperature dependent, the sample temperature is controlled at 35°C. The sample is then left to pre-concentrate for 5 minutes, allowing equilibration to the optimum sampling conditions. This ensures that each sample is tested under the same conditions, minimising sample to sample variation. A measurement is then taken and displayed as a concentration in parts per million (ppm).

Sampling apparatus

- Plastic Pasteur pipette (Part number Fisher Scientific FB 55345)
- Analytical balance
- 120ml glass sampling vessel (bottle)
- O-ring (Part number Owlstone 50-0510)

Directions

- Load an empty glass bottle into the Lonestar(Figure 2). Place bottle into the at-line sampling module bottle holder, fit bottle holder into the Lonestar and tighten the securing nut until snug.

Figure 2 – Loading sample bottle

- The Lonestar analyzer screen appears as shown in Figure 3. On the drop down menu labelled ‘Method’, select the Methanol Content Configuration if not already selected.
- Click the ‘Check Cleandown’ button. The button will only be selectable if the top banner is green. If it is red, one or more parameter does not match the method file, consult troubleshooting guide.

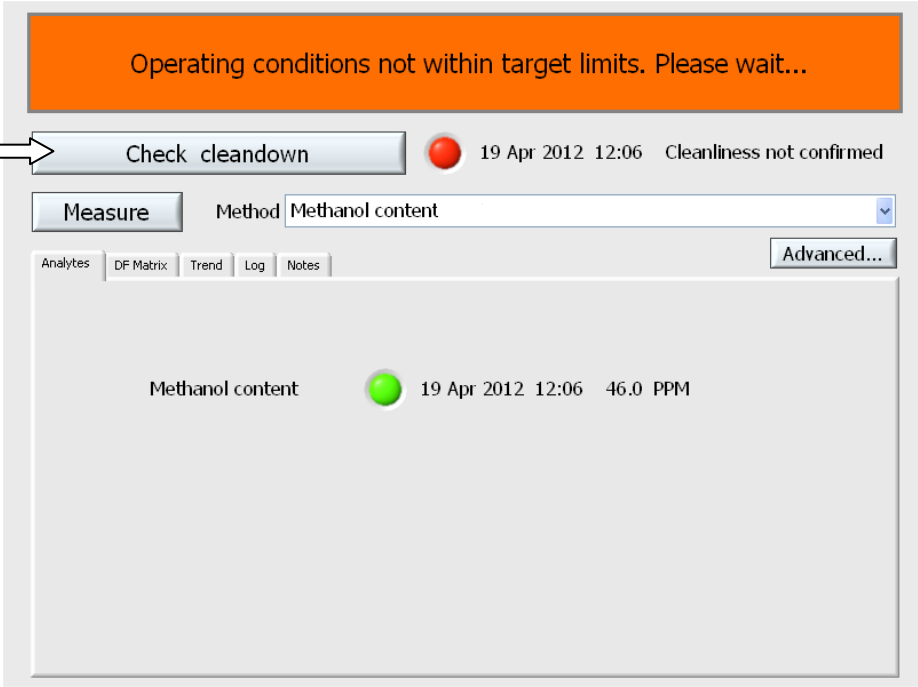


Figure 3 – Lonestar analyser Screen

- A pop up message will appear, click the 'OK' button to continue. The software will then check that the system is clean and ready to begin a measurement.
- If the bottle and system is clean, the light by the 'Check' button will switch from red to green and a time stamped 'Cleanliness Confirmed' message will appear. The system is now ready to receive a sample - it can be left in this state almost indefinitely, but if the time exceeds 4 hours it is recommended that the check is rerun before taking the sample. The time to carry out a check is less than 2 minutes. The light will be green and the 'Measure' button will no longer be greyed out.
- Unload the sample by releasing the securing nut.
- Using a plastic Pasteur pipette, weigh 10g of a representative crude oil sample into the glass sampling vessel.
- Load the sample into Lonestar as before, place bottle into bottle holder, fit bottle holder onto interface on the Lonestar and spin the securing nut until tight.
- Select the 'Measure' button on the analyser screen (Figure 4, left), this will trigger a pop up window that asks for a filename. Name the file and then click ok (Figure 4, right).

