IFSTL International Food Safety Training Laboratory | parera

parera
Food Risk Analysis and Regulatory Excellence Platform

INAF Institute of Nutrition and Functional Foods

Université Laval
Faculty of Agriculture and Food Sciences

Confirmation Methods for Organic Chemical Contaminants

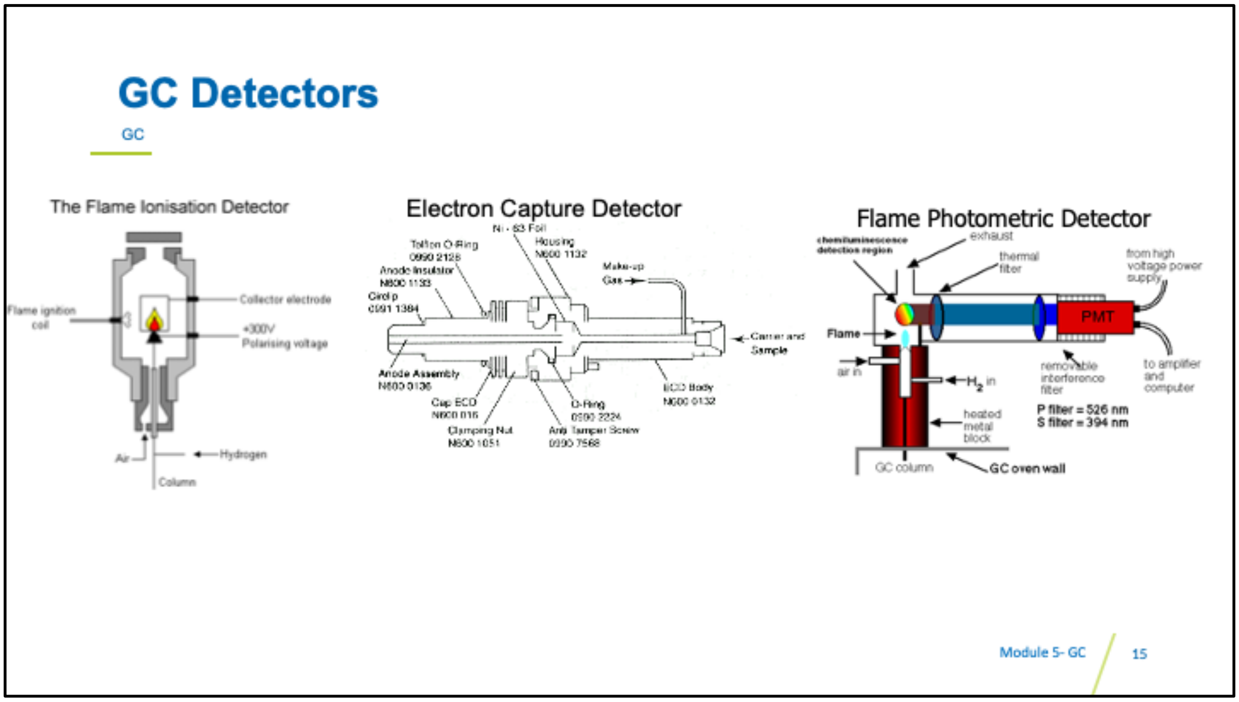
Module 5

Welcome to module 5 of this training on confirmation methods for organic chemical contaminants. This module discusses the principles of gas chromatography.

