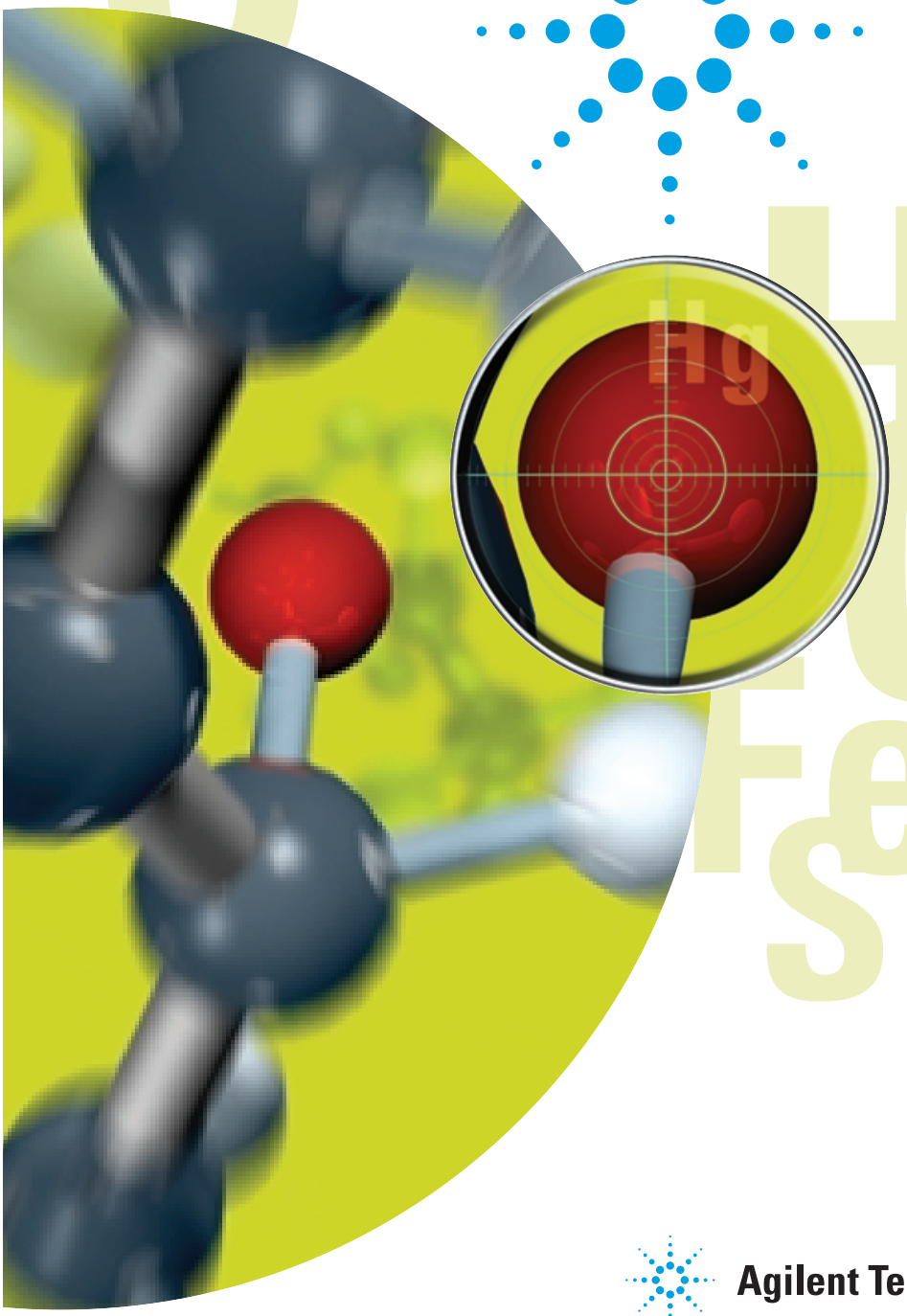
The Third Dimension of Information Vol. IV

SIMPLY SMART SOLUTIONS

Applications with the Agilent Technologies Atomic Emission Detector

jas joint analytical systems



Agilent Technologies

The Third Dimension of Information Vol. IV

Applications with the Agilent Technologies Atomic Emission Detector

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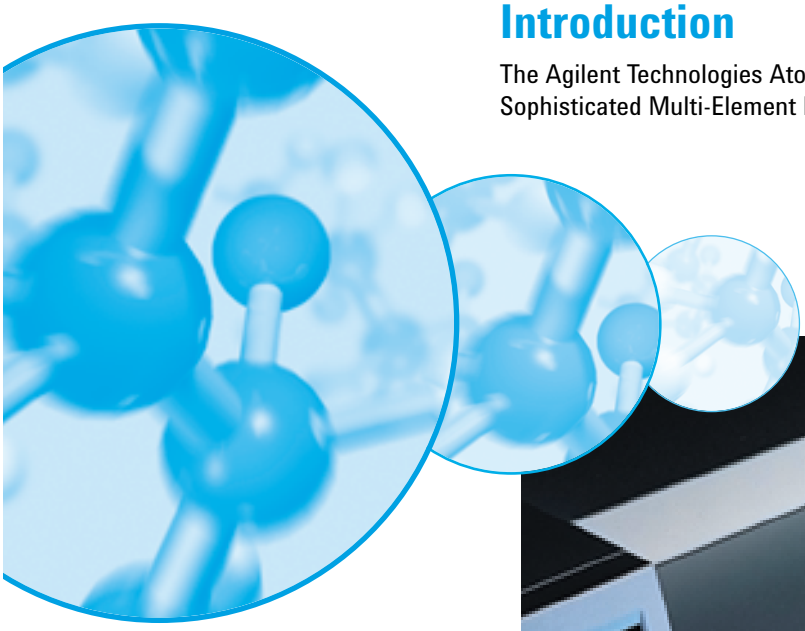
Introduction

The Agilent Technologies Atomic Emission Detector for Gas Chromatography, Sophisticated Multi-Element Detection for Routine or Research Analyses



Product Summary

Agilent Technologies Atomic Emission Detector (AED) is the world's only commercially available atomic emission detector for gas chromatography.
The first generation of AED, the HP 5921A Atomic Emission Detector was introduced in 1989. As a second-generation instrument, the G2350A AED has been substantially redesigned to broaden the scope of applications, enhance data handling and integration, and increase the analytical utility. Additionally, the AED is much easier to use and maintain, more reliable and smaller in size and weight.

Features

The Agilent Technologies AED allows the detection of virtually all elements (except helium) within any volatized compound at picogram-levels and with excellent selectivity.

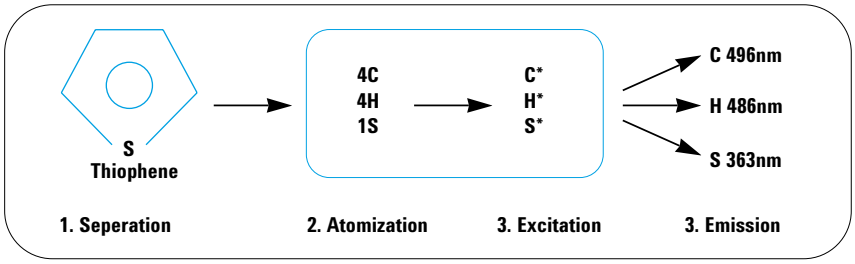
Capabilities of the AED

- Selectively detect compounds containing any of about 25 preset elements including organo-metallic species and compounds labeled with stable isotopes.
- Enhance analytical confidence by confirming the presence of elements in compounds using atomic emission spectra.
- Obtain up to six element chroma tograms from a single injection.
- Automatically profile a sample by sequential detection of any number of elements in the sample.
- Perform quantitative analysis using almost constant response factors, it's possible to calibrate with any readily available compound containing the elements of interest.
- Estimation of empirical formulas.

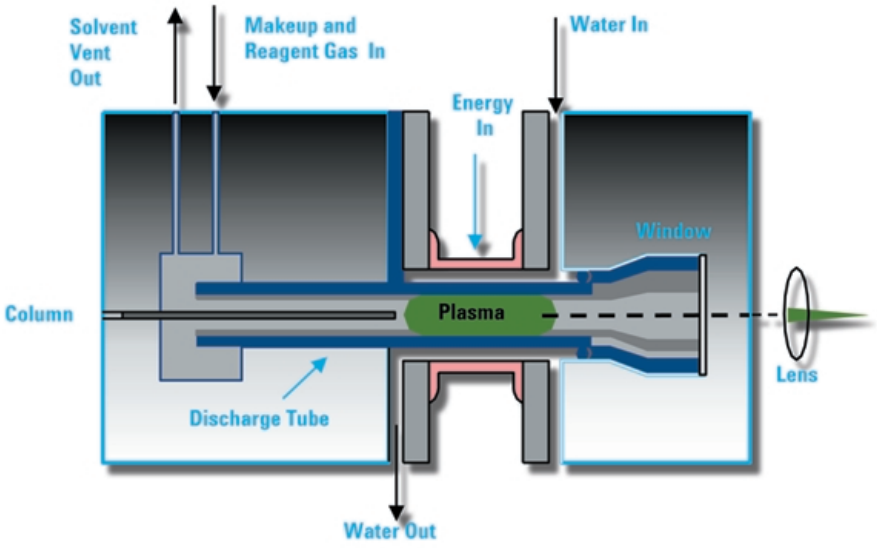
Sensitivity and selectivity of the Atomic Emission Detector

- About five times more sensitive for carbon than GC-FID
- About ten times more sensitive, with more linearity than GC-FPD for sulfur.
- For some elements it is more sensitive and selective than GC-MS in SCAN mode.
- Typically more selective than GC-NPD and GC-ECD for complex matrices.