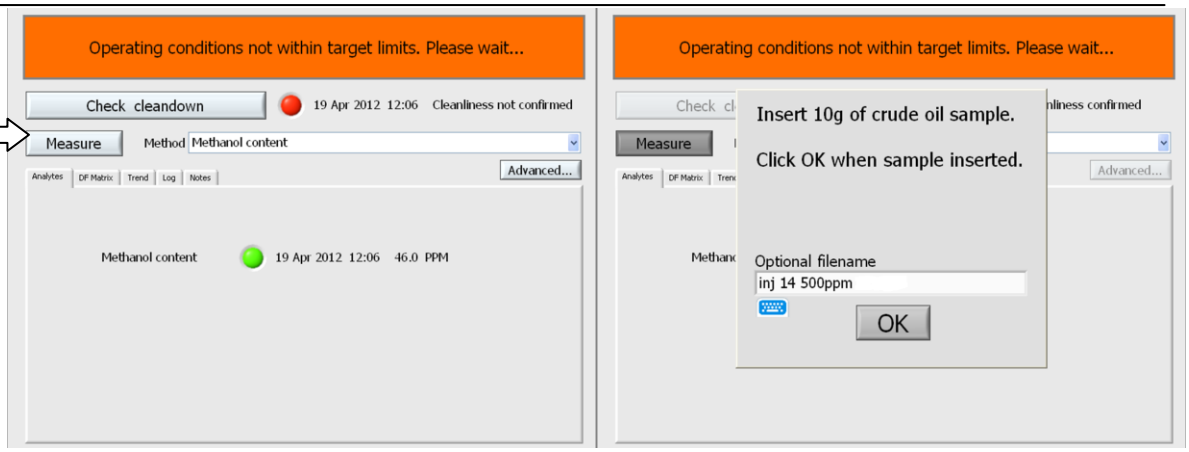


Figure 4 - Select measure button

- Analysis time is approximately 7 minutes including the pre-concentration waiting period. Upon completion, the screen is updated with the measured concentration and a time stamp. The cleanliness of the system will switch to 'Unconfirmed' and the indicator will turn red waiting for another blank bottle.

Figure 5 – Results screen

- Remove the sample from Lonestar and swap in a fresh clean bottle to allow the system to blank.
- Select the 'Check Clean' button on the analyser screen.
- The system is then ready for the next sample.

Lonestar - Calibration check standard

Principles

In order to check the system functionality a test sample is created at a mid-range concentration for the application. The analyzer output for the sample should be within the 10% of the expected signal (the specified accuracy for the method), if it fails then a calibration adjustment will be required.

Reagents and Apparatus

- Methanol CAS No:- 67-56-1
- Crude oil
- 2-100µl positive displacement pipette & pipette tips
- 120ml glass sampling vessel
- O-ring
- Analytical balance
- Stirring plate set to 400RPM
- Fridge to store sample
- Glass double ended magnetic spinner 40mm (Part number Fisher Scientific FB55628)
- 100ml Duran bottle (Part number Fisher scientific FB 33144) with lid

Directions (100ppm check standard)

- Place magnetic stirrer into 100ml Duran bottle
- Using an analytical balance weigh out 50g of crude oil into 100ml Duran bottle using a plastic Pasteur
- Using the 2-10ul positive displacement pipette, pipette 6.3ul of methanol into the 50g of crude oil.
- Place lid on top of Duran bottle & label
- Invert sample 3 times and place on stirring plate
- Set plate to 400RPM and leave for 40 minutes
- When sample has finished stirring place in the fridge set to 4°C and leave until needed for sampling. Allow at least 10 minutes for sample to cool down before first sample run.
- Note that this sample should be kept refrigerated at all times as the methanol has a very low boiling point, allowing this to build up into the headspace of the Duran bottle therefore destroying the sample immediately when opened.
- Each standard will run a maximum of 4 samples.
- Load sample into Lonestar and run sample as in the method above
- Analyser output should be 100ppm +/-10%. If outside of this range, first repeat sampling on a fresh sample and then refer to the troubleshooting guide.

Appendix A: FAIMS Technology at a Glance

Field asymmetric ion mobility spectrometry (FAIMS), also known as differential mobility spectrometry (DMS), is a gas detection technology that separates and identifies chemical ions based on their mobility under a varying electric field at atmospheric pressure. Figure 6 is a schematic illustrating the operating principles of FAIMS.