SECTION 2

Detectors for GC

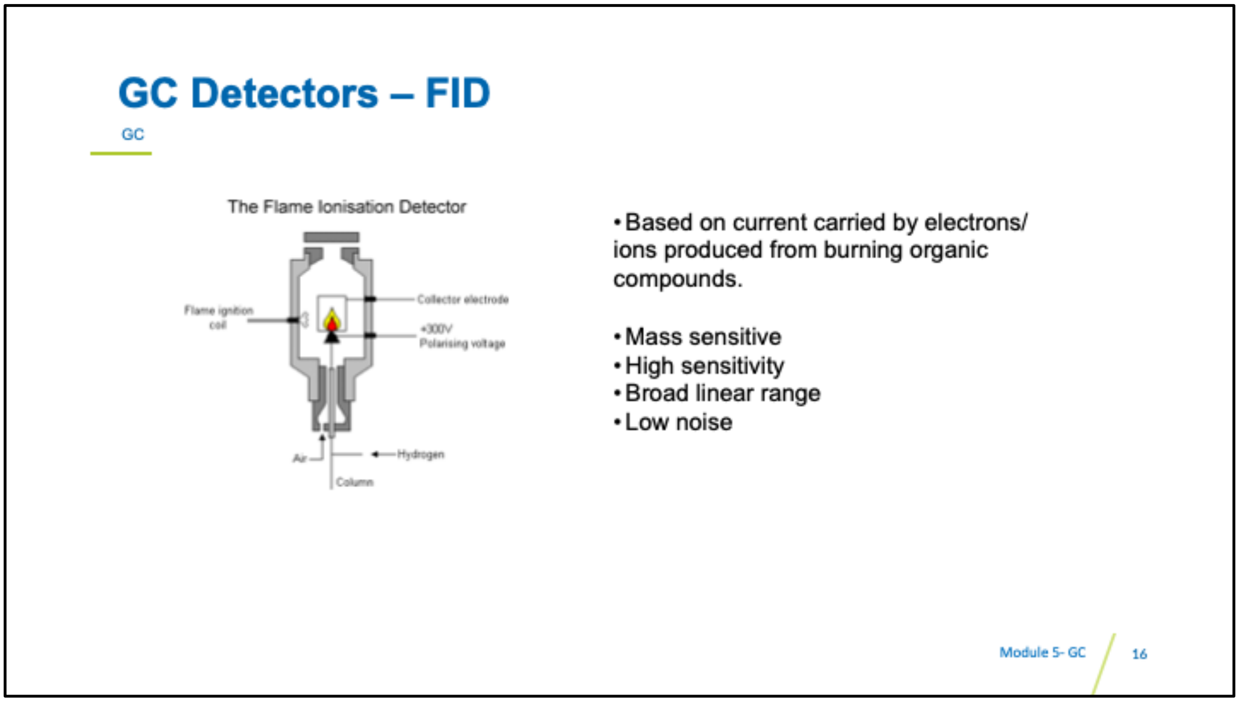
Section 2: Detectors for GC



GC Detectors

GC

The detector the measuring component of the GC system. In some cases, the detector measures everything that comes out of the column, regardless of what it is. This would describe a detector with low selectivity or specificity. In other cases, the detector is only sensitive to certain chemicals and will show no response to others. Fluorescence and absorbance detectors fall in this category. Finally, there are those detectors that add a step of selection (or exclusion) prior to the actual measurement, such as the mass spectrometry detector.



GC Detectors – FID

GC

The Flame Ionisation Detector

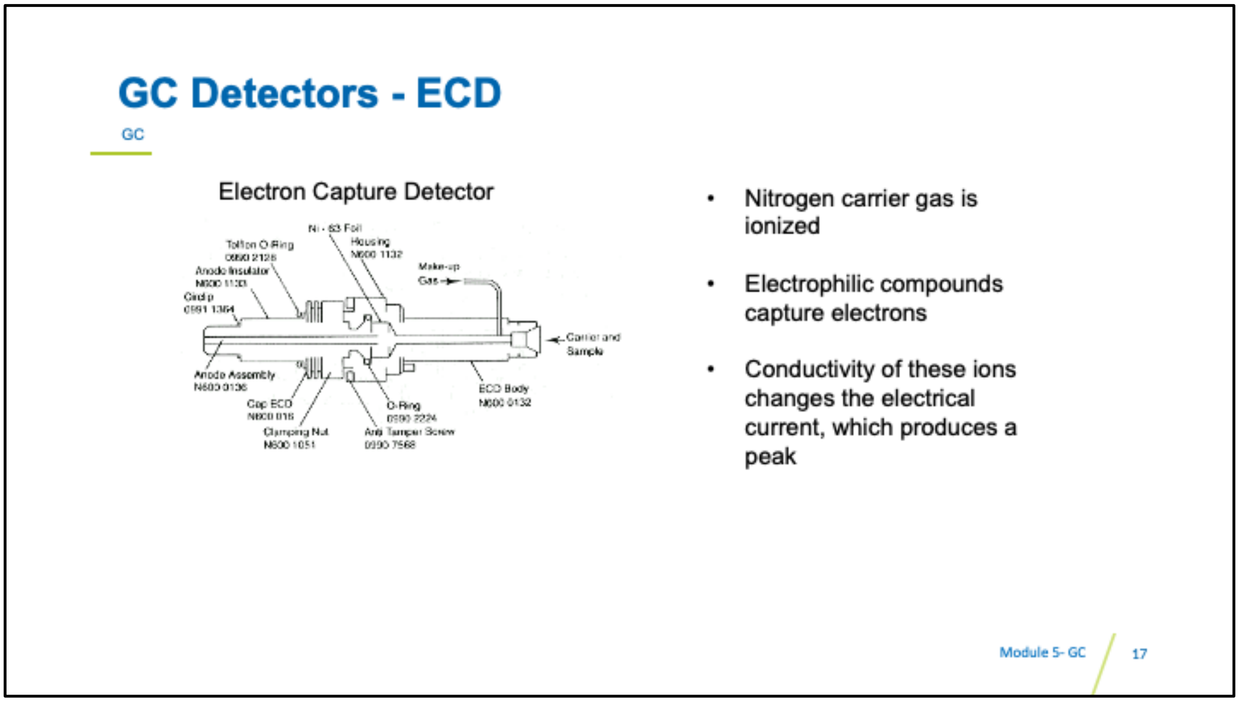
- Based on current carried by electrons/ ions produced from burning organic compounds.