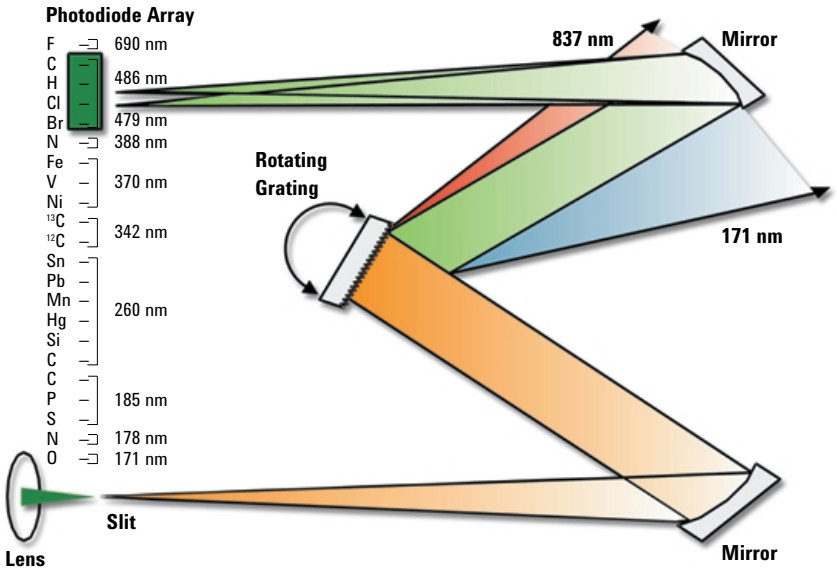
GC - Atomic Emission Process:



AED Cavity and Plasma Source:



Detection System:



The AED is designed to interface with the 6890 series of gas chromatographs. Users can program both GC and AED parameters from the Windows-based ChemStation. Electronic control of many of the system parameters, such as precise control of all gases, make it possible to optimize performance of the GC-AED and to rapidly change analytical methods. The increased versatility further enables the GC-AED to be used as a universal analysis tool that can serve as an alternative to multiple GC's equipped with element-specific detectors.

The highest SENSITIVITY and SELECTIVITY for Element Detection

The AED uses atomic emission spectroscopy to detect elements in compounds eluting from a GC. The helium plasma fragments all compounds, with the resulting excited atoms producing characteristic emission lines. A lens focuses the light produced onto the entrance slit of the spectrometer. The rotating grating varies the elemental light spectrum covered by a fixed-position Photo Diode Array (PDA) that can measure up to six elements simultaneously.

The next three pictures show the main operation principles of the AED.

GC-AED / GC-MSD

There are often analytical problems where the characterization of complex mixtures by GC-MSD Total Ion Chromatograms (TIC) can be difficult for some of the compounds. In these situations, the GC-AED can be used to corroborate MS library searching results by identifying the elements present in the compounds.

Quantitation

Most detectors require construction of calibration curves using "target analytes" as standards. Calibration for comparable analyses using the AED in most cases requires only that the standard contain the elements of interest; there is no need for employing target analytes, which might be difficult to obtain. The use of compound-independent calibration is made possible by the linear relationship between AED response and element concentration, which is virtually independent of molecular structure.

Analysis of Organo Tin Compounds

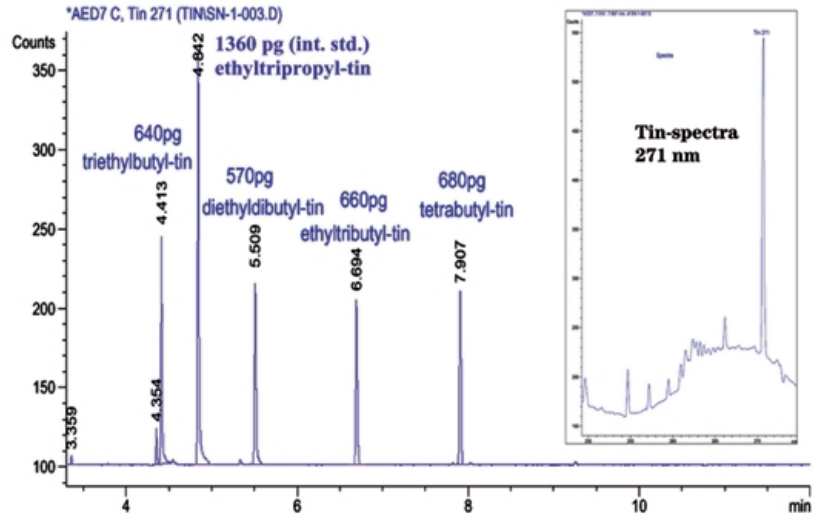
Sensitive and selective determination of TBT and other organo-tin compounds in different matrixes.

Analytical Problem

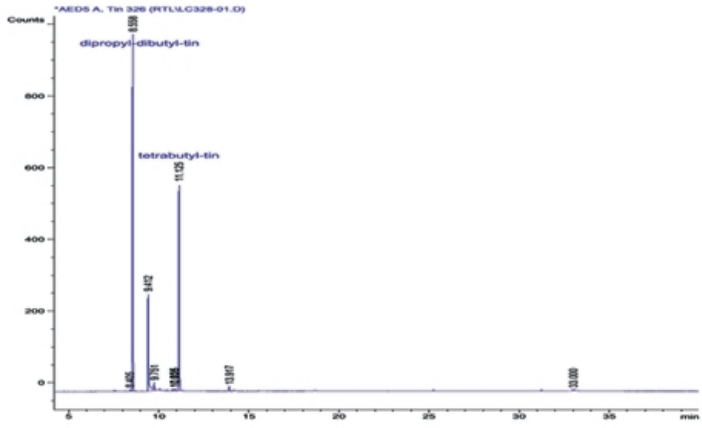
Chemical organo-tin compounds are generally toxic. The most common compound in this category is tributyl-tin (TBT).
TBT was heavily used as an antifouling agent, mainly for ships, until 1980. But also textiles such as carpets or clothes have been impregnated with TBT, which is not only highly toxic but is also an endocrine disrupter. Usage of TBT all over the world has been severely restricted and the International Marine Organization (IMO) have banned the use of TBT after 2003. Nevertheless there is still a requirement to measure TBT and other tin compounds in the environment.

There are several methods used to analyze tin compounds in different matrixes, but most of them have some limitations. Some detectors such as ICP or AAS, will measure only the total tin content of a certain matrix, including the insoluble and therefore less toxic compounds. Others, such as FPD (with tin filter) or MSD, are often not selective enough to detect low levels of organo-tin compounds in complex matrixes.

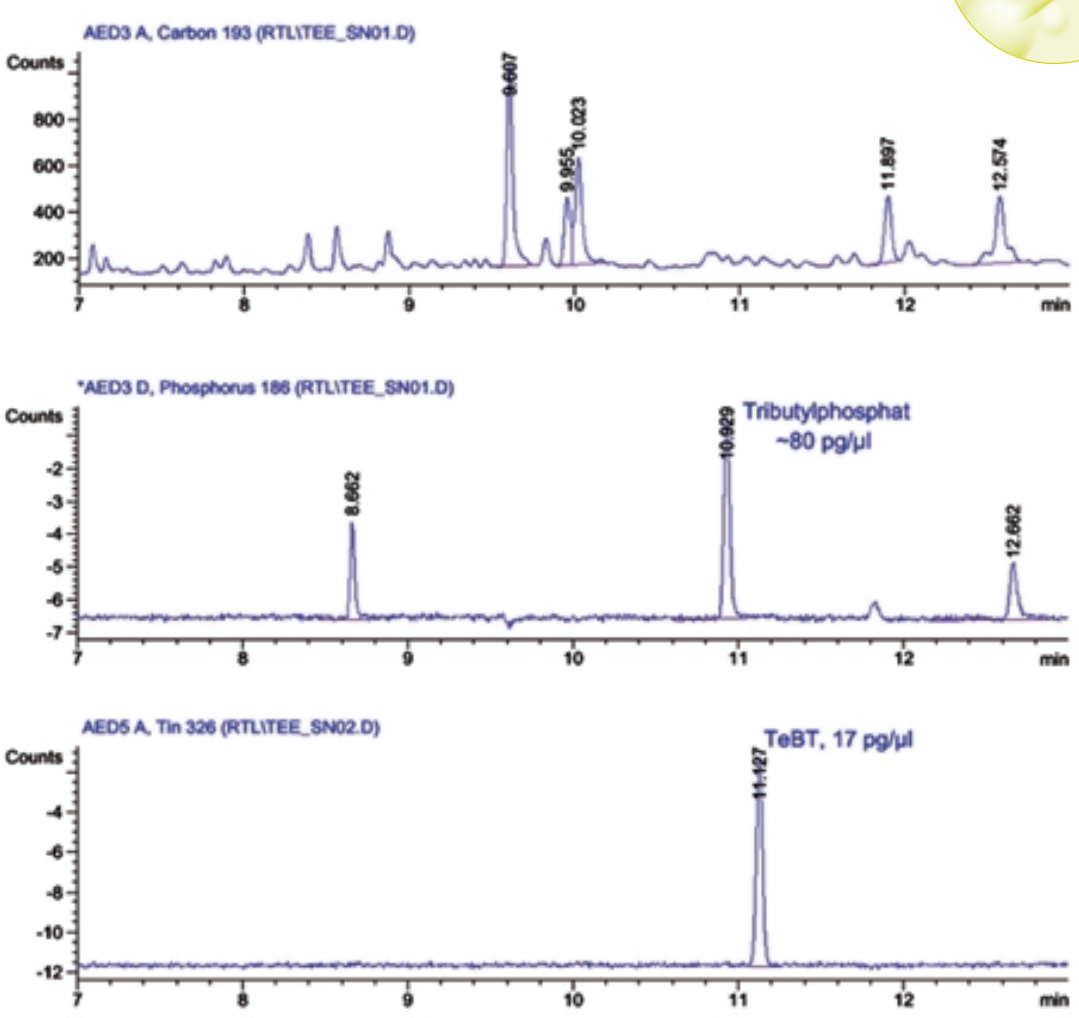
Tin standard (~650 pg each) with GC/AED at 271 nm