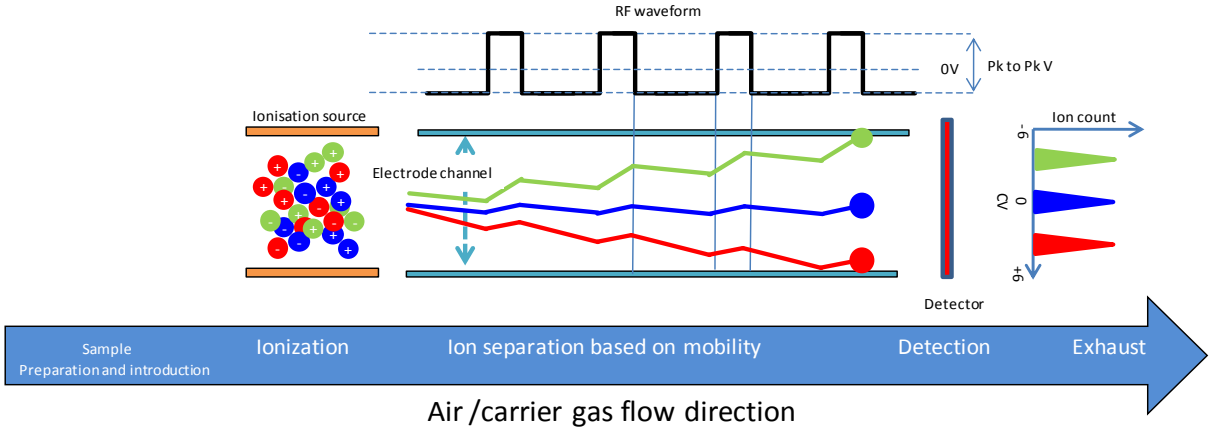


Figure 6 FAIMS schematic. The sample in the vapour phase is introduced via a carrier gas to the ionisation region, where the components are ionised via a charge transfer process or by direct ionisation, dependent on the ionisation source used. It is important to note that both positive and negative ions are formed. The ion cloud enters the electrode channel, where an RF waveform is applied to create a varying electric field under which the ions follow different trajectories dependent on the ions' intrinsic mobility parameter. A DC voltage (compensation voltage, CV) is swept across the electrode channel shifting the trajectories so different ions reach the detector, which simultaneously detects both positive and negative ions. The number of ions detected is proportional to the concentration of the chemical in the sample

Sample preparation and introduction

FAIMS can be used to detect volatiles in aqueous, solid and gaseous matrices and can consequently be used for a wide variety of applications. The user requirements and sample matrix for each application define the sample preparation and introduction steps required. There are a wide variety of sample preparation, extraction and processing techniques each with their own advantages and disadvantages. It is not the scope of this overview to list them all, only to highlight that the success of the chosen application will depend heavily on this critical step, which can only be defined by the user requirements.

There are two mechanisms of introducing the sample into the FAIMS unit: discrete sampling and continuous sampling. With discrete sampling, a defined volume of the sample is collected by weighing, by volumetric measurement via a syringe, or by passing vapor through an adsorbent for pre-concentration, before it is introduced into the FAIMS unit. An example of this would be attaching a container to the instrument containing a fixed volume of the sample. A carrier gas (usually clean dry air) is used to transfer the sample to the ionization region. Continuous sampling is where the resultant gaseous sample is continuously purged into the

FAIMS unit and either is diluted by the carrier gas or acts as the carrier gas itself. For example, continuously drawing air from the top of a process vat.

The one key requirement for all the sample preparation and introduction techniques is the ability to reproducibly generate and introduce a headspace (vapour) concentration of the target analytes that exceeds the lower limits of detection of the FAIMS device.

Carrier Gas

The requirement for a flow of air through the system is twofold: Firstly to drive the ions through the electrode channel to the detector plate and secondly, to initiate the ionization process necessary for detection.

As exhibited in Figure 7, the transmission factor (proportion of ions that make it to the detector) increases with increasing flow. The higher the transmission factor, the higher the sensitivity. Higher flow gives a larger full width half maximum (FWHM) of the peaks but also decreases the resolution of the FAIMS unit (see Figure 8).