- Mass sensitive
- High sensitivity
- Broad linear range
- Low noise

Module 5- GC 16

In the flame ionization detector, the effluent from the column is mixed with hydrogen and air, and ignited. Ions and electrons are produced are the organic compounds burn; these conduct electricity through the flame. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any and all organic compound is measured.

One important advantage of FID is that it is mass sensitive rather than concentration sensitive; this gives the advantage that changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range, and low noise. It is also robust and easy to use, for almost all organic compounds, which have C-H or C-N structure.



GC Detectors - ECD

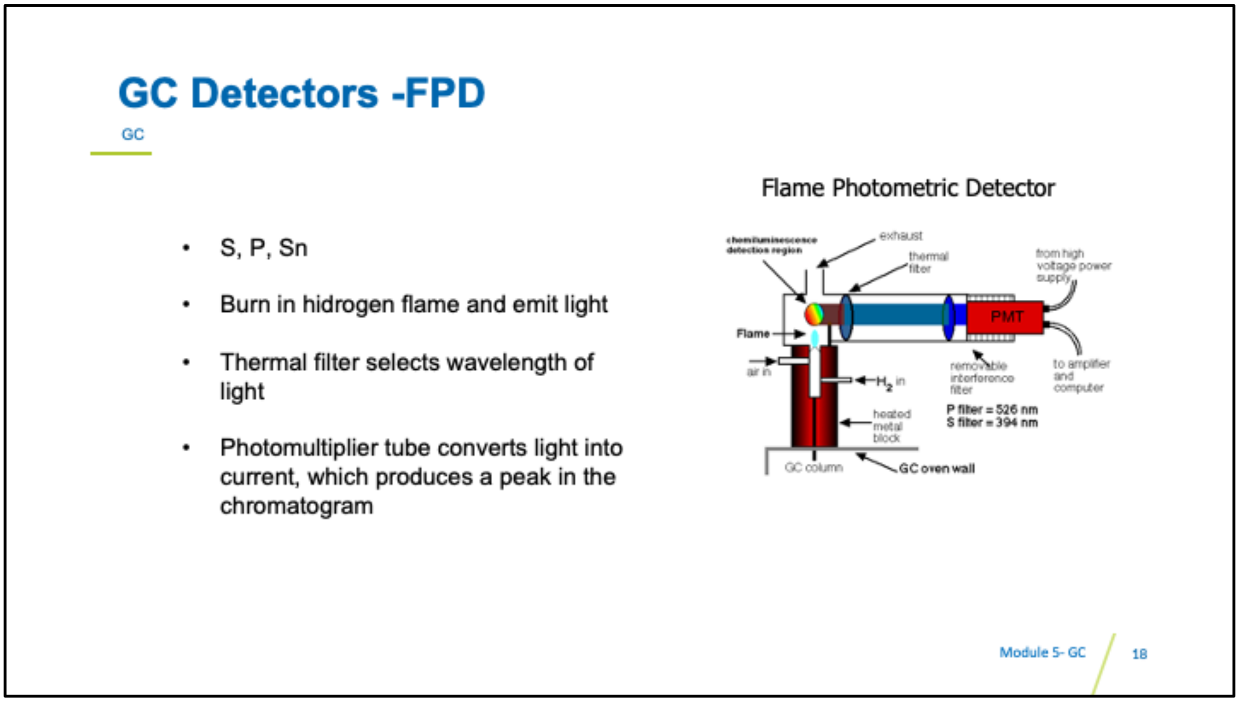
GC

Electron Capture Detector

- Nitrogen carrier gas is ionized
- Electrophilic compounds capture electrons
- Conductivity of these ions changes the electrical current, which produces a peak

In the electron capture detector, the nitrogen carrier gas is ionized by a beta ray, and the electrons released are captured by the electrophilic compounds that results in a negative ion. These ions are conductive and the change in the current produces a peak.

This detector is used in food safety for pesticides and environmental contaminants.