Shoe Insole Extract, 5µl solvent vent, Tin 326 nm



Spiked Sn and P at low levels in black tea extract (5µl injection)



Agilent 6890 GC/AED conditions

6890 GC:

PTV inlet: 5µl solvent vent, 80°C (0.02 min.) 700°C/min. to 270°C, vent flow 20 ml/min. He

Oven: 70°C (2 min.) 25°C/min. to 150°C, 3°C/min. to 200°C, 8°C/min. to 280°C (10 min.)

Column: 30m x 0.25mm x 0.25µm HP5-MS, constant pressure at 27.6 psi

AED:

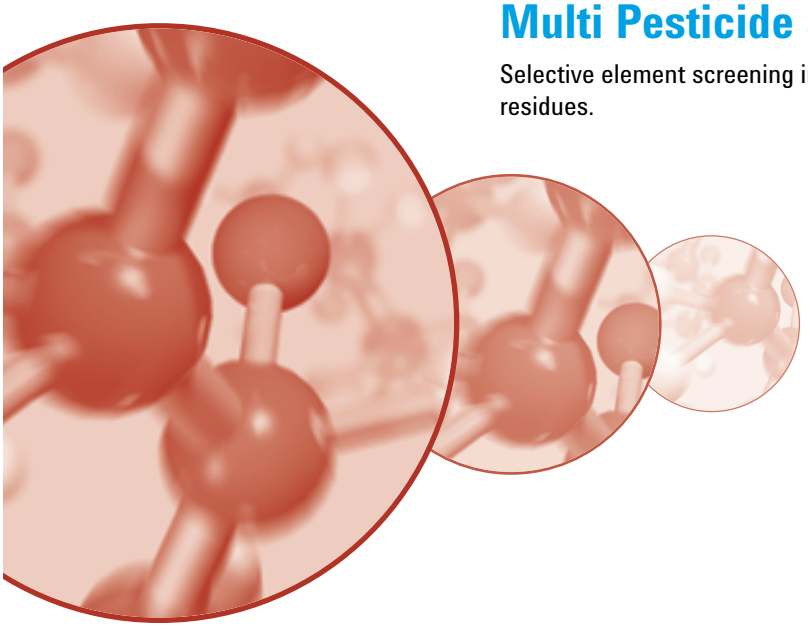
Carbon	193 nm
Phosphorus	186 nm
Tin	271 nm
Tin	326 nm

Cavity 310°C, Transfer line 300°C
Solvent vent on: 0.1 min., off 4.0 min.

How the Agilent Atomic Emission Detector can help

After suitable derivatisation to ensure detection of all volatile ethyl- or propyl/butyl tin compounds, selective detection with the AED, at different wavelengths, will be possible.
Tin detection at 271nm allows simultaneous analysis of C, Si, Hg, Mn and Pb together with Sn from a single injection. This is extremely useful for the screening of metallo-organics in environmental samples.

The most sensitive and selective detection of tin can be performed at 326 nm. At this wavelength, tin can be detected below 1 pg/sec with a selectivity of more than 3 000 000 against carbon. This allows measurement of very small concentrations of tin even in very complex matrixes such as clothes, carpets or sludge.



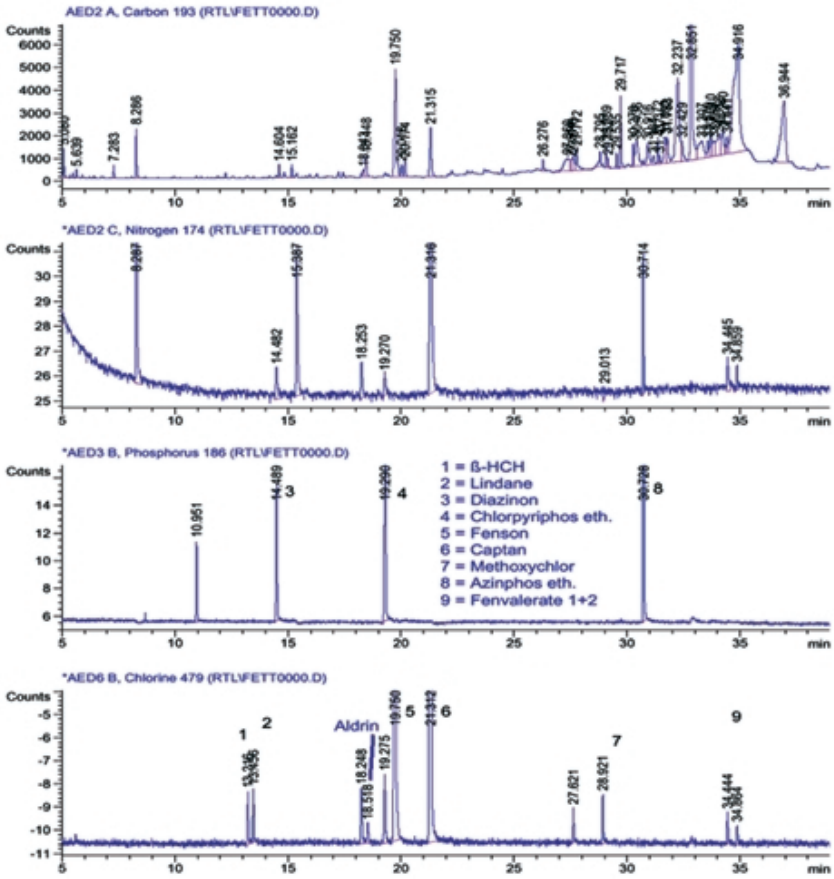
Multi Pesticide Screening in Food Samples

Selective element screening in food samples for the determination of pesticide residues.