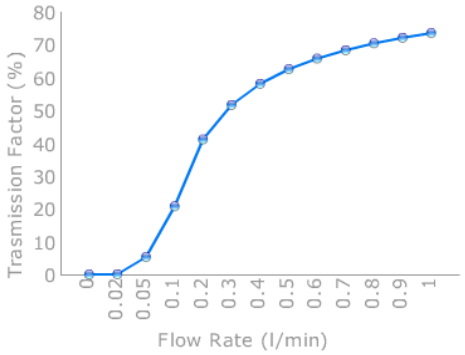


Figure 7 Flow rate vs. ion transmission factor

The air/carrier gas determines the baseline reading of the instrument. Therefore, for optimal operation it is desirable for the carrier to be free of all impurities (< 0.1 ppm methane) and the humidity to be kept constant. It can be supplied either from a pump or compressor, allowing for negative and positive pressure operating modes.

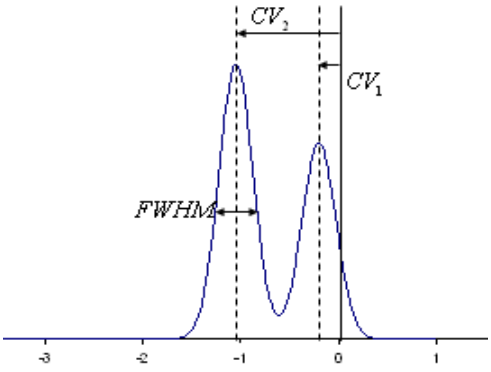


Figure 8 FWHM of ion species at set CV

Ionisation Source

There are three main vapor phase ion sources in use for atmospheric pressure ionization; radioactive nickel-63 (Ni-63), corona discharge (CD) and ultra-violet radiation (UV). A comparison of ionization sources is presented in Table 1.

Ionisation Source	Mechanism	Chemical Selectivity
Ni^{63} (beta emitter) creates a positive / negative RIP	Charge transfer	Proton / electron affinity
UV (Photons)	Direct ionisation	First ionisation potential
Corona discharge (plasma) creates a positive / negative RIP	Charge transfer	Proton / electron affinity

Table 1 FAIMS ionization source comparison

Ni-63 undergoes beta decay, generating energetic electrons, whereas CD ionization strips electrons from the surface of a metallic structure under the influence of a strong electric field. The generated electrons from the metallic surface or Ni-63 interact with the carrier gas (air) to form stable +ve and -ve intermediate ions which give rise to reactive ion peaks (RIP) in the positive and negative FAIMS spectra (Figure 9). These RIP ions then transfer their charge to neutral molecules through collisions. For this reason, both Ni-63 and CD are referred to as indirect ionization methods.

For the positive ion formation:

$N_2 + e^- \rightarrow \mathbf{N_2^+} + e^-$ (primary) + e^- (secondary)
$\mathbf{N_2^+} + 2N_2 \rightarrow \mathbf{N_4^+} + N_2$
$N_4+ + H_2O \rightarrow 2N_2 + \mathbf{H_2O^+}$
$H_2O+ + H_2O \rightarrow \mathbf{H_3O^+} + OH$
$H_3O+ + H_2O + N_2 \leftrightarrow \boldsymbol{H^+(H_2O)_2} + N_2$
$H^+(H_2O)_2 + H_2O + N_2 \leftrightarrow \boldsymbol{H^+(H_2O)_3} + N_2$

For the negative ion formation:

$O_2 + e^- \rightarrow \mathbf{O_2^-}$
$B + H_2O + \mathbf{O_2^-} \leftrightarrow \boldsymbol{O_2^-(H_2O)} + B$
$B + H_2O + O_2^-(H_2O) \leftrightarrow \boldsymbol{O_2^-(H_2O)_2} + B$

The water based clusters (hydronium ions) in the positive mode (blue) and hydrated oxygen ions in the negative mode (red), are stable ions which form the RIPs. When an analyte (M) enters the RIP ion cloud, it can replace one or dependent on the analyte, two water molecules to form a monomer ion or dimer ion respectively, reducing the number of ions present in the RIP.

Monomer Dimer

$$H^+(H_2O)_3 + M + N_2 \leftrightarrow M\boldsymbol{H^+(H_2O)_2} + N_2 + H_2O \leftrightarrow M_2\boldsymbol{H^+(H_2O)_1} + N_2 + H_2O$$

Dimer ion formation is dependent on the analyte's affinity to charge and its concentration. This is illustrated in Figure 9A using dimethyl methylphsphonate (DMMP). Plot A shows that the RIP decreases with an increase in DMMP concentration as more of the charge is transferred over to the DMMP. In addition the monomer ion decreases as dimer formation becomes more favourable at the higher concentrations. This is shown more clearly in Figure 9B, which plots the peak ion current of both the monomer and dimer at different concentration levels.