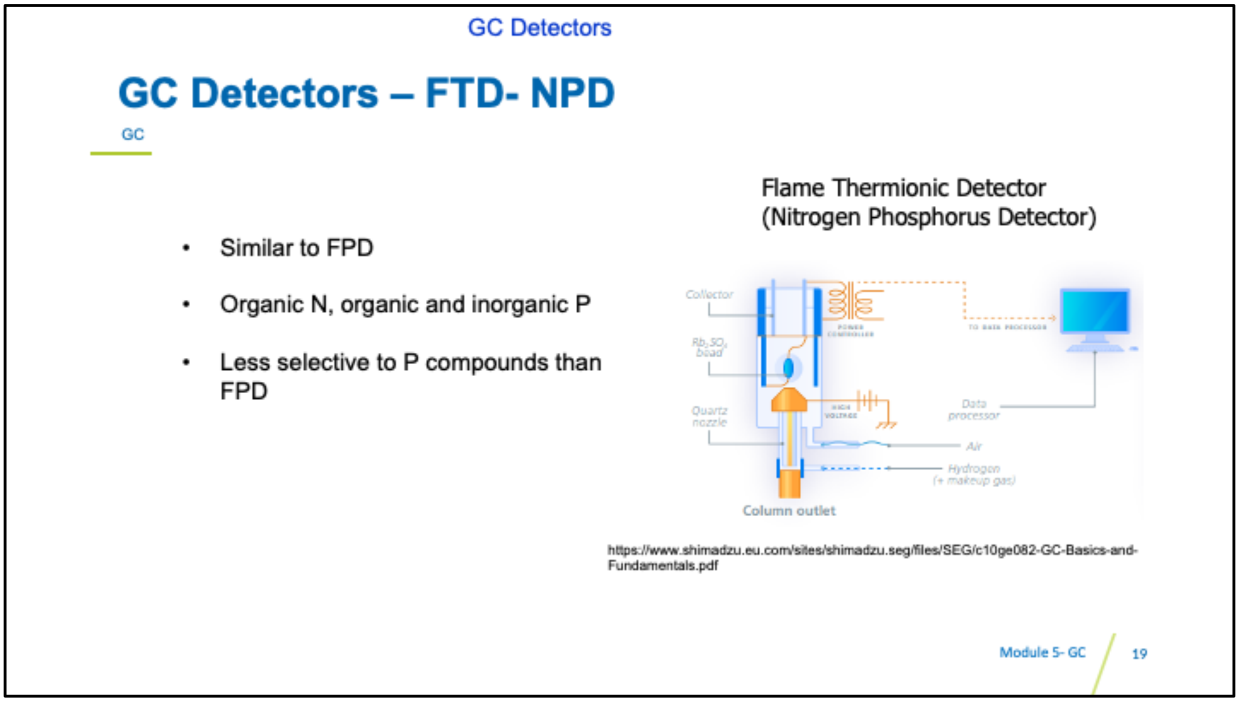
GC Detectors -FPD

GC

- S, P, Sn
- Burn in hidrogen flame and emit light
- Thermal filter selects wavelength of light
- Photomultiplier tube converts light into current, which produces a peak in the chromatogram

Flame Photometric Detector

The flame photometric detectors, FPD, are good for sulphur, phosphorus, tin and a few other elements that burn to specific colors (or wavelengths) in a hydrogen flame. FPD is highly sensitive and selective which makes it well suited for food contaminants and their usually low concentrations. In addition, it is a very stable detector. It is especially useful in the food safety laboratory to measure phosphorus pesticides



GC Detectors

GC Detectors – FTD- NPD

GC

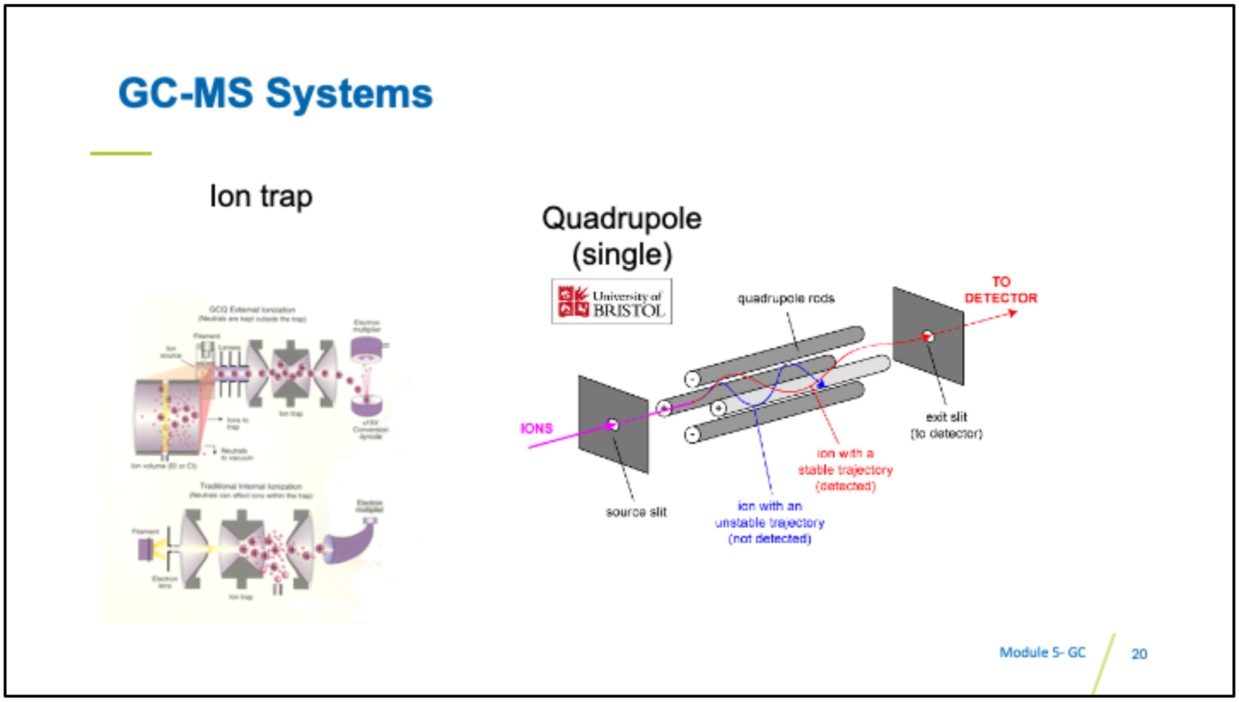
- Similar to FPD
- Organic N, organic and inorganic P
- Less selective to P compounds than FPD