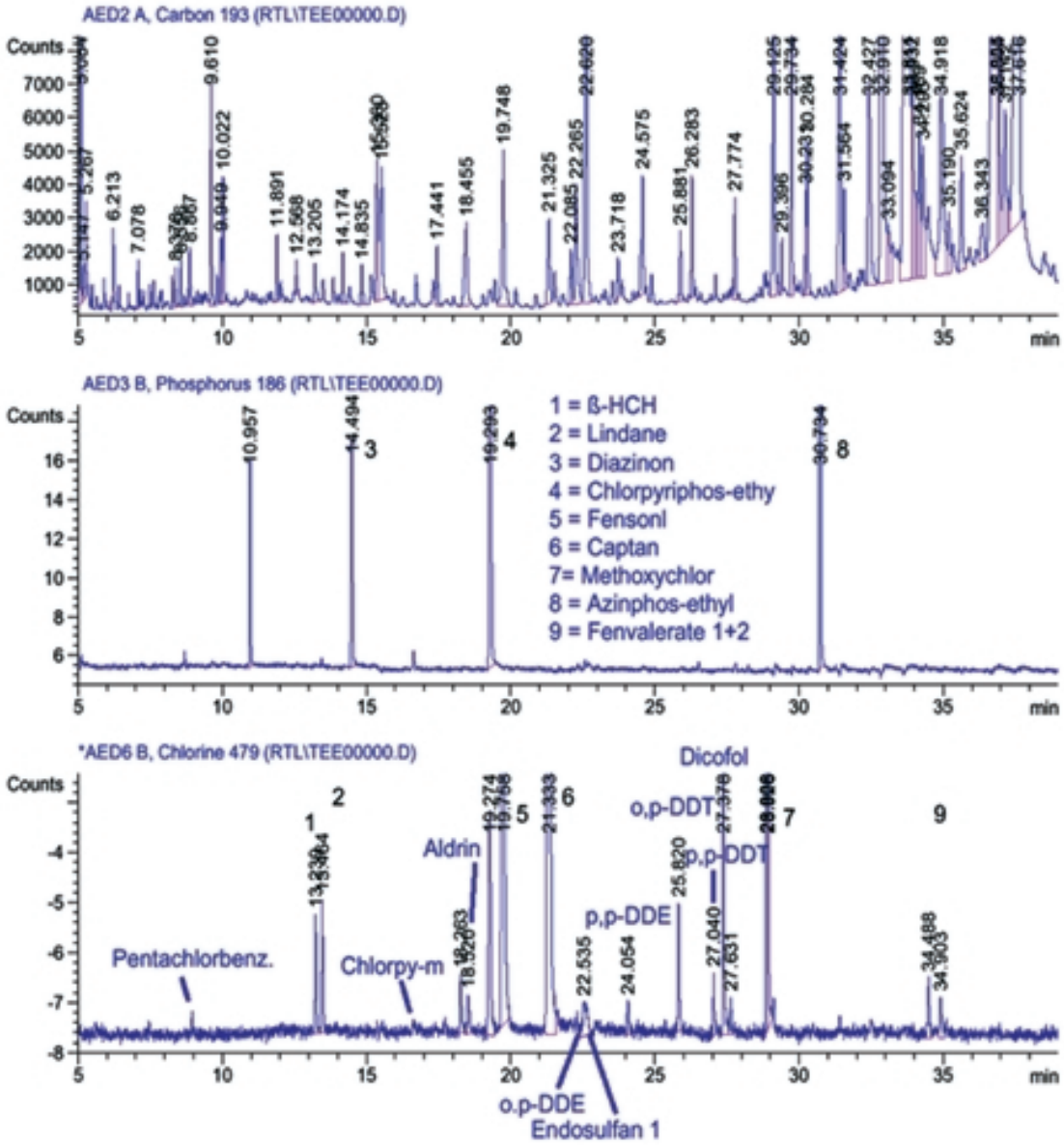
Analytical Problem

More than 750 compounds are listed currently in the pesticide manual as active ingredients in various pesticide formulations. Many of them are no longer used, but still persist in the environment. To protect the environment and human health, acceptable limits have been set by the different governments around the world. Numerous methods have been developed to screen for pesticide contamination in food and the environment. Most laboratories that analyze for pesticides in food, screen for only a few dozen compounds because it is very difficult to screen for more. Even GC/MSD methods, which are gaining in popularity, still have some limitations, either using selected ion monitoring (SIM) for target compounds or Scanning Methods.

N, Cl and P- Pesticides spiked into a pork fat extract with AED, 5µl solvent vent



