

Real Time Monitoring of VOC and Odours Based on GC-IMS at Wastewater Treatment Plants

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Emissions of VOCs and odours at wastewater treatment plants are a frequent cause of concern due to their general proximity to residential areas. An increase in environmental awareness and the existence of regulations can lead to greater complaints amongst citizens. In addition, odours that are considered as unpleasant can be perceived as being linked to health concerns in local populations. Thus, VOC and odour emission control has become an issue of utmost importance at wastewater treatment plants, and subsequently the monitoring of emissions is an equally significant task.

The aim of this study is to evaluate a GC-IMS (Gas Chromatography - Ion Mobility Spectrometer) as a tool for continuous monitoring emissions from wastewater treatment plants, offering the possibility of producing fast measurements for the determination of chemical fingerprints of VOCs and odorous compounds. Air samples from different process units at a metropolitan wastewater treatment plant in the UK were collected and analysed by GC-IMS and dynamic olfactometry according to EN 13725. The GC-IMS system was used to determine magnitude of individual VOC emissions and investigate whether process types could be characterised by unique VOC fingerprints. The results showed different chemical fingerprints of volatiles in each sample and a correlation between the magnitudes of VOCs detected against results obtained by olfactometry. This suggests that GC-IMS has the potential for use as a beneficial analytical technique for the monitoring odour compounds, with greater potential than conventional electronic noses due to its higher sensitivity.

1. Introduction

There is a permanent concern related to the emissions of Volatile Organic Compounds (VOCs) and unpleasant odours originating from wastewater treatment plants because of their general proximity to residential areas. Increased environmental awareness and the existence of environmental standards can lead to greater complaints amongst citizens.

Moreover, odours that are considered as unpleasant can be perceived as being linked to health concerns in local populations and in the case of VOCs, they are usually considered as environmental pollutants (Lehtinen and Veijanen, 2011). For these reasons, Thus, VOC and odour emission control has become an issue of utmost importance at wastewater treatment plants, and subsequently the monitoring of emissions is an equally significant task

Currently, the measurement of VOCs and odour are carried out using two different analytical methods: instrumental and sensorial (Zarra et al., 2008). Whilst sensory methods are essential in understanding the magnitude of odours from the perspective of human perception, it is not possible to determine which substances generate neither the odour nuisance nor its concentration. Through instrumental analysis methods, it is possible to obtain information identification and quantification of chemical species associated with odours. The most commonly used technique is Gas Chromatography coupled to a Mass Spectrometer, known as GC-MS. This technique is able to detect, identify and quantify VOCs reaching the detector (MS) after the sample is introduced into the gas chromatograph (Vera et al., 2013). One of the main advantages of

this technique is its sensitivity and robustness, however its limited portability and large times of analysis per sample impede ideal monitoring measurements *in situ*.

Electronic noses are an alternative for measurements and monitoring of some VOCs and odours *in situ* with a big advantage being portability. These systems comprise of a series of sensors of different materials (e.g. metal oxides, conductive polymers, catalytic metals) capable of generating responses to thousands of chemical species resulting in an odour profile or fingerprint. However, the main disadvantage of these systems is its limited sensitivity, an extremely critical condition for odorous molecules, which can be perceived by the human nose at very low concentrations.

An interesting alternative is gas chromatography coupled with ion mobility spectrometry (GC-IMS). This instrument uses a similar technology for chemical detection to that used by mass spectrometry time of flight (ToFMS). The main characteristic of these instruments is the good selectivity, detection and quantification of a wide range of chemical species, the instrument is not affected by humidity (which can be an issue with other sensors): and has the following advantages; a) a high sensitivity, detection down to low ppbv levels (Gygax and Mannebeck, 2015), b) it can perform fast analysis (3-10 minutes) and c) its size and the fact that it is operated at ambient pressure enables it to be easily portable. The latter two characteristics are ideal for *in-situ* monitoring. Additional advantages, unlike other portable instruments, are that IMS ionizes the molecules at ambient pressure and when used with a GC column, a bi-dimensional representation of signals can be achieved that is useful for representing and clearly visualizing the composition of a mixture.