Flame Thermionic Detector
(Nitrogen Phosphorus Detector)

https://www.shimadzu.eu.com/sites/shimadzu.seg/files/SEG/c10ge082-GC-Basics-and-Fundamentals.pdf

The flame thermionic detector is a highly selective and sensitive detector for organic nitrogen compounds, and inorganic and organic phosphorus compounds. It is also known as a nitrogen phosphorus detector (NPD) because it detects nitrogen and phosphorus compounds.

Its selectivity to phosphorus compounds is lower than FPD. The main applications of FTD include the analysis of drugs, nitrogen pesticides, and phosphorous pesticides.



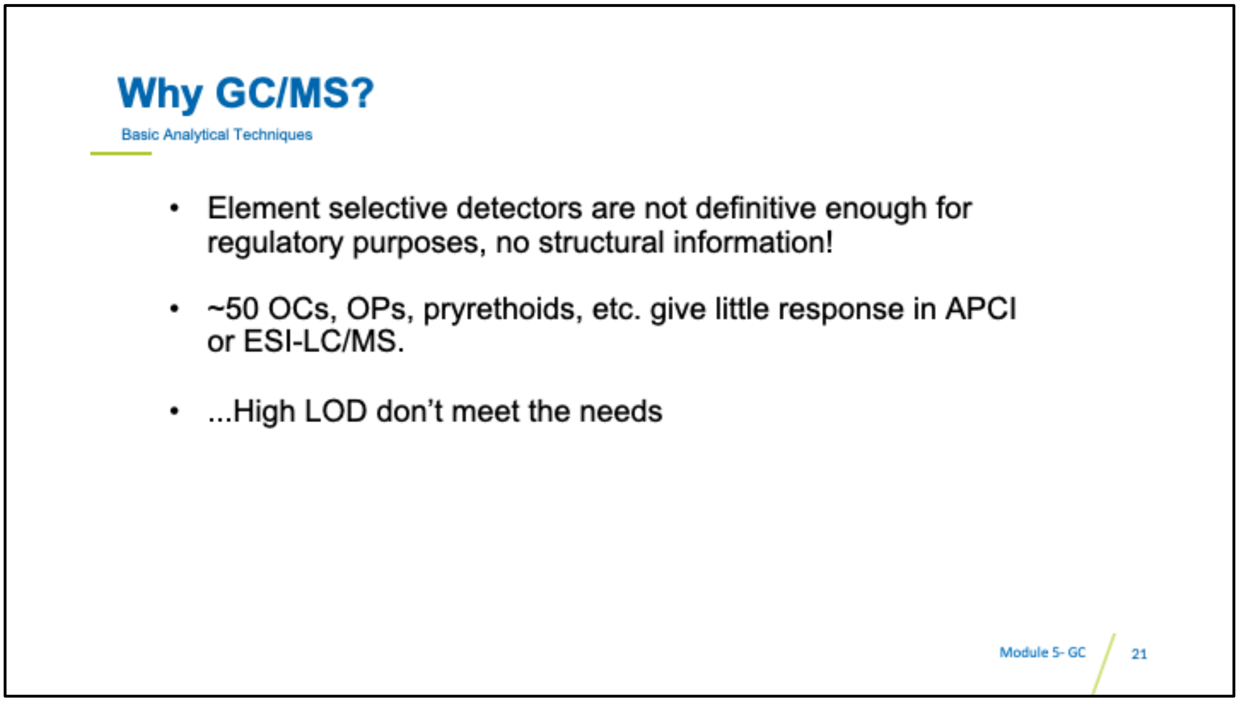
GC-MS Systems

Ion trap

Quadrupole (single)

The mass spectrometry component of a GC-MS system is the same as described in Module 4 dedicated to HPLC and in the upcoming Module 6. Briefly, a quadrupole maintained under high vacuum uses radio frequency and polarity switches to guide ions of a particular mass-to-charge ratio to a detector. This type of detector is highly selective because it will only allow one mass to charge ratio through, but we must bear in mind that more than one chemical compound may produce ions of this M/Z. Combining two quadrupoles are a collision chamber between them increases the selectivity even more, which is why this combination is considered to provide sufficient information for confirmation of identity.