Pesticides found and spiked in a black tea extract



Small portion of the RTL Pesticide database

```
==========================================================================
Results of RT Table Search
==========================================================================
Search results for 13.151 +/- 0.100 minutes
Contains elements:          CL:                                  Does
not contain elements:  BR:N:P:S:                              RTT file
searched:           C:\HPCHEM\RTL\PEST.RTT
RTTable Title:              HP Pesticide RT Table Release Candidate 5
FID_RT   Compound Name                                              MW       13.176
BHC beta isomer                                          290.83        CAS #
319-85-7                                                            Formula
C:6,H:6,Cl:6,                                                       MSD_RT       13.2
     HP Inventory Number  HP2207
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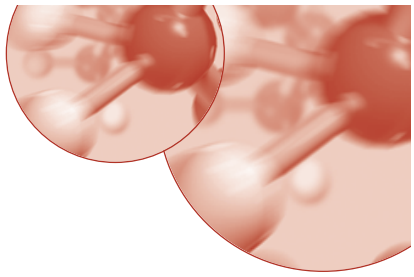

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not contain elements:  BR:N:P:S:                          RTT file
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RTTable Title:              HP Pesticide RT Table Release Candidate 5
FID_RT    Compound Name                                                MW      13.429
Lindane                                                      290.83       CAS #
58-89-9                                                                   Formula
C:6,H:6,Cl:6,                                                             MSD_RT
13.461
     HP Inventory Number  HP2041


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not contain elements:  BR:CL:                             RTT file
searched:           C:\HPCHEM\RTL\PEST.RTT
RTTable Title:              HP Pesticide RT Table Release Candidate 5
FID_RT    Compound Name                                                MW      14.465
Diazinon                                                       4.34       CAS #
333-41-5                                                                  Formula
C:12,H:21,N:2,O:3,P:1,S:1,                                                MSD_RT
14.466
     HP Inventory Number  HP2065
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Agilent 6890 GC/AED conditions

6890 GC:

PTV inlet: 5µl solvent vent, 80°C (0.2 min.) 700°C/min. to 270°C, vent flow 20 ml/min. He

Oven: 70°C (2 min.) 25°C/min. to 150°C, 3°C/min. to 200°C, 8°C/min. to 280°C (10 min.)

Column: 30m x 0.25mm x 0.25µm HP5-MS, constant pressure at 27.6 psi

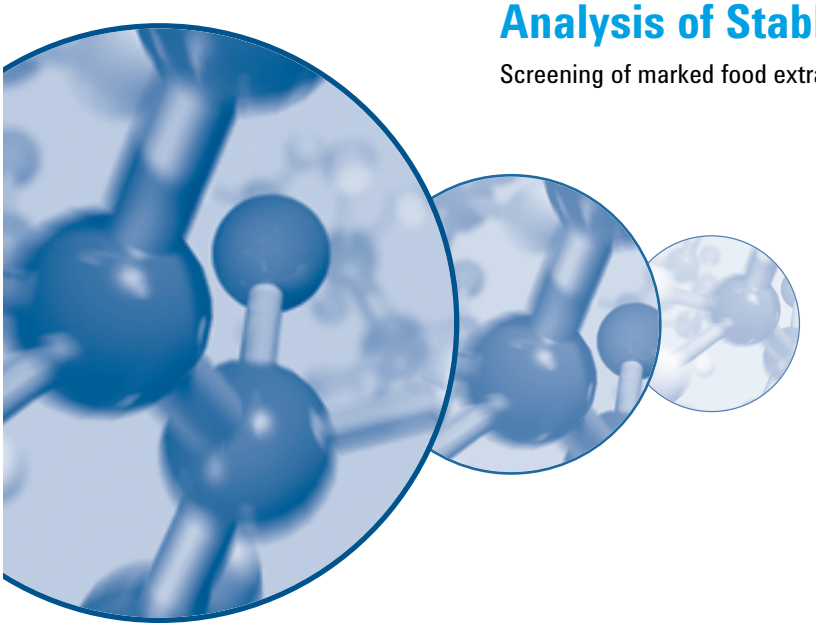
AED:

Carbon	193 nm	Group 1
Nitrogen	174 nm	
Sulphur	181 nm	
Phosphorus	186 nm	Group 2
Chlorine	479 nm	Group 3
Bromine	478 nm	
Hydrogen	486 nm	

Cavity 310°C, Transfer line 300°C
Solvent vent on: 0.1 min., off 4.0 min.

How the Agilent Atomic Emission Detector can help

The AED together with the universal pesticide method, in principle, can be used to screen for any pesticide, metabolite or endocrine disrupter that elute from a gas chromatograph. The screening procedure relies on a technique called retention time locking (RTL) with database searching based on retention times and elemental content. This procedure is used to narrow the identity of a pesticide to a few or even single possibility.
Confirmation can be performed afterwards by GC-MS, where identical retention times on both systems will simplify the identification dramatically.