The functioning principle of the IMS technology is illustrated in Figure 1. IMS is a technique of ionization to form a 'reactive ion' species from the carrier gas employed by the system (air or N₂). These groups of reactive ions can lead to the ionization of the molecules present in the sample, thus forming groups of characteristic ions or packages.

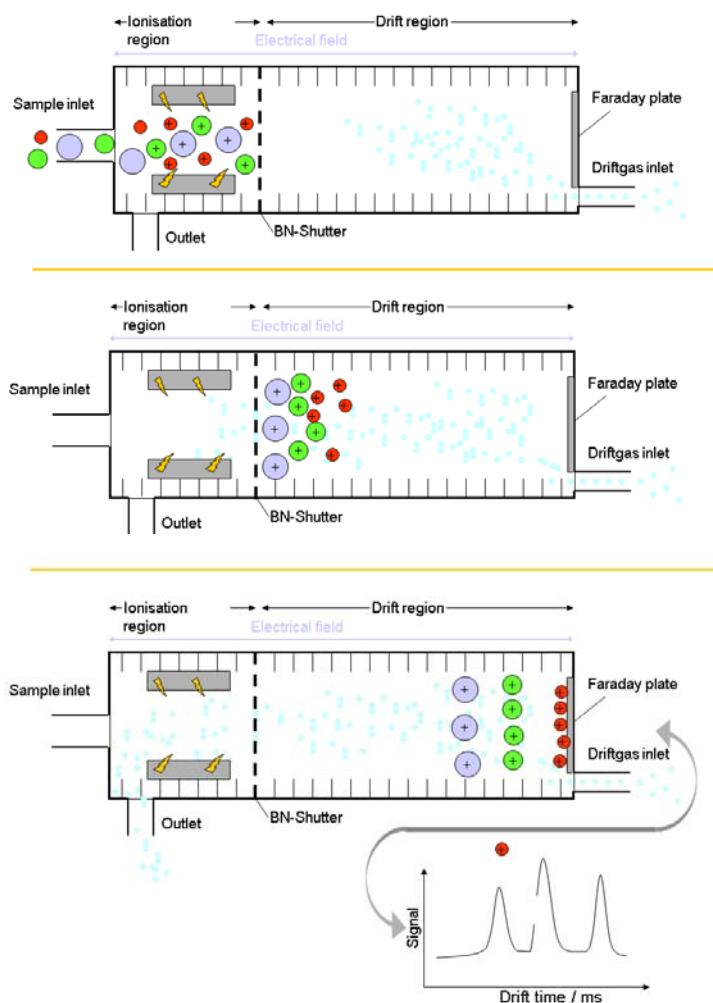


Figure 1. Functioning principle of the IMS technology

A small package of ions thus formed in the instrument are injected into a drift region where they travel against the flow of a drift gas towards a detector under the influence of an electrostatic field. Ions travel through the drift region at characteristic velocities related to the size, shape and charge of the groups of ions. Upon reaching the detector, each ion species generates a specific signal, and the ion current is measured as a function of time of arrival. The IMS spectrum is recorded and mobility information is extracted in real time within the instrument.

When a chromatographic column is inserted between sample introduction and ionization step a GC-IMS system is formed. The preliminary chromatographic stage provides an additional component in separation (in addition to the drift time) based on retention time allowing a bi-dimensional visualization of the chromatograms obtained (Figure 2).

As the analysis results in both GC separation and IMS separation, a 3 dimensional chromatogram is produced. In Figure 2 below the upper image shows such a 3D chromatogram. The y axis represents time associated with GC separation, the x axis represents IMS drift time and the z axis represents the detector response (related to the amount of each component present). A useful visualisation tool to represent the results is a 'heat map' 2D fingerprint, as shown in the lower image in Figure 2. In this image a 3D output has been converted into a 2D representation by transforming the z axis data into a colour signature for each detection signal, i.e. a heat spot for each component detected. The higher the detector response (which is related to the amount of compound detected) the more intense the heat spot.

The dotted lines in the 3D illustration can be traced to see how the peaks are represented in the corresponding 2D visualisation of results.