The very small size of the sample effectively making it through the GC column sometimes justifies the use of a concentration step such as an ion trap, which will be discussed in Module 6.



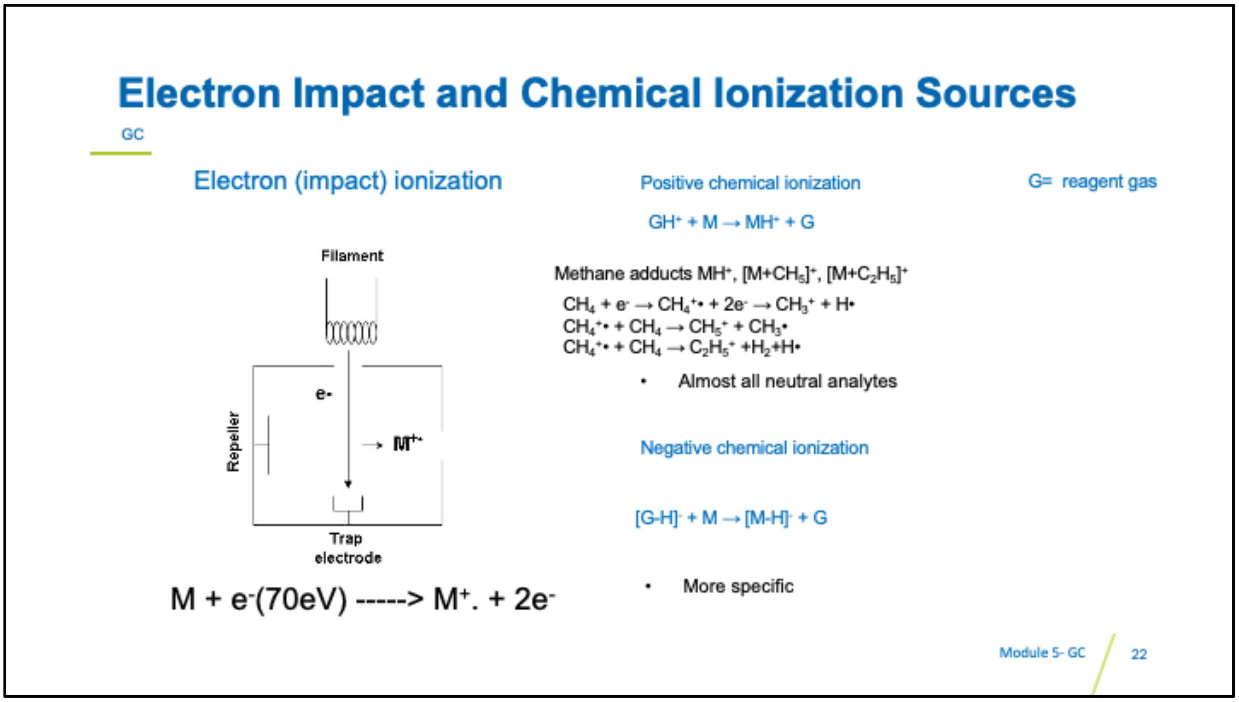
Why GC/MS?

Basic Analytical Techniques

- Element selective detectors are not definitive enough for regulatory purposes, no structural information!
- ~50 OCs, OPs, pryrethoids, etc. give little response in APCI or ESI-LC/MS.
- ...High LOD don't meet the needs

Gas chromatography has s solid place in the food safety laboratory for a number of reasons. While the absence of structural information limits the confirmation capabilities with older detectors to just matching retention times with multiple columns, mass spectrometry really bridges this gap. Obviously, the ~50 pesticides that are not amenable to LC analysis could be justification enough. But some older mostly phased-out pesticides such as organochlorides and organophosphates still require testing because they are either still registered for use in some countries or because they are found in the environment. And these are also not doable on HPLC. Some pesticides can be brought into HPLC-MS methods, but challenges still exist for very low concentrations.

The combination of GC with mass spectrometry has expanded the scope of use to confirmation analysis in a single method; this has contributed to make GC highly desirable again in the food safety laboratory, especially for pesticide residue analysis. When the scope of the laboratory more broadly covers food analysis, the strength of GC for oil analysis and its powerful detection and confirmation of pesticide residues give it even more value for a lower cost than the liquid chromatography equivalent.



