

Do we always need mass spectrometry with gas chromatography ?

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Abstract : The detector , as well as being an essential supporting device for the gas chromatography (GC) has also played a critical role in the development of the technique as a whole. The mass spectrometer (MS) is still the commonly praised detector as before. In fact , the information of fragmentation patterns is seldom used in practice , and the GC-MS instrument is even more expensive. For today ' s analytical problems , it seems that element specific detectors can and should be used for many applications rather than GC-MS.

Key words : gas chromatography (GC) ; mass spectrometry (MS) ; detector

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1 Issues raised

In all too many applications of gas chromatography (GC) , there is a need for supporting confirmation of a result. Retention time alone is simply not definitive enough. What to do ? Occasionally the issue has been studied and a secondary confirmatory column has been documented and recommended. This may require running a sample again. This may be practical , but also is time consuming. If the need is infrequent , then starting up the confirmatory chromatograph will be time consuming. Often the start up time extends the analysis time to a second shift , thus introducing the variance of different analysts.

For these reasons , many laboratories in the developed world have opted to use a mass spectrometer (MS) as the secondary or confirmatory detector especially in GC. Indeed , when MS is suitable , it is a fine detection technology. However , the acquisition cost is high , as is the running cost , and the analyst needs to be proficient in interpreting GC-MS spectra. This often means that the laboratory needs a GC-MS specialist , which is often several pay grades higher. Also , MS instruments do benefit from experienced operators and service staff. For this reason , many

vendors recommend a service interval as short as two months.

2 Element specific detector for GC

Rather than focusing on MS detection , experienced gas chromatographers can select from a list of highly discriminating detectors for GC to supplement and thus confirm results from the flame ionization detector (FID) and thermal conductivity detector (TCD). Some detector options are presented in Table 1. In many cases , the element specific detector might be sufficient , since the analytes of interest may all have an element in common , other than carbon and hydrogen , of course. For example , if the analytes of concern are all halocarbons such as polychlorinated biphenyls (PCBs) , then one could select the thermionic surface ionization detector (TID-7) and really simplify the chromatography.

The selective detectors for gas chromatography are shown in Table 1. One can use the element specific detector to selectively focus on a particular analyte class. For example , if the problem is to detect oxygenated compounds in fuels , then running the a dual detector GC with an TID-1 (which is not destructive) followed by FID. The latter will provide a profile of the hydrocarbons.

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Table 1 Selective detectors for gas chromatography (excluding MS)

Detection type	Vendor	Detection process	Significant application
Electron capture detector	Agilent Technologies , Santa Clara , CA	beta ray capture	halogenated analytes
Flame photometric detector	Agilent Technologies , Santa Clara , CA or O. I. Analytical , College Station , TX	upon burning , sulfur containing analytes emit photons that are detected with photomultiplier tube	sulfur containing analytes , less sensitive for P
Helium discharge detector	VALCO Instrument Company , Inc. , Houston , TX	photons from a helium discharge ionize analytes	high sensitivity detection
Nitrogen chemiluminescence detector	Agilent Technologies , Santa Clara , CA	oxidize organonitrogen compounds to NO. NO reacts with ozone to produce light	organonitrogen analytes
Photoionization detector	PID Analyzers , Pembroke , MA	photons from a ultraviolet lamp ionize analytes	industrial hygiene even in coal mines
TID-1 detector	DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	oxygenated and nitro hydrocarbons
TID-2 detector	Agilent Technologies , Santa Clara , CA or DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	phosphorus and nitrogen compounds
TID-3 detector	DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	volatile halogenated organics including trihalomethanes
TID-4 detector	DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	best response for nitrogen analytes
TID-5 detector	DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	Br and I organics , suppressed resp. to Cl
TID-6 detector	DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	phosphorus organics suppressed resp. to N
TID-7 detector	DETECTOR Engineering & Technology , Walnut Creek , CA	thermionic surface ionization	halogenated pesticides , polychlorinated biphenyls (PCBs) , polybrominated diphenylethers (PBDEs)

Oxygenated analytes will stand out in the response from the TID-1. Or one can run the two detectors in parallel , but this requires a splitter.