To identify the components of the sample, a number of options are available including using the NIST library based on Kovats indices (i.e through GC separation), or by the "drift time" based on a database provided by the instrument manufacturer, or simply generating an internal library based on the analysis of standard mixtures

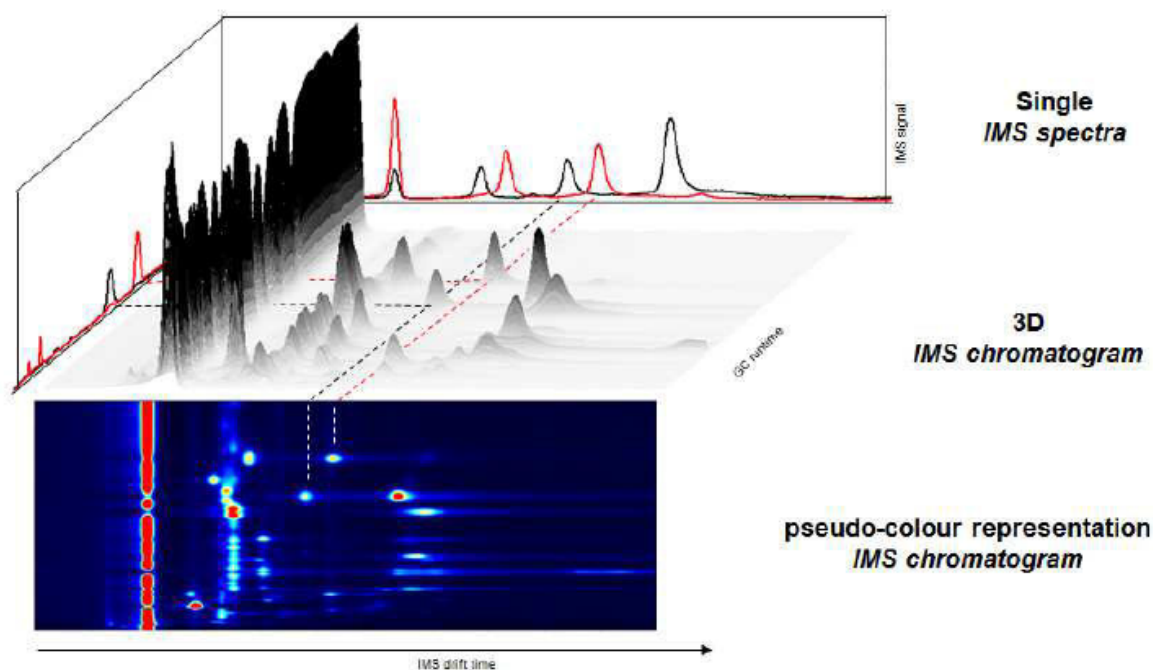


Figure 2. Bi-dimensional chromatogram obtained by GC-IMS

The aim of this study is to determine if it is possible through the use of GC-IMS, to perform fast measurements to differentiate between chemical traces of VOCs and odors originating from different processing units in a wastewater treatment plant and its potential use as a tool in continuous monitoring of odorants.

2. Materials and methods

Five air samples from different locations in a wastewater treatment plant (WWTP) in a metropolitan area in the United Kingdom were collected. A description of sample types can be found in Table 1. Sources were chosen to cover a range of source types including storm water storage, preliminary sewage processing, sludge storage and a comparison of treated and untreated emissions.

Table 1: Summary of sampling locations

| Sample ID | Source Name | Nature of source |
|-----------|------------------------------------|---|
| AAM | Covered storm tank headspace | Storm tanks covered and odorous air extracted to OCU. |
| BAM | Inlet pumping station | Air from an enclosed inlet pumping station is extracted to OCU. Sample was collected from OCU inlet (untreated) airstream |
| DAM | Sludge pumping station | Digested sludge is stored prior to pumping offsite for dewatering. Odorous air extracted to OCU. Sample was collected from OCU inlet (untreated) airstream |
| EAM | Preliminary and primary OCU outlet | The OCU serves preliminary, primary effluent handling plus storm water storage operations. Tanks are covered and odorous air extracted to OCU. This large OCU (design flow in excess of 100,000 m ³ /hr) is a 2 stage system comprising of chemical scrubber followed by carbon adsorption beds. Samples were collected from both the inlet (untreated) and the outlet (treated) airstreams of the system. |
| FAM | Preliminary and primary OCU inlet | |

A cylinder of synthetic air was used as drift gas within the measurements and blank samples were run from Nalophan bags containing synthetic air between samples.