Electron Impact and Chemical Ionization Sources

GC

Electron (impact) ionization

$M + e^-(70eV)$ -----> $M^+. + 2e^-$

Positive chemical ionization

G= reagent gas

$GH^+ + M \rightarrow MH^+ + G$

Methane adducts MH^+, $[M+CH_5]^+$, $[M+C_2H_5]^+$

$CH_4 + e^- \rightarrow CH_4^{+\bullet} + 2e^- \rightarrow CH_3^+ + H\bullet$
$CH_4^{+\bullet} + CH_4 \rightarrow CH_5^+ + CH_3\bullet$
$CH_4^{+\bullet} + CH_4 \rightarrow C_2H_5^+ + H_2 + H\bullet$

- Almost all neutral analytes

Negative chemical ionization

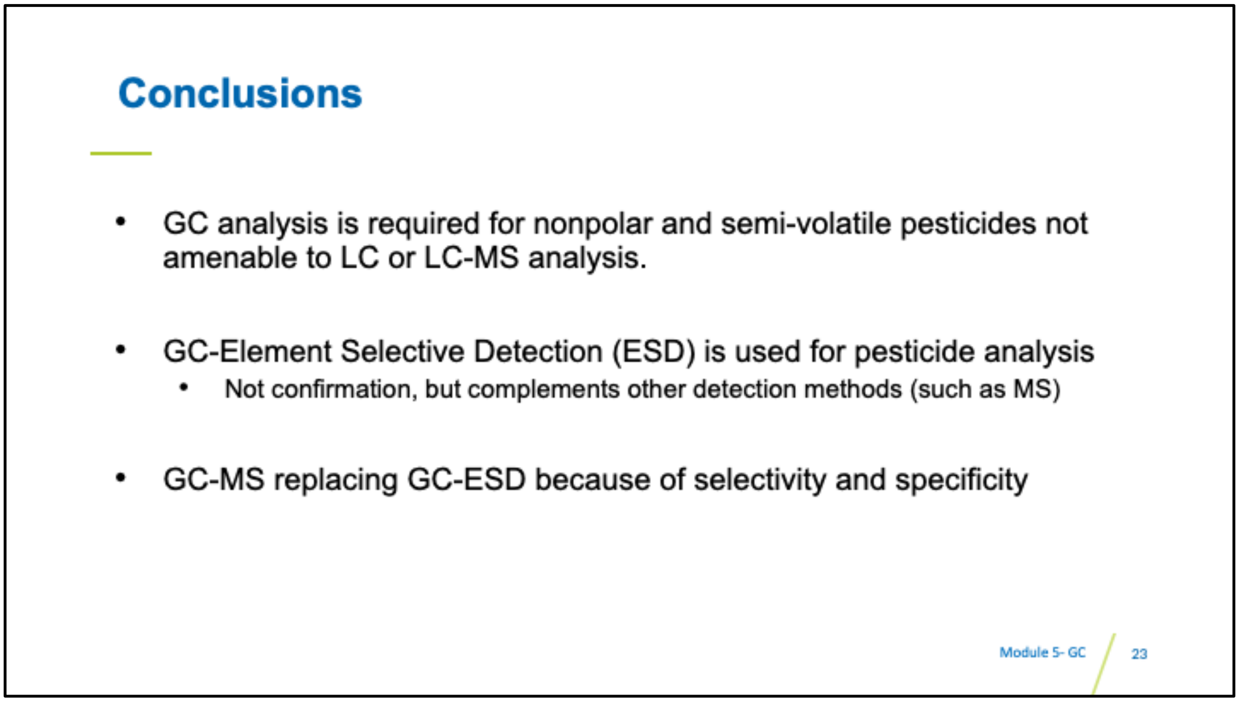
$[G\text{-}H]^- + M \rightarrow [M\text{-}H]^- + G$

- More specific

Typical sources used for mass spectrometry following GC separation are electron impact and chemical ionization. Electron ionization, formerly known as electron impact ionization is a hard ionization technique. A metal filament is heated, which produces highly energetic electrons. These electrons meet the analytes from the GC in a chamber filled with a gas, usually methane, that slows down the highly energetic electrons. When they meet, the remaining high level of energy causes a fragmentation of the analyte molecules. The first fragment is usually one where electrons are knocked off the analyte, but many smaller fragments are generated as well. It is the pattern of fragmentation, a highly reproducible process, that enables the identification of the compound.

Chemical ionization is a soft ionization, like electrospray in LC/MS. In this source, a gas is ionized, usually methane gas, by an electron beam. When the ionized gas meets the analyte, a hydrogen molecule is transferred, which produces a quasi-molecular ion [MH] and some other ions in much smaller quantity. This is the positive mode of chemical ionization. Its advantage is that almost all analytes compatible with GC are compatible with positive CI.