3 Capabilities of detectors

3.1 Helium ionization

The pulsed discharge detector operates in two modes , both of which provide opportunities for selective detector tuning. In the electron capture mode , the compounds with a high electron affinity such as halocarbons entering the detection cell decrease the standing current. Typical detection limits fall in the range of 10^{-15} g to 10^{-12} g. In the pulsed discharge mode , high energy photons from a helium discharge ionize the analytes. The liberated electrons cause changes in the standing current which are amplified for the detector signal.

Detection sensitivity is superior to conventional sources such as ^{63}Ni .

3.2 Electron capture

Electron capture detectors qualify as the classic selective detector , having been invented in the late 1950s. A radioisotope such as ^3H or ^{63}Ni is placed in a cell with a collection anode [1]. In the absence of analyte , a small finite “ standing ” current flows from the beta ray source to the collection anode. However , when analytes with high electro affinity are present , the electrons are captured , which reduces the standing current. The loss of current is amplified and displayed as the response.

3.3 Photoionization

Photoionization detectors are conceptually similar to the pulsed discharge detector , except that

the ultraviolet light directly illuminates the content of the detector cell [2]. The light ionizes all molecules that have an ionization energy equal to or less than the energy of the light emitted from the lamp. The electrons are attracted to the anode and the resulting current is amplified for the detector output.

3.4 Flame photometry and nitrogen chemiluminescence

Flame photometric detectors burn the column effluent in a flame. Photons from the flame are converted to an electric current with photomultiplier tube. Detection limit for sulfur is about 4 pg/s. Detection of phosphorous is more than 10 times worse.

Nitrogen chemiluminescence detection relies on the reaction of NO with ozone to produce a photon which is measured with a photomultiplier.

These detectors are quite popular since they are so specific to the elements. They are moderately expensive , however.

3.5 Thermionic surface ionization

Thermionic surface ionization describes a class of chromatographic transducers that utilize hot ceramic surfaces where small differences in work function produce element specific ionization [3]. These detectors (TID-1 – TID-7 , Table 1) differ by the composition of the active surface. Small ceramic beads are heated in a detector that resembles a cell for an FID , but without the flame. The column effluent passes over the hot surface. Analytes that possess the right functional group for the bead , contact the surface and are ionized [4 5]. Ionization changes the standing current passing through the cell , which is amplified as with an FID. Typically , the life time of the ceramic bead is a few years. Beads are easily replaced and recycled. The chromatographer can identify peaks based upon the retention time and

relative response (response ratio) of the peaks detected by a universal detector such as an FID and an element specific detector. The price of a typical TID is less than 5% of the cost of a MS detector. Plus , maintenance is easier and less demanding.

4 Conclusion

If element specific detectors are so good , why is GC-MS so popular ? MS does provide more information , especially if fragmentation patterns are considered. But this information is seldom used in practice , since the analytes are usually well known and can be identified by comparing the retention time with standards. MS achieved its popularity 20 years before the thermionic detectors became easily available. And fortunately for MS , many occidental economies can afford the expensive instrumentation. Things would probably be quite different if the thermionic detection preceded the introduction of GC-MS.

For today 's analytical problems , it seems that element specific detectors can and should be used for many applications rather than GC-MS. In short , why waste money just to follow the herd ? Element specific detectors save money , are easy to use , and allow people with less training to make good decisions. This is what separation science is all about.

References :

- [1] Electron capture detector. http://en.wikipedia.org/wiki/Electron_capture_detector
- [2] Photoionization detector. http://en.wikipedia.org/wiki/Photo-ionization_detector
- [3] Vijaya Saradhi U , Suryanarayana M , Gupta A , et al. J Chromatogr A , 2001 , 911(1) : 63
- [4] Hill H , McMinn D. Detectors for Capillary Chromatography. New York : John Wiley & Sons , 1992 : 139
- [5] DETectro Engineering & Technology , Inc. <http://www.det-gc.com/DetectionPrinciples.htm>