Replicate samples were collected and analysed by olfactometry measurements for odour concentration according to EN13725.

3. Results

Figure 3 shows two representative samples; from the inlet pumping station (BAM) and sludge pumping station (DAM), (i.e. the weakest and the strongest samples from an odour and VOC concentration perspective). In these spectra, the peaks are represented by colored spots against the predominant blue background. Light colors represent low intensity peaks, with the red color representing high intensity peaks.

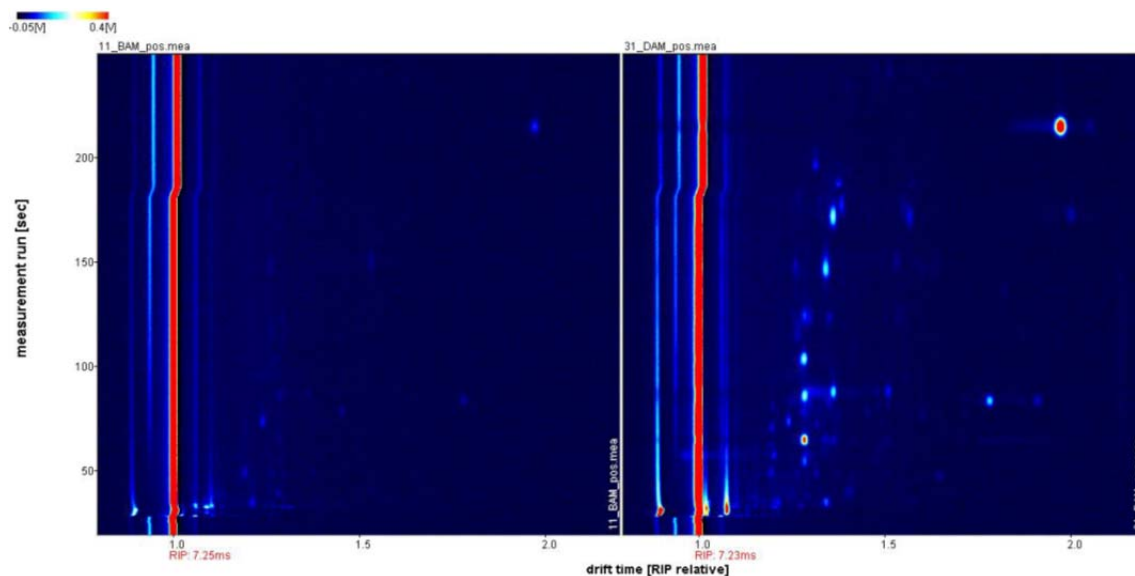


Figure 3. GC-IMS spectra of BAM (left) and DAM (right)

In figure 3 a clear difference can be seen in the response area of sample DAM (right) compared to the BAM shows (left). Thus, a defined chemical fingerprint information is obtained.

Each of the scans were inspected to identify visible signals which were then selected for comparison between samples. The areas of interest are highlighted in Figure 4 below and the gallery plot comparing the relative concentration of each signal is presented in Figure 5. The areas of interest have been labelled in accordance to their IMS drift time, e.g. mark '1_28ms' has a drift time of 1.28 ms.