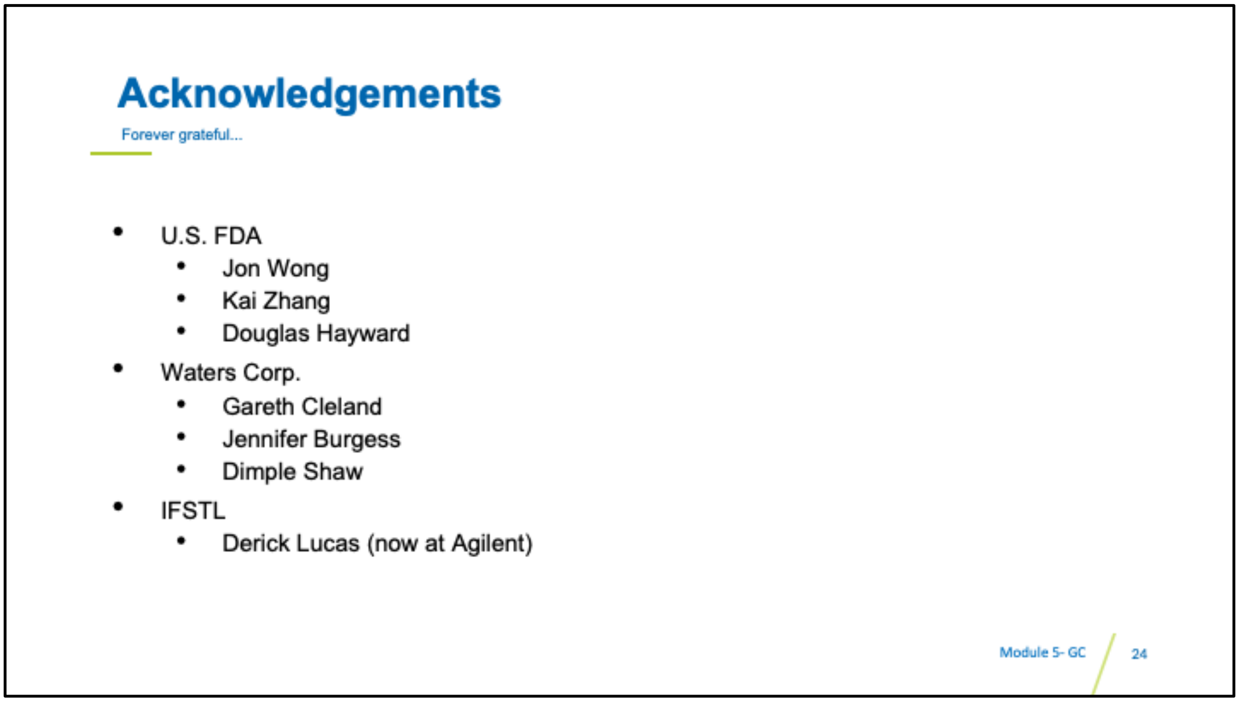
Negative CI is more selective in the sense that not all analytes will produce a stable negative quasi-molecular ion. It is very effective with environmental contaminants such as PCBs and fire retardants, as well as pesticides.



Conclusions

- GC analysis is required for nonpolar and semi-volatile pesticides not amenable to LC or LC-MS analysis.
- GC-Element Selective Detection (ESD) is used for pesticide analysis
  - Not confirmation, but complements other detection methods (such as MS)
- GC-MS replacing GC-ESD because of selectivity and specificity

The gas chromatograph is an important instrument in the food safety laboratory because, equipped with appropriate detectors, it enables the analysis of a large number of semi volatile compounds for which regulations exist. Liquid chromatography and gas chromatography are complementary techniques in the sense that they target molecules that are nonvolatile for LC, and semi volatile or volatile for GC. The selection of the detector is critical and as described in this module many detectors exist that are suitable for specific chemical contaminants of food. However, mass spectrometry in the form of a single or tandem quadrupole is playing an increasingly important role for the identification and quantification of a wide variety of chemical contaminants. Have however the high cost this type of detector, the higher cost of maintenance, and most importantly the specialized workforce tat is hard to find mean that there will be a need for the other detectors for many years to come.



Acknowledgements

Forever grateful...

- U.S. FDA
  - Jon Wong
  - Kai Zhang
  - Douglas Hayward
- Waters Corp.
  - Gareth Cleland
  - Jennifer Burgess
  - Dimple Shaw
- IFSTL
  - Derick Lucas (now at Agilent)

Many people have contributed slides or contributed ideas or reviewed various parts of this module, and for that, I am forever grateful.

Section 2
End

Next: SECTION 3
GC for Pesticide Residues