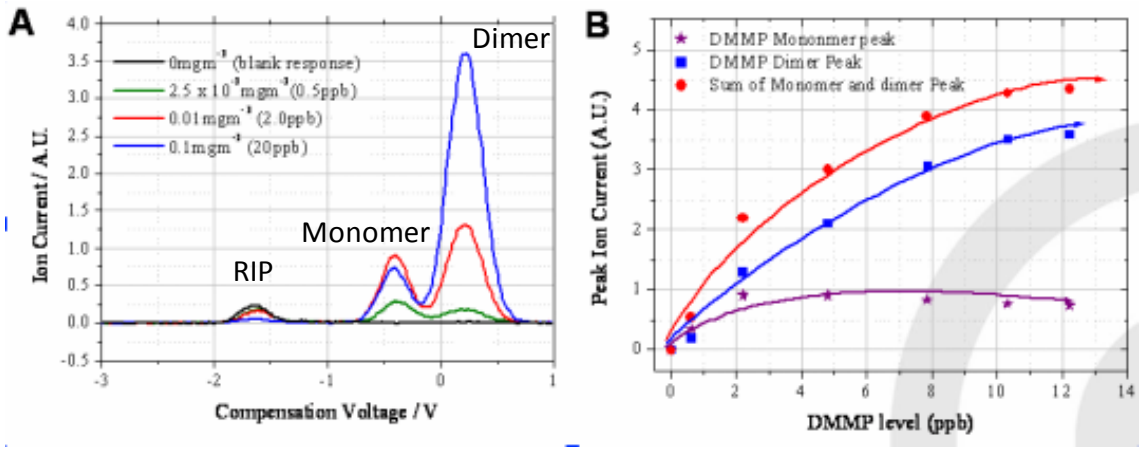


Figure 9 DMMP Monomer and dimer formation at different concentrations

The likelihood of ionization is governed by the analyte's affinity towards protons and electrons (Table 2 and Table 3 respectively).

In complex mixtures where more than one chemical is present, competition for the available charge occurs, resulting in preferential ionisation of the compounds within the sample. Thus the chemicals with high proton or electron affinities will ionize more readily than those with a low proton or electron affinity. Therefore the concentration of water within the ionization region will have a direct effect on certain analytes whose proton / electron affinities are lower.

Chemical Family	Example	Proton affinity
Aromatic amines	Pyridine	930 kJ/mole
Amines	Methyl amine	899 kJ/mole
Phosphorous Compounds	TEP	891 kJ/mole
Sulfoxides	DMS	884 kJ/mole
Ketones	2- pentanone	832 kJ/mole
Esters	Methly Acetate	822 kJ/mole
Alkenes	1-Hexene	805 kJ/mole
Alcohols	Butanol	789 kJ/mole
Aromatics	Benzene	750 kJ/mole
Water		691 kJ/mole
Alkanes	Methane	544 kJ/mole

Table 2 Overview of the proton affinity of different chemical families

Chemical Family	Electron affinity
Nitrogen Dioxide	3.91eV
Chlorine	3.61eV
Organomercurials	
Pesticides	
Nitro compounds	
Halogenated compounds	
Oxygen	0.45eV
Aliphatic alcohols	
Ketones	

Table 3 Relative electron affinities of several families of compounds

The UV ionization source is a direct ionization method whereby photons are emitted at energies of 9.6, 10.2, 10.6, 11.2, and 11.8 eV and can only ionize chemical species with a first ionization potential of less than the emitted energy. Important points to note are that there is no positive mode RIP present when using a UV ionization source and also that UV ionization is very selective towards certain compounds.

Mobility

Ions in air under an electric field will move at a constant velocity proportional to the electric field. The proportionality constant is referred to as mobility. As shown in Figure 10, when the ions enter the electrode channel, the applied RF voltages create oscillating regions of high ($+V_{HF}$) and low ($-V_{HF}$) electric fields as the ions move through the channel. The difference in the ion's mobility at the high and low electric field regimes dictates the ion's trajectory through the channel. This phenomenon is known as differential mobility.