The high selectivity of the AED for the selected elements allows pesticide screening, even in very complex matrixes like food extracts down to the ppb level. Using this method, there is a high probability to find and identify even unexpected or unknown pesticides.



Analysis of Stable Isotopes

Screening of marked food extracts for compounds including stable isotopes.

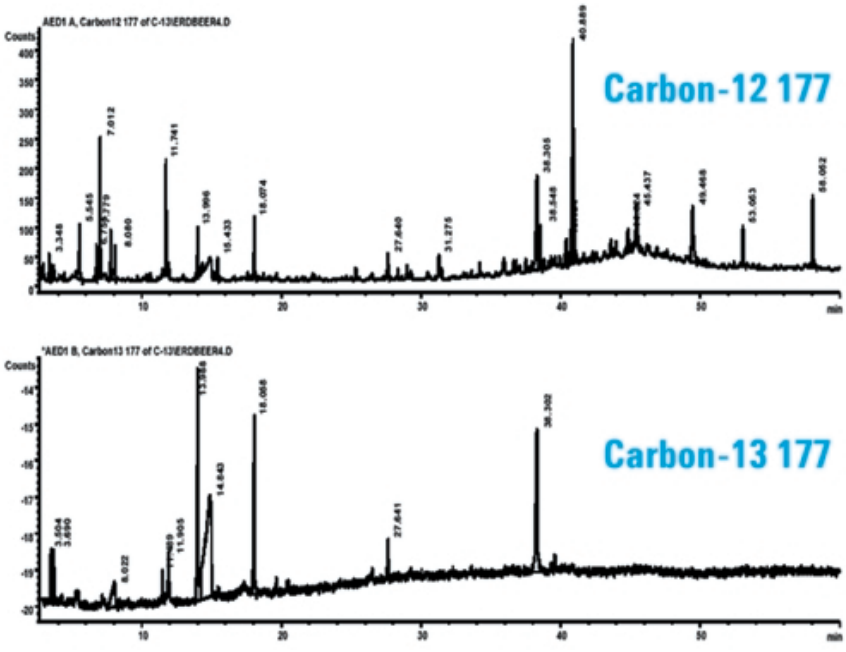
Analytical Problem

Fruits or vegetables with a reduced amount of flavour are a well-known problem. Breeding to produce more resistant plants and green-house-cultivation of the plants are often associated with this lack of flavour and aroma.

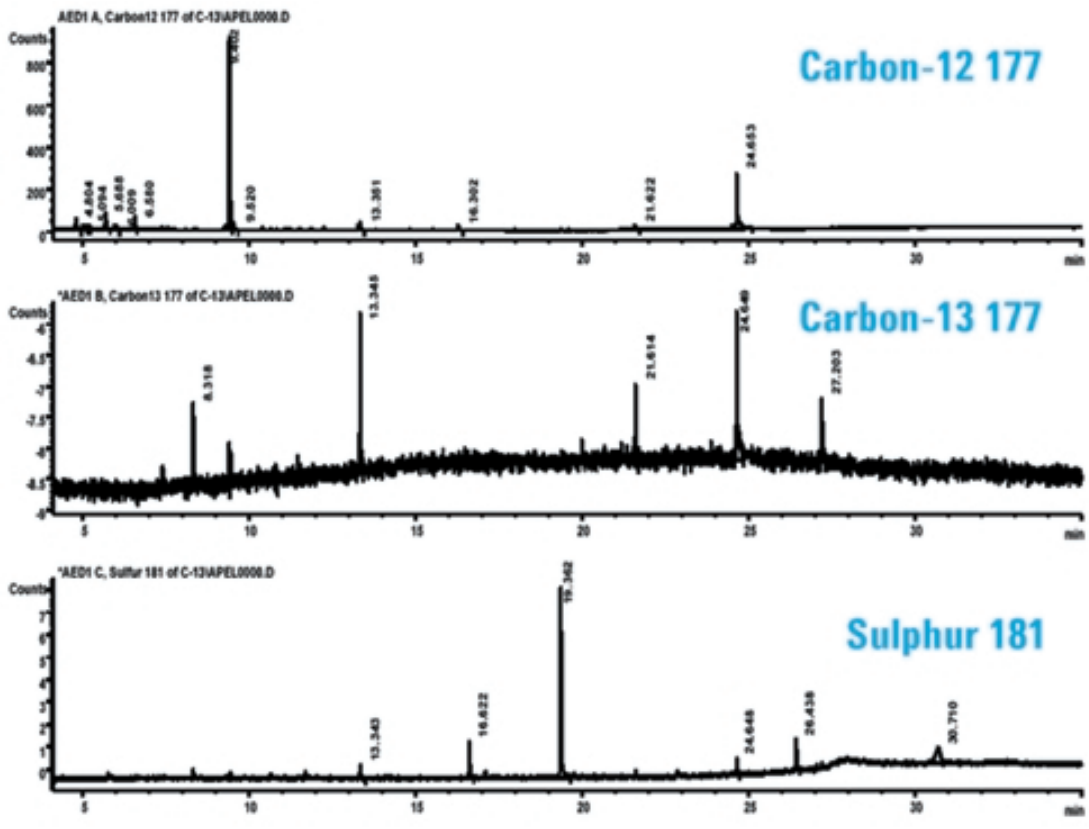
Agriculture researchers often spike plants with isotopic marker compounds to detect variations in flavour and aroma during the growth cycle. Modification of the compounds, including the stable isotope labelled compounds, must be detected to evaluate the formation of flavour or aroma active compounds.

With GC-MS analysis it is possible to measure the mass changes in a certain compound including isotopes, but on the other hand it is very difficult to find all compounds, including isotopically labelled compounds, in a complex matrix. Isotope-ratio-MS can also be used, but this technique is relatively expensive and more difficult to handle.

Selective analysis of carbon-13 marked flavour compounds in a strawberry extract



Analysis of carbon-13 marked flavour and additional sulphur compounds in an apple extract



Agilent 6890 GC/AED conditions

6890 GC:

Split/Splitless inlet: 240°C, 1µl split 10:1

Oven: 50°C (2 min.) 5°C/min. to 240°C (15 min.)

Column 1: 30m x 0.25mm x 0.25µm HP5-MS, 1.5 ml/min. constant flow

Column 2: 60m x 0.25mm x 0.25µm HP-INNOWax, 2.5 ml/min. constant flow

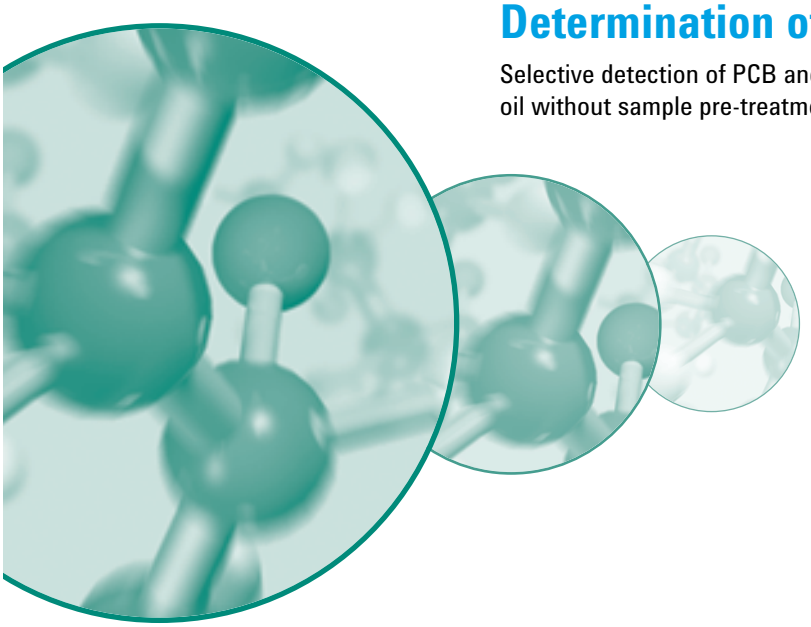
AED:

Carbon-12 177 nm
Carbon-13 177 nm
Sulphur 181 nm

Cavity 260°C, Transfer line 250°C
Solvent vent on: 0.1 min., off 4.0 min.

How the Agilent Atomic Emission Detector can help

The AED provides selective GC detection of compounds with excess carbon-13, nitrogen-15 or deuterium content. Compounds with a level higher than the natural abundance can be determinated easily. Even chromatographic overlap of labelled with unlabelled peaks can be still detected with this technique.
The ability to screen for these important tracer isotopes, together with multi-element atomic detection, makes the AED an important complement to mass and infrared spectral detection.
Labelled compounds detected with the AED can be subsequently identified much easier with a GC/MSD system or even by calculating the empirical formula from the elemental response.
A detection limit for carbon-13 of about 10 pg/sec. can be expected and a selectivity vs. carbon-12 of about 1200. The system is set normally to suppress the natural abundance of 13-C in a compound.



Determination of PCB in Transformer Oil

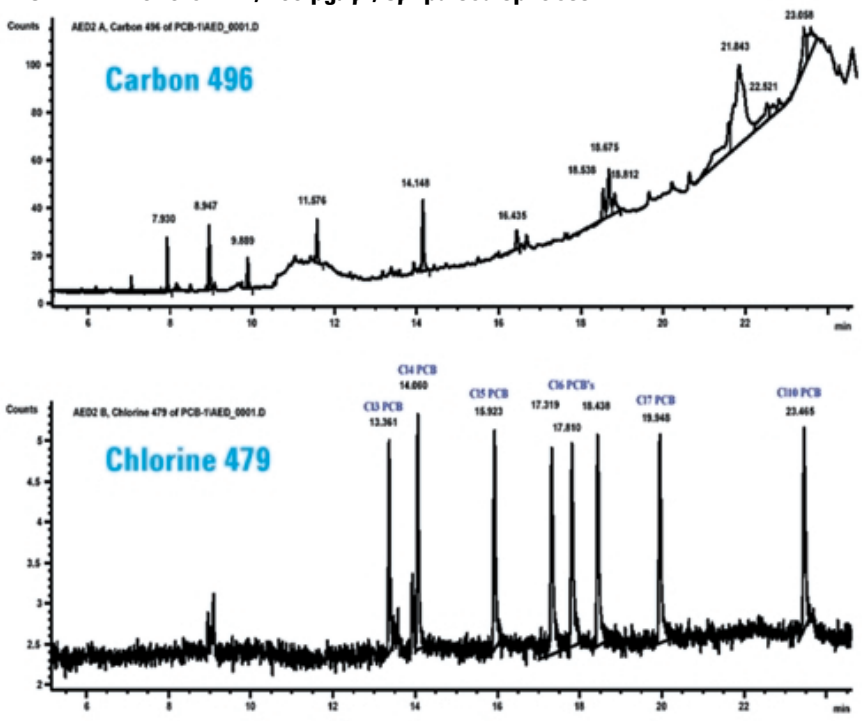
Selective detection of PCB and other chlorinated compounds in transformer oil without sample pre-treatment.

Analytical Problem

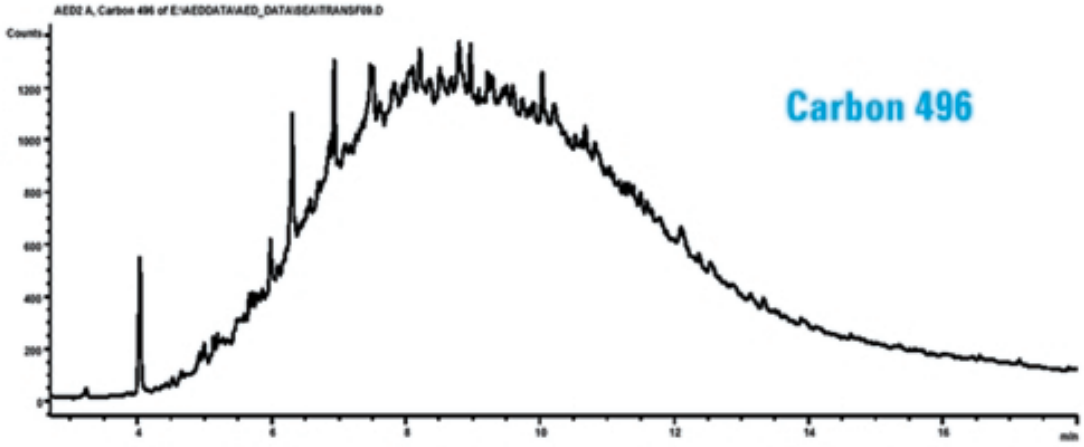
Polychlorinated biphenyls (PCB's) are a very important and widespread group of environmental pollutants. PCB's have a wide range of chemical properties and toxicity with more than 200 different congeners. PCB'S are thermally stable and excellent electrical insulators and are widely used in electrical appliances, such as power transformers, because of their dielectric (insulating) properties.

