GC(GCMS), the Multi Tool for Environmental Analyses

For decades and through the whole laboratory industry, chromatography has been a widely used separation technique for analytical and preparation purposes. Chromatography refers to the words chromos (Latin for colour) and graphic (visual registration). Lines or dots of, for example, a green or orange marker on a wet sheet of paper, divided into their primary colours yellow/blue and yellow/red. This is the basic process that takes place during chromatography.

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There are several chromatographic techniques like Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Thin Layer Chromatography (TLC), Gel Permeation Chromatography (GPC) or Chemical Electrophoresis (CE).

This article will focus on GC and GCMS (GC combined with a Mass Selective detector) analysis in the environmental industry.

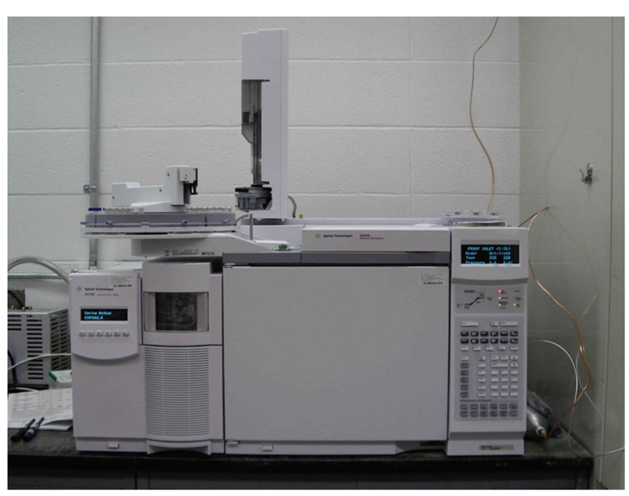

Image 1: A complete GCMS system of Agilent

Instruments and usage for environmental analysis

GC is a common analysing technique to separate organic compounds that are volatile, without decomposing, out of a complex mixture from other substances like lipids, acids, minerals and proteins. To achieve reliable results of the amount of target compound(s), a GC contains various basic elements.

In the beginning samples were injected manually into an injector of a GC. To manage larger amounts of samples, to increase accuracy and efficiency and to automate pre-treatment handlings, manufacturers developed different kinds of robotic samplers called Auto Samplers.

Sample introduction into the system, or the injector, evaporates a sample solution into a vapour and injects it into the separation column. For environmental usage there are three common types, Split/ Split less (S/SL), Cold On Column (COC) and Programmable Temperature Vaporiser (PTV).

For the separation column in a GC there can be two kinds available, capillary (used for sample solutions or extracts) or packed (used for gases). A column is packed or coated with a stationary phase. In this phase the separation takes place by difference in affection of the target compound(s) with the stationary phase. This phase is mostly a cross-linked polymer.

The carrier gas (mobile phase) transports the target compound and the other substances through the separation column (stationary phase). This gas must be inert because otherwise it will react with the target compound or materials in the GC or cause problems in the detector.

Helium is commonly used for GC analyses thanks to several benefits like costs and being safer to use. Hydrogen and nitrogen are also used. For hydrogen you have to take extra safety arrangements like a hydrogen detector. Nitrogen is less used, creating longer analysis.

The separation column is placed into the temperature programmable oven. The chromatographic separation can be optimised using a temperature programme for critical pairs of target compounds which separate at a constant temperature.

The detector counts the target compounds coming out of the column. For GC there are two kinds of detectors, specific (like the Electron Capture Detector, ECD, very sensitive for halogen containing target compounds) and non-specific (like the Mass Selective Detector, MSD or MS, every molecule or ion has a mass).

To calculate results a computer is required to handle the data, especially for a GCMS . In some situations a recorder is enough for registration or report purposes.