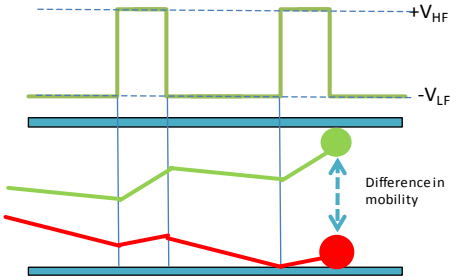


Figure 10 Schematic of a FAIMS channel showing the difference in ion trajectories caused by the different mobilities they experience at high and low electric fields

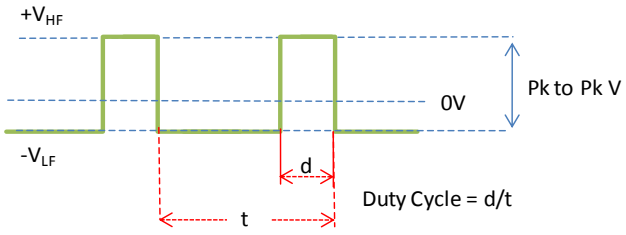


Figure 11 Schematic of the ideal RF waveform, showing the duty cycle and peak to peak voltage (Pk to Pk V)

The physical parameters of a chemical ion that affect its differential mobility are its collisional cross section and its ability to form clusters within the high/low regions. The environmental factors within the electrode channel affecting the ion's differential mobility are electric field, humidity, temperature and gas density (i.e. pressure).

The electric field in the high/low regions is supplied by the applied RF voltage waveform (Figure 11). The duty cycle is the proportion of time spent within each region per cycle. Increasing the peak-to-peak voltage increases/decreases the electric field experienced in the high/low field regions and therefore influences the velocity of the ion accordingly. It is this parameter that has the greatest influence on the differential mobility exhibited by the ion.

It has been shown that humidity has a direct effect on the differential mobility of certain chemicals, by increasing/decreasing the collision cross section of the ion within the respective low/high field regions. The addition and subtraction of water molecules to analyte ions is referred to as clustering and de-clustering. Increased humidity also increases the number of water molecules involved in a cluster ($MH^+(H_2O)_2$) formed in the ionisation region. When this cluster experiences the high field in between the electrodes the water molecules are forced away from the cluster reducing the size (MH^+) (de-clustering). As the low field regime returns so do the water molecules to the cluster, thus increasing the ion's size (clustering) and giving the ion a larger differential mobility. Gas density and temperature can also affect the ion's mobility by changing the number of ion-molecule collisions and changing the stability of the clusters, influencing the amount of clustering and de-clustering.

Changes in the electrode channel's environmental parameters will change the mobility exhibited by the ions. Therefore it is advantageous to keep the gas density, temperature and humidity constant when building detection algorithms based on an ion's mobility as these factors would need to be corrected for. However, it should be kept in mind that these parameters can also be optimized to gain greater resolution of the target analyte from the background matrix, during the method development process.

Detection and Identification

As ions with different mobilities travel down the electrode channel, some will have trajectories that will result in ion annihilation against the electrodes, whereas others will pass through to hit the detector. To filter the ions of different mobilities onto the detector plate a compensation voltage (CV) is scanned between the top and bottom electrode (see Figure 12). This process realigns the trajectories of the ions to hit the detector and enables a CV spectrum to be produced.

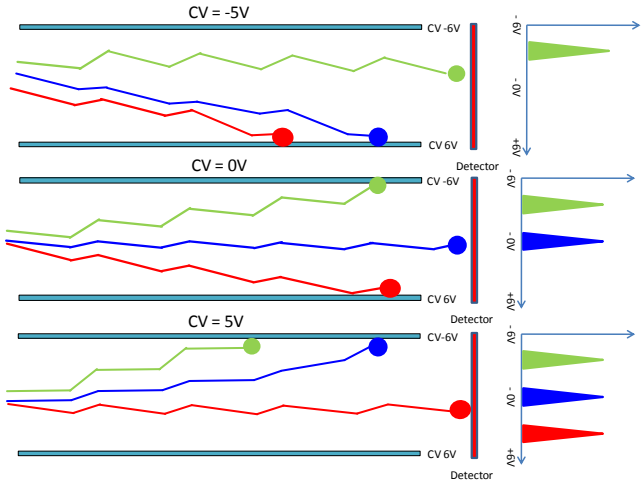


Figure 12 Schematic of the ion trajectories at different compensation voltages and the resultant FAIMS spectrum

The ion's mobility is thus expressed as a compensation voltage at a set electric field. Figure 13 shows an example CV spectrum of a complex sample where a de-convolution technique has been employed to characterize each of the compounds.