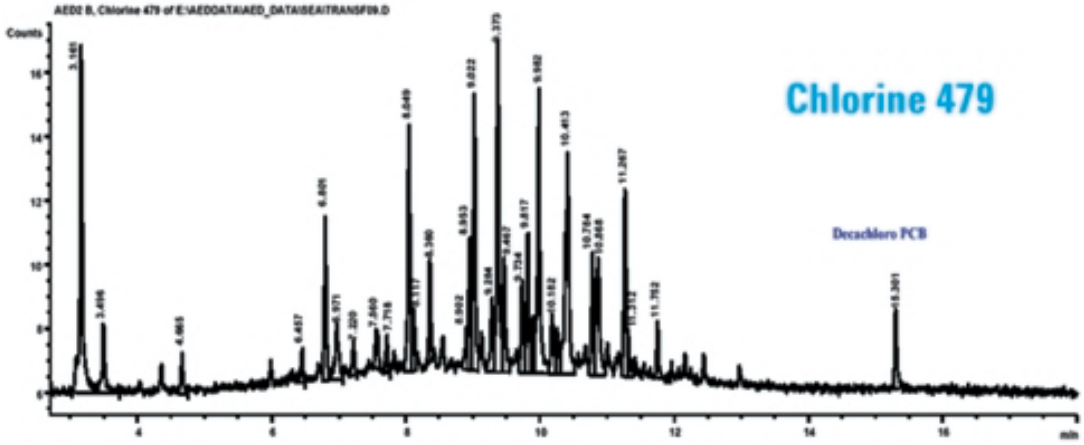
To analyse PCB mixtures in transformer oils, significant sample extraction and clean up is normally required, even when using selective detectors such as ECD or MSD in conjunction with gas chromatographic separation.

PCB Mix with the AED, 100 pg/µl, 3µl pulsed splitless



Selective Analysis of PCB's and other Chlorinated Compounds in Transformer Oil, 3µl pulsed splitless





Agilent 6890 GC/AED conditions

6890 GC:

Split/Splitless inlet: 280°C, 3µl pulsed splitless, tapered liner with glass wool

Oven: 50°C (1min.) 15°C/min. to 180°C (0 min.) 7.5°C/min. to 300°C (5min.)
or: 90°C (1min.) 30°C/min. to 180°C (0 min.) 10°C/min. to 300°C (5min.)

Column: 30m x 0.25mm x 0.25µm HP-5MS, 1.0ml/min. He, constant flow

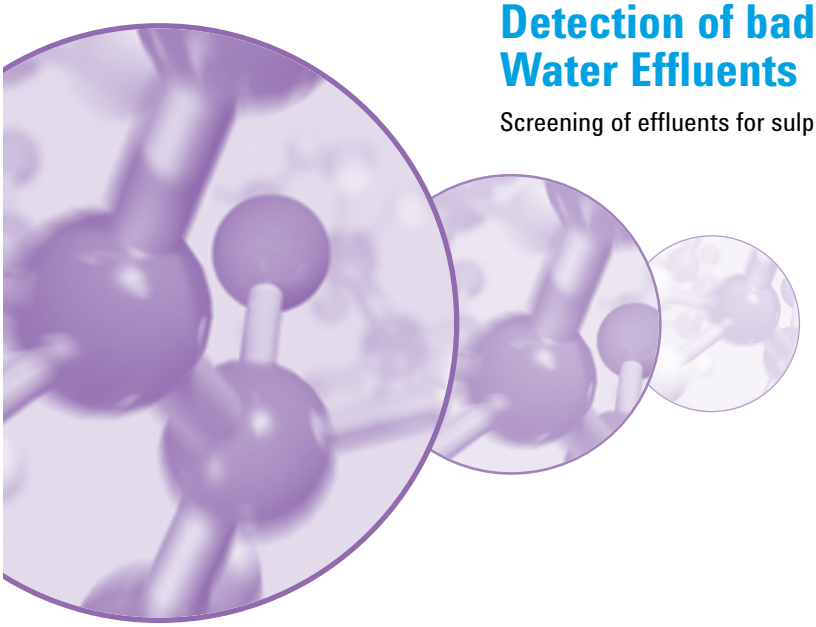
AED:

Carbon 496 nm
Chlorine 479 nm

Cavity: 320°C, Transfer line 310°C
Solvent vent on: 0.1 min., off 5.0 (3.0) min.

How the Agilent Atomic Emission Detector can help

Even though the AED is not as sensitive for most of the poly halogenated compounds as an ECD, the AED can be a very powerful tool in detecting chlorinated compounds in a complex matrix like transformer oil.
In such a complex sample, selectivity against the matrix compounds is often much more important than absolute sensitivity.
Both chlorine lines (479 and 837 nm) of the AED are very selective against carbon or hydrocarbons. With optimised reagent gas settings, a selectivity of 4 to 5 orders of magnitude vs. carbon can be reached. This allows detection of PCB'S directly in a 1:10 diluted transformer oil sample in hexane without any further sample preparation.
The huge amount of hydrocarbons in the oil sample, which can not separated by the GC column show nearly no influence on the chlorine 479 nm trace of the AED. The base line of the chlorine trace is still very stable and the individual chlorinated compounds can easily be detected and quantified after a calibration with a PCB standard.



Detection of bad Odour Compounds in Water Effluents

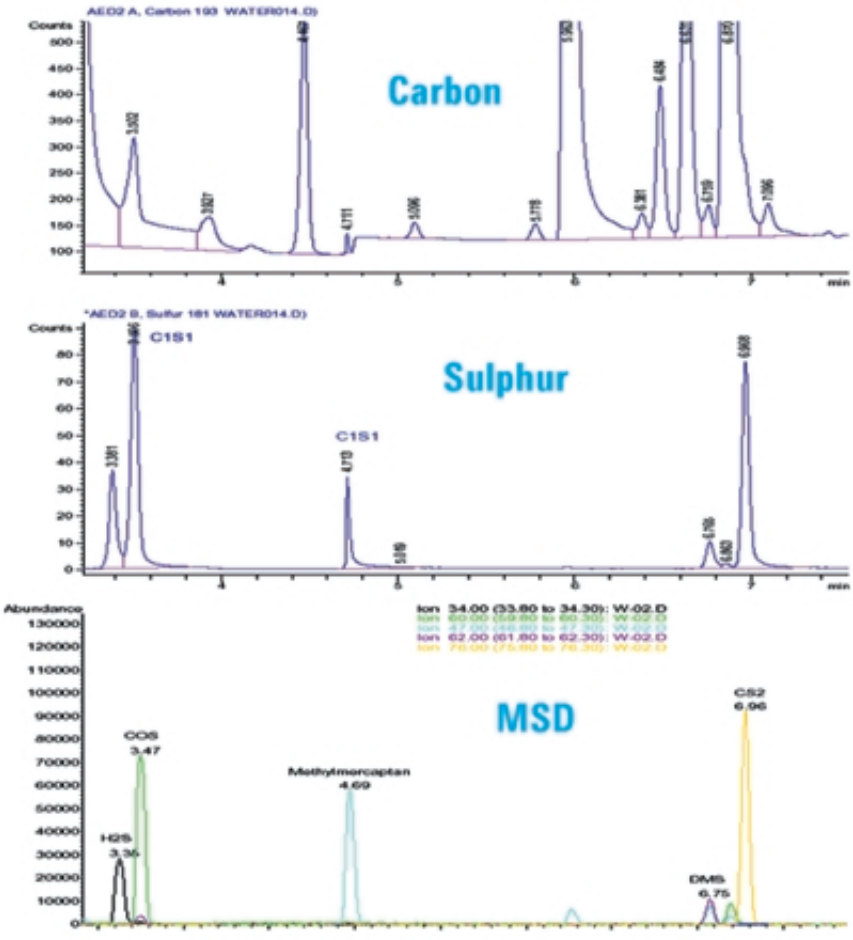
Screening of effluents for sulphur and nitrogen containing off odour compounds.

Analytical Problem

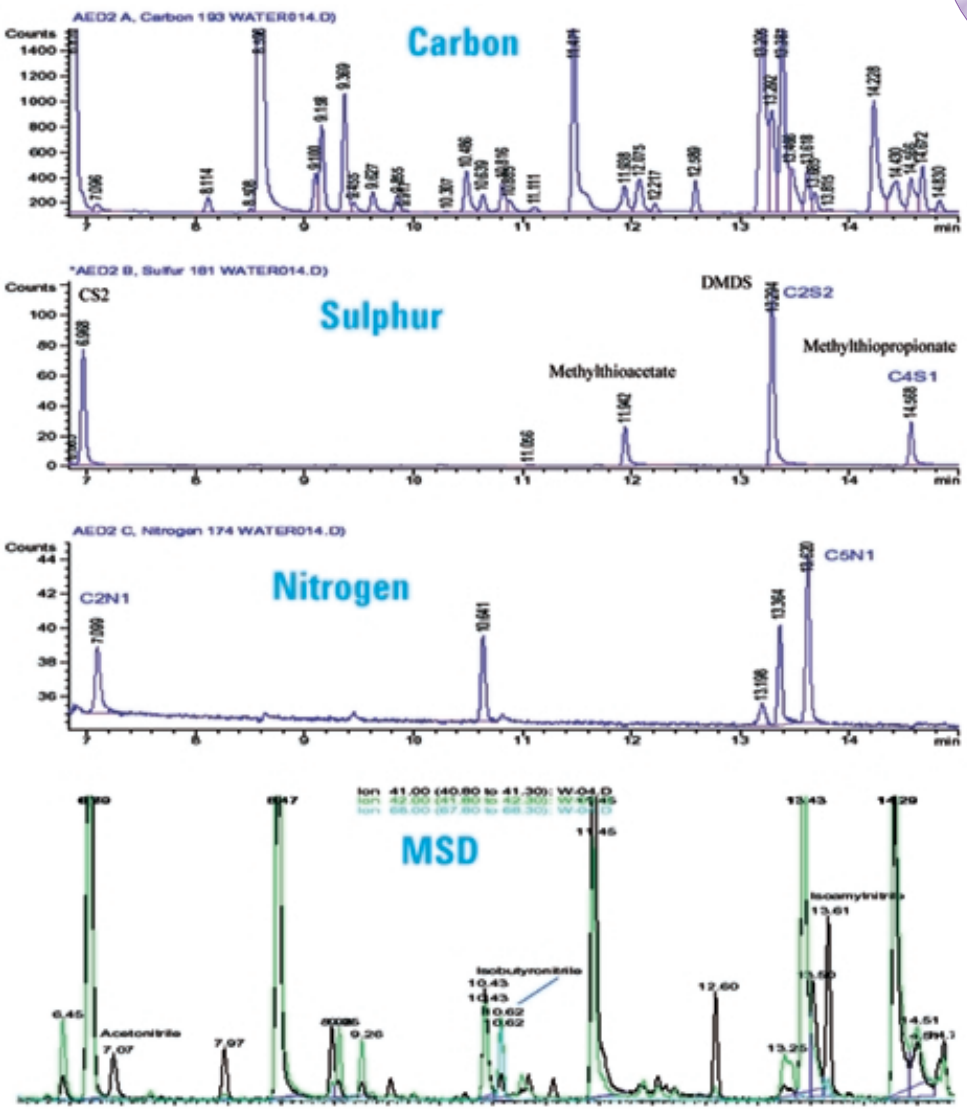
Water effluents from food manufacturers can contain sulphur or nitrogen compounds that sometimes produce a strong off-odour in the water.
To detect these compounds in purification plants, or in the effluents flowing into rivers, highly selective and sensitive analytical methods are absolutely necessary.

With standard GC detectors, at least two analyses must be performed for selective determination of sulphur (FPD) and nitrogen (NPD) containing odour compounds. However, NH3 cannot be detected with the nitrogen and phosphor selective NPD.
With the AED, both nitrogen and sulphur containing compounds can be measured from a single injection, at high sensitivity and selectivity using Headspace sampling.

Food effluent with HSS/GC/AED (C and S) and MSD



Food effluent with HSS/GC/AED (C, S and N) and MSD



Agilent 6890 GC/AED conditions

7694 HSS:

10 ml water + 6g Na2SO4

Oven: 80°C, Valve 110°C, Transfer line 150°C
Vial heating 15 min. with high shake, 1 ml sample loop

6890 GC:

Split/Splitless inlet: 180°C, split 3:1, direct liner

Oven: 35°C (3 min.) 8°C/min. to 220°C (9 min.)

Column: 60m x 0.32mm x 1.8µm HP-624, He 2.8 ml/min. constant flow

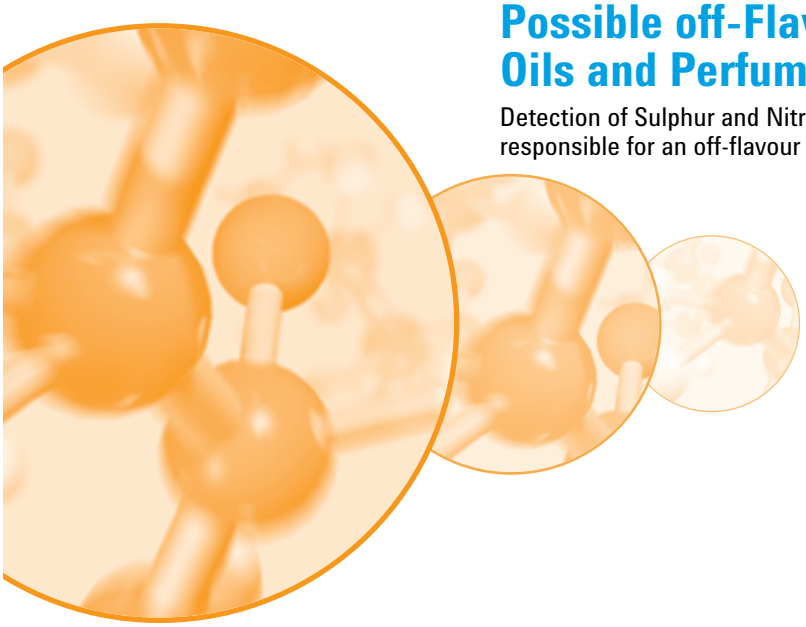
AED:

Carbon 193 nm
Sulphur 181 nm
Nitrogen 174 nm

Cavity 250°C, Transfer line 240°C