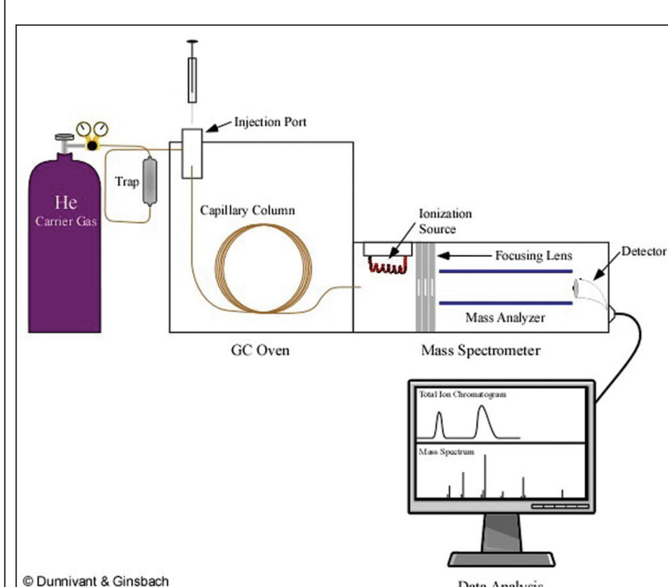

Image 2: A scheme of a GCMS system

Before a GC analyses can be performed on an environmental sample, the sample needs to be pre-treated to be suitable for analyses.

In general, analysis by a GC (GCMS) is performed as follows. The sample extract is injected into a preheated injector. The organic solvent, target compounds and other substances are vaporised into the injector. This vapour will be, partly or in total lead over the separation column by the carrier gas. All the different substances, including the target compounds, will be separated from each other, supported by the heat of the GC oven in the column. Finally the target compounds will be detected by a detector. For calculations and reporting of the results, the data is sent to a PC or recorder.

Modern gas chromatography was invented in 1952 and in 1954 with

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Perkin Elmer being the first manufacturers to introduce a complete GC system. Not long after that, other manufacturers like Shimadzu, came with their GC system. Nowadays the GC market consists of manufacturers like Agilent, Bruker, CTC, HTA, Leco Corporation, Perkin Elmer, Shimadzu, Thermo Scientific and other smaller manufacturers.

In the environmental industry, GC is the preferred analysing technique for pollutants such as Mineral Oil (MO), Poly Chlorinated Dibenzo Dioxins (PCDDs), Volatile Organic Compounds (VOCs) or Organic Chlorinated Pesticides (OCPs) in for instance surface water, wastewater, sludge or soil.

For all these analysis there is a suitable configuration for the GC system in order to achieve correct results. GC (GCMS) analysis is only part of the whole analysis method (including pretreatment) for a target compound or a group of target compounds. Depending on the purpose, there are various standard methods available for different kinds of compounds suitable for several types of environmental samples. There are international and national standard methods available as EN (European), ISO, ASTM (Both International), EPA (U.S.A.) and DIN (German).

The leading aim for GC (GCMS) methods is to achieve the required detection limit to get reliable results from the target compound in relevant environmental samples. The method is built up in reverse order.

You select a suitable detector which is sensitive and selective enough to detect the target compound(s). The separation column must have enough affinity with the target compound to get the required separation of the target compounds and substances. Manufacturers of columns have a large variety of length, internal diameter, stationary phase and column material available. The GC oven has to be powerful enough to ramp the temperature (heating up) to what is needed to separate critical pairs which can be difficult to separate.

Which injector type is suitable for the method? The choice is dependent on how many target compounds need to be brought into the separation column to get a signal that fits the range for the detector. A PTV injector is used when you are expecting a low presence of target compounds. You can inject more extracts, for example 50 µl, compared to a S/SL injector (1 or 2 µl). The injection technique is also dependent on the target compounds. When you have target compounds with high boiling points, you can pre-separate the target compound from the compound and solvent with a much lower boiling point using a PTV injector.

Finally a suitable auto sampler needs to be chosen to complete the configuration of your GC(GCMS) system. For environmental use there are three options;

- An auto sampler for liquid samples (extracts of samples for semi and less volatile compounds)
- An auto sampler for Head Space (HS) samples (vapour sample above a liquid sample for volatile compounds)
- A hybrid auto sampler like the Combipal sampler from CTC. This is a XYZ robotic auto sampler and very versatile. There are different modules available such as a liquid module, a HS module and a Solid Phase Extraction (SPE) module.