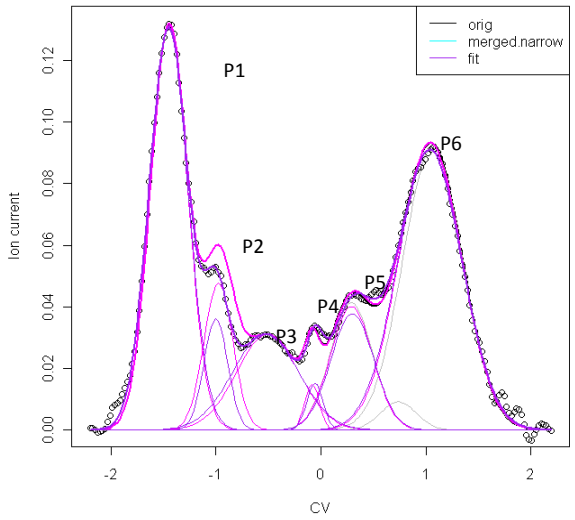


Figure 13 Example CV spectra. Six different chemical species with different mobilities are filtered through the electrode channel by scanning the CV value

Changing the applied RF peak-to-peak voltage (electric field) has a proportional effect on the ion's mobility. If this is increased after each CV spectrum, a dispersion field matrix is constructed. Figure 14 shows two examples of how this is represented; both are negative mode dispersion field (DF) sweeps of the same chemical. The term DF is sometimes used instead of electric field. It is expressed as a percentage of the maximum peak-to-peak voltage used on the RF waveform. The plot on the left is a waterfall image where each individual CV scan is represented by compensation voltage (x-axis), ion current (y-axis) and electric field (z-axis). The plot on the right is the one that is more frequently used and is referred to as a 2D color plot. The compensation voltage and electric field are on the x, and y axes and the ion current is represented by the color contours.

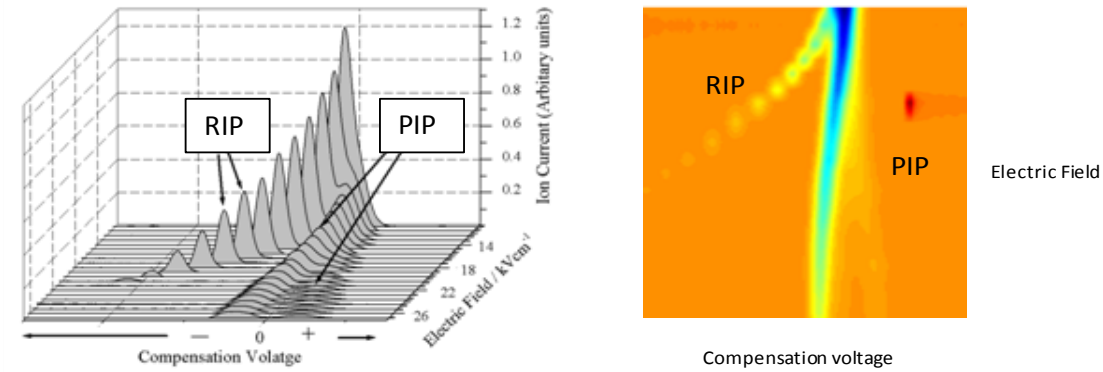


Figure 14 Two different examples of FAIMS dispersion field matrices with the same reactive ion peaks (RIP) and product ion peaks (PIP). In the waterfall plot on the left, the z axis is the ion current; this is replaced in the right, more frequently used, colorplot by color contours

With these data rich DF matrices a chemical fingerprint is formed, in which identification parameters for different chemical species can be extracted, processed and stored. Figure 15 shows one example: here the CV value at the peak maximum at each of the different electric field settings has been extracted and plotted, to be later used as a reference to identify the same chemicals. In Figure 16 a new sample spectrum has been compared to the reference spectrum and clear differences in both spectra can be seen.