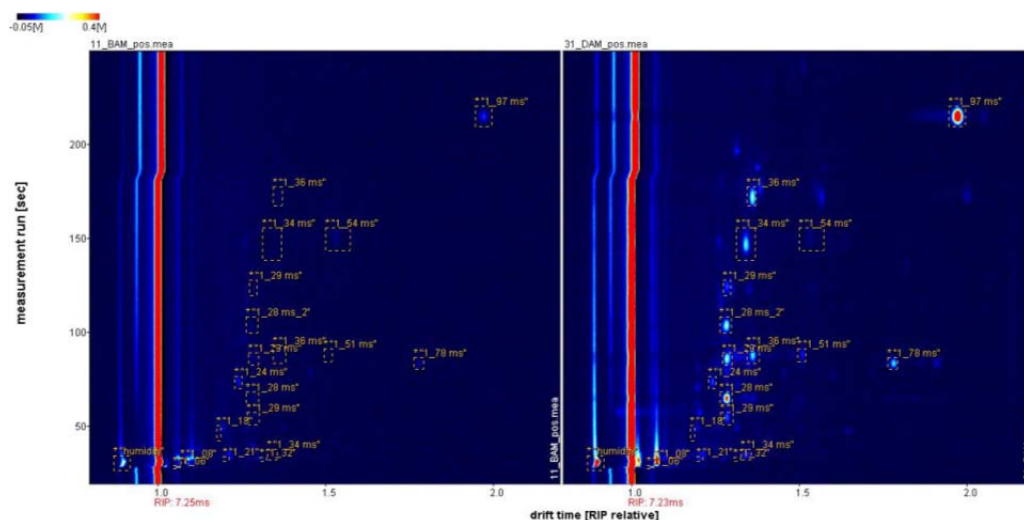


Figure 4. GC-IMS spectra of BAM (left) and DAM (right) with 'area mark-up'

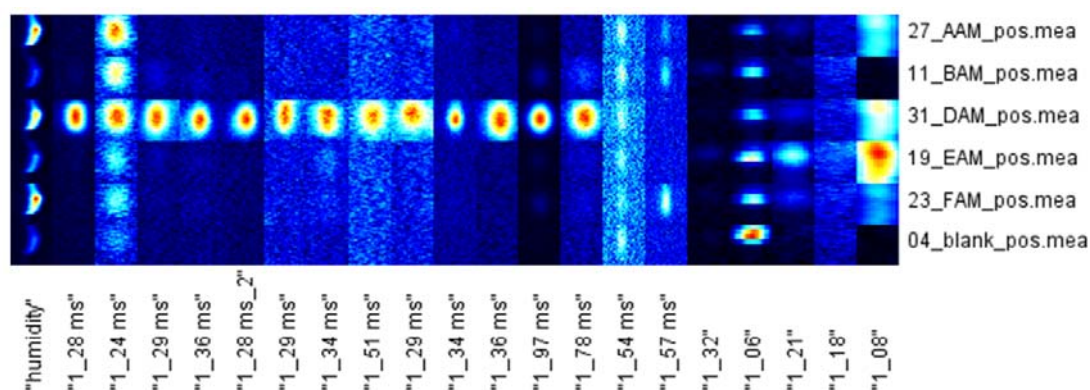


Figure 5. Gallery plot to compare relative peak intensity between samples

The graphical comparison in Figure 4 shows a more prominent presence of visible signals on the DAM sample, which is in line with expectations of the olfactometric results, where the concentration of odour in DAM sample is 25-80 times higher to the remainder (Table 2). Based on this, it can be observed the GC-IMS displays a good sensitivity of detecting odoriferous compounds, with some compounds detectable even at very low concentrations.

Table 2: Olfactometric results

| Sample ID | Odour concentration [ou _E /m ³] |
|-----------|--|
| AAM | 3875 |
| BAM | 1203 |
| DAM | 103594 |
| EAM | 1448 |
| FAM | 2266 |

The GC-IMS spectra show multiple components, and initial evaluation of results indicates that samples from effluent sources should be distinguishable from sludge based sources (certain peaks associated with sludge sources are not present in effluent spectra and vice versa) and a correlation between the magnitudes of VOCs detected against results obtained by olfactometry is observed. Furthermore, analysis by GC-IMS of a larger number of samples from each location could provide more definitive chemical fingerprint for VOCs and/or a "smell print" for odour compounds, useful for monitoring tasks.

The next step is the chemical identification and quantification of the compounds responsible for the signals that make up the chemical fingerprint of each sample (focusing on odorous compounds).

4. Conclusions

Through analysis of GC-IMS at different locations in a wastewater treatment plant, it was possible to detect different two-dimensional representations of VOCs based on the sampled source, which would allow the assignment of different "fingerprints" to different odour sources. Based on these preliminary results, it should be possible to identify individual odorants and use peak intensity data in support of olfactometry analysis. This indicates that GC-IMS shows potential to be used as alternative or even an improved analytical technique to electronic noses, since it is portable, offers higher sensitivity with short analysis times, and is therefore ideal for monitoring applications.

References

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