The first two types of auto samplers are dedicated samplers and are economically the best choice and most suitable for routine analyses. The third type of auto sampler like, the Combipal, is more expansive but is also suitable for routine analyses. The strength of the Combipal is the significant possibility to automate pre-treatment. SPE for example is a pre-treatment method to extract your target compounds out of a liquid sample. A liquid sample is then poured into a column with the solid phase. When the solid phase is nearly dry, the target compounds are simply washed of the solid phase with an organic solvent. A Combipal can do all this for you and more, such as adding injection standard solution to the extract before injection or derivation. Derivation is a chemical modification method to make target compounds suitable for (GC) analysis.

Image 3: A Combipal auto sampler with HS module on a Agilent GC

Benefits

There are many benefits when using GC or GCMS for environmental analysis such as;

- High throughput of routine samples. Environmental contract laboratories are capable of keeping operating costs low by automating and optimising their analyses.
- High accuracy and sensitivity. GC's are highly sophisticated. Manufactures are continuously developing their GC's and all new models have new features and better performance.
- Multiple parameter analyses. It's possible with a GC to quantify several kinds of different compounds in one single run like Organic Chlorinated Pesticides (OCPs) and Poly Chlorinated Biphenyl's (PCBs) or over a hundred different organic compounds.
- Qualification. Besides the usual quantification of target compounds, you can use a GCMS to qualify unknown compounds.
- Low detection limit. A GC is capable of quantifying target compounds at a very low level e.g. Parts Per Trillion (ppt).
- Second life. A GC is flexible. In many cases a second hand GC can be easily adapted to fit for another purpose by chancing detector(s), auto samplers or injectors.
- Coupling. For specific purposes, GC's are sometimes coupled to other analytical instruments like Inductive Coupled Plasma-MS, ICP-MS (instrument to analyse elements) and LC (coupled to the front of a GC in combination with large volumes injected to perform clean-up of the extract).

Opportunities and developments for the future

Besides all the benefits of using GC or GCMS, it may be obvious that there are still some opportunities for improvements and development with GC or GCMS analysis in general, but also for environmental use too.

In general GC analyses is used for compounds with a boiling point of 500 degrees Celsius. This range could be extended in the future by using other injection techniques.

Water can be disastrous for the stationary phase of the separation column. Other injection techniques can prevent water reaching the column or even make it possible to inject aquatic samples. At the same time manufacturers could improve their column to be less sensitive for water.

Some target compounds, compounds that are familiar to the target compound or other compounds which are present in the sample (matrix) are hard to separate from each other. In that case these compounds leave the column (almost) at the same time the target compounds leaves. This effect is called co-elution and affects the result even causing a false positive result. When optimising the oven program, changing columns or other qualifiers (specific fragment for a target compound when using an MS) doesn't help, you can look for better pre-treatment techniques or use GC x GC. Two GC's are coupled to each other. The compounds that co-elute are lead to another GC with another column, where the separation starts over to desperate them.

Depending on the target compounds, separation and numbers of compounds, a GC run can take a view minutes to more than an hour. Fast GC analysis performed in TV CSI episodes are an illusion. When you want to analyse more samples or analyses in shorter time, manufacturers are developing small GC ovens with heating coils on the outside or columns on a chip. The benefit of this is that the column is heated in seconds to reach a preset temperature compared to a couple of minutes with a regular oven. This kind of development has lead to accurate GC analyses in less time.

More data of characteristic materials or samples will enable the (future) analyst to perform better identification. With comprehensive GCMS (a 3D plot of a sample) or pyrolysis (burning a material or solid sample) give characteristic information of a sample.

Manufacturers are constantly developing their GC's and their equipment, such as detectors, to get lower detection limits in order to trace the slightest amounts of target compounds. MSD's are developing like Triple Quad MS (Three Quadrupoles placed in series) or Time Of Flight MS (measures the time of flight of the ions). Flame Ionisation Detectors (FID) are also gaining sensitivity.

GC analysis is commonly performed in a laboratory on a bench top GC. For analysing volatile organic compounds in air samples, there are portable GCMS systems available. The main advantage is that the sampling and analysis is performed at the same time, limiting losses of target compounds. For the manufacturers this could be a big challenge.

In the University of Amsterdam there is a faculty under the supervision of Professor Peter Schoemakers. They are studying ways to increase the working field of chromatography like GC and GCMS. These studies will lead to more applications for GC and GCMS in the future. GC's and GCMS are essential multi-tools for environmental analysis, both now and in the future.

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