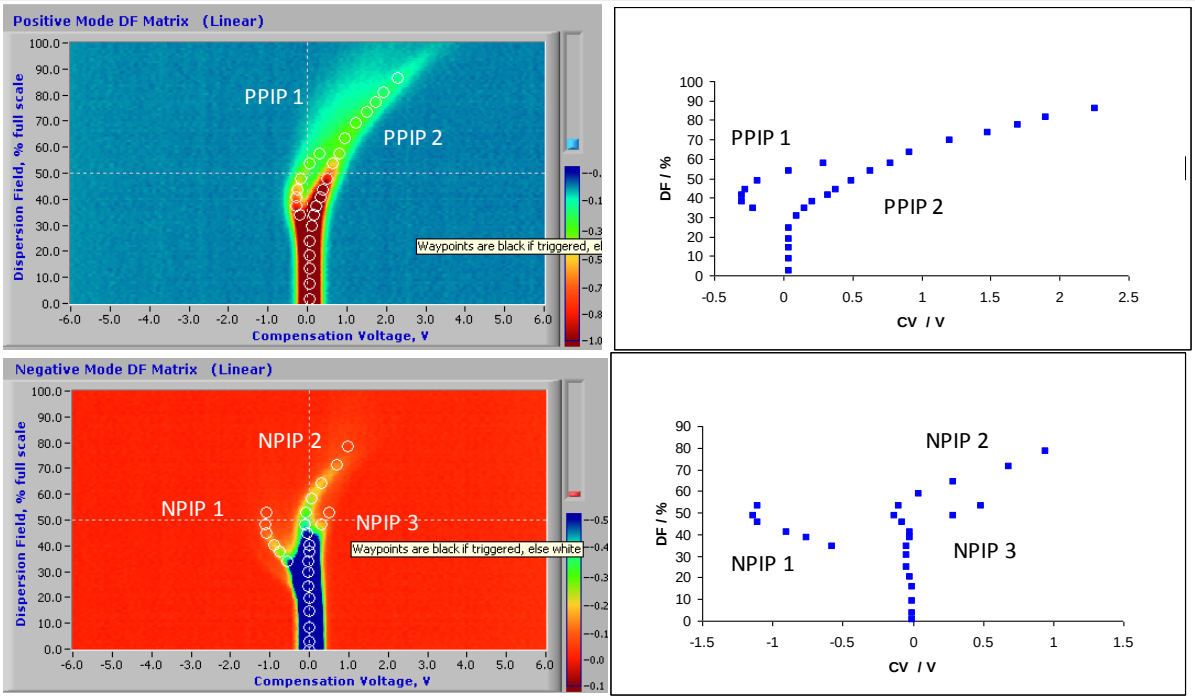


Figure 15 On the left are examples of positive (blue) and negative (red) mode DF matrices recorded at the same time while a sample was introduced into the FAIMS detector. The sample contained 5 chemical species, which showed as two positive product ion peaks (PPIP) and three negative product ion peaks (NPIP). On the right, the CV at the PIP's peak maximum is plotted against % dispersion field to be stored as a spectral reference for subsequent samples.

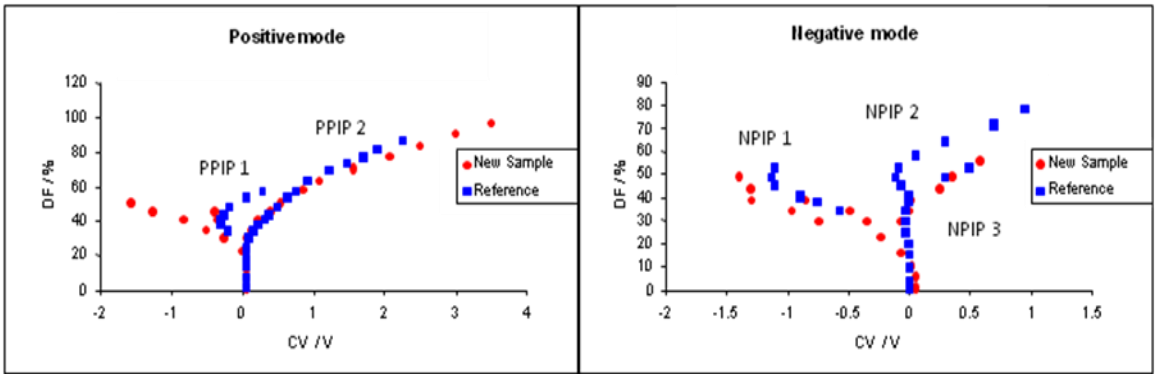


Figure 16 Comparison of two new DF plots with the reference from Figure 10. It can be seen that in both positive and negative modes there are differences between the reference product ion peaks and the new samples