No solvent vent was used

How the Agilent Atomic Emission Detector can help

Most of the volatile off flavour compounds from food effluents are known to contain sulphur or nitrogen atoms. The AED is a perfect tool to perform elemental screening in a wide variety of different matrices.
Using a headspace sampler, the volatile odour compounds could easily be detected using the AED. Nitrogen and Sulphur containing molecules can be measured simultaneously in a single analysis. Afterwards, the empirical formula can be calculated for some of the compounds by injecting a standard with known sulphur and nitrogen contents.
Identification of the different odour compounds was then performed using a 6890/5973 GC/MSD. This was relative easy since the elution order and exact retention times for the individual compounds, detected using the GC/AED, can be exactly repeated using the GC/MSD by using retention time locking methods (RTL) on both systems. Therefore it is not necessary to calibrate the system with each single sulphur or nitrogen compound prior to the analyses of the food effluent samples.
This example shows that GC/AED and GC/MSD are highly complementary techniques for the identification of unknown compounds in complex matrices.



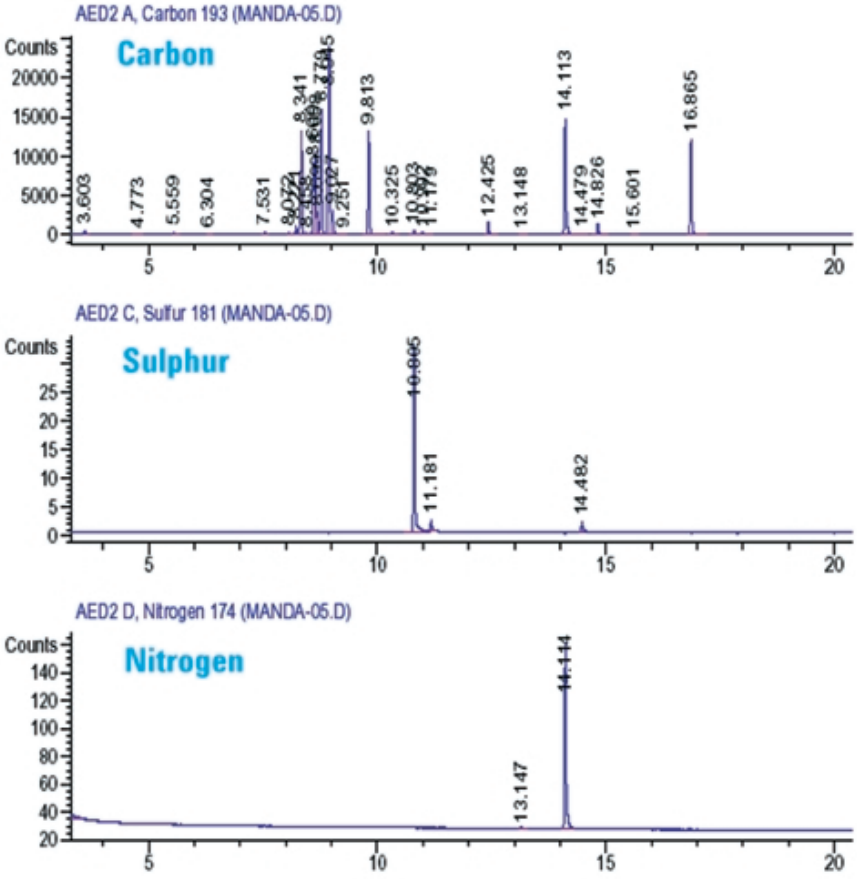
Possible off-Flavour Compounds in Fruit Oils and Perfumes

Detection of Sulphur and Nitrogen containing compounds in natural fruit oils responsible for an off-flavour

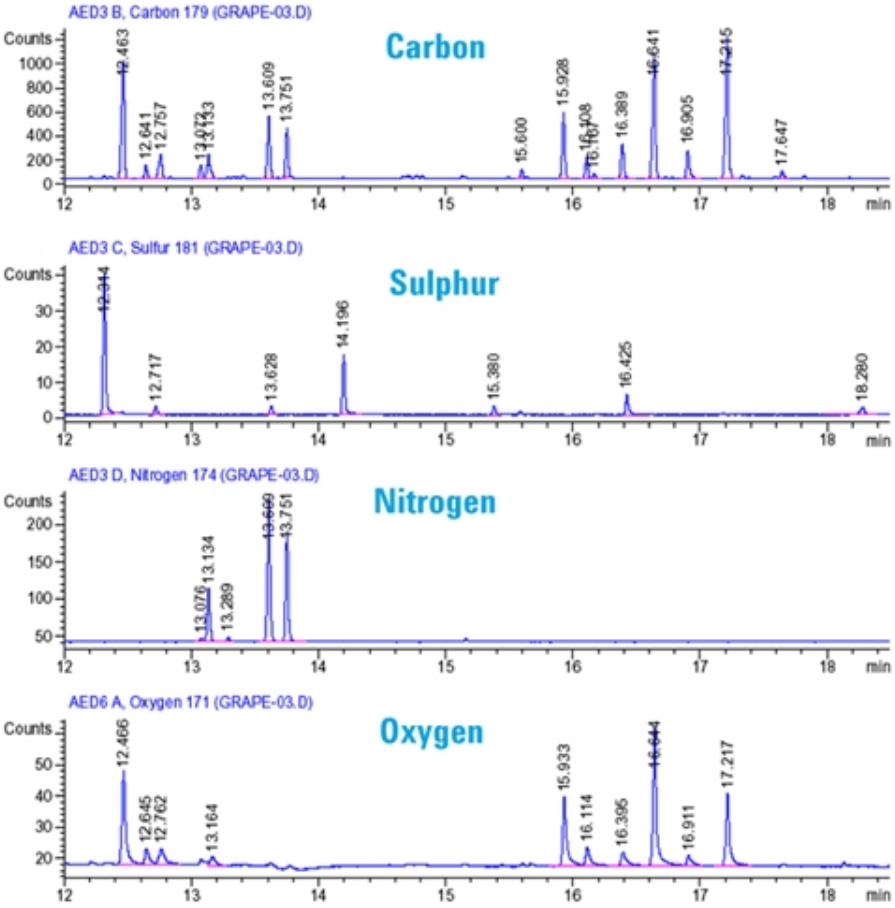
Analytical Problem

Natural fruit oils contain a large number of different compounds such as esters, alcohols, aldehydes, ketones and fatty acids, which are responsible for the aromatic character.
On the other hand some sulphur and nitrogen containing compounds can add a strange off-flavour. The concentrations of these compounds are often very low in the complex fruit oil matrix and so they are very difficult to analyse.

Carbon Sulphur and Nitrogen trace from Mandarin oil



C, S, N and O determination in Grapefruit oil



Agilent 6890 GC/AED conditions

6890 GC:

PTV inlet: 0.2µl split 150:1, 60°C (0.02 min.) 700°C/min. to 280°C

Oven: 45°C (0 min.) 10°C/min. to 300°C (9.5 min.)

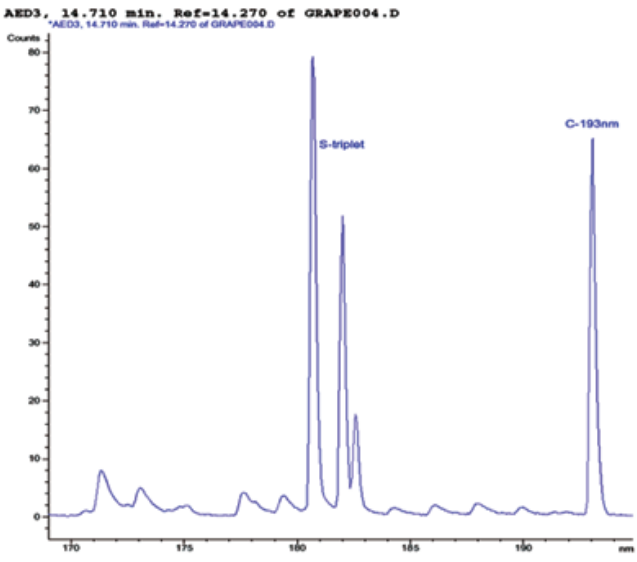
Column: 50m x 0.20mm x 0.33µm HP-5, He 1.6 ml/min. constant flow

AED:

Carbon 179 nm
Sulphur 181 nm
Nitrogen 174 nm
Oxygen 171 nm (additional run)

Cavity 310°C, Transfer line 305°C
Solvent vent on: 0.5 min., off: 3.9 min.

AED sulphur spectrum (triplet)



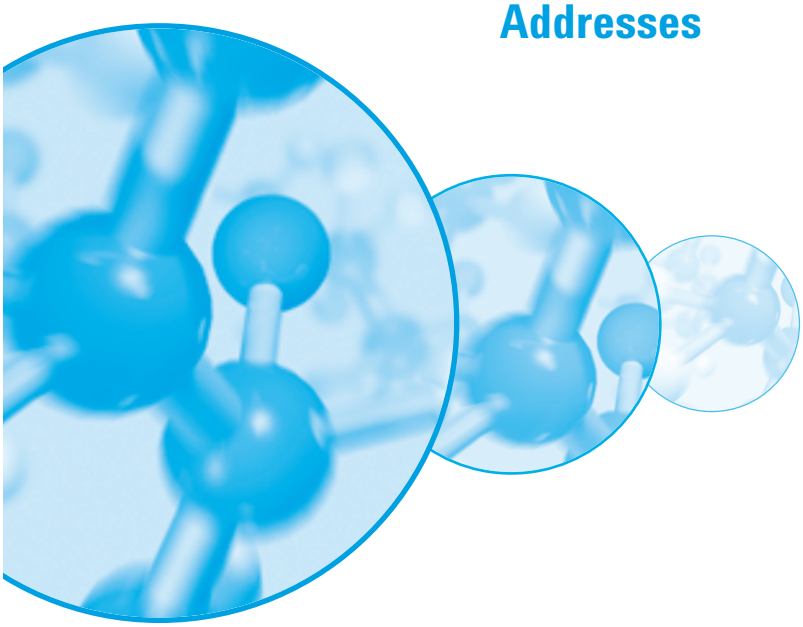
How the Agilent Atomic Emission Detector can help

Detection of the very low levels of compounds responsible for an off-flavour in a complex matrix, such as natural fruit oils, can be a real challenge for the analyst. The sulphur containing compounds have such a low odour level that detection of them even with an FPD can be very difficult, or even impossible.

The high sensitivity, selectivity and liner response of the AED for sulphur compounds enables their direct detection in the fruit oil samples without any additional sample preparation. Only a split injection (150:1) was used to adjust the concentration level.

The examples above clearly indicate, that the detected sulphur compounds are very low in the overall concentration of the fruit oils. These compounds are virtually undetected in the carbon trace.

Addresses



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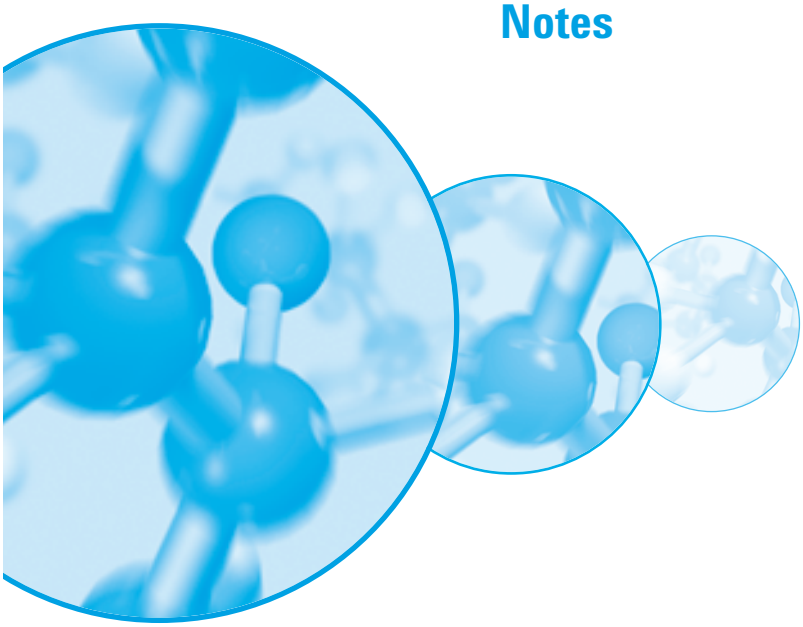
Notes



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