Thanks for your interest in this presentation!

“THE LATEST IN FIRE DEBRIS ANALYSIS - GC/MS/MS”

This presentation was initially presented and very well received at the inaugural “FRENZY” conference (Forensic Sciences and Crime Scene Technology) May, 2000 in Washington, D.C., USA

In the spring of 2001, it was enhanced and presented directly to the National Centre for Forensic Science and the International Institute for Forensic Sciences

I wish we could present this in person to you, in lieu of that we have included these additional white slides to give you more narration.
“THE LATEST IN FIRE DEBRIS ANALYSIS - GC/MS/MS”

In mid 2001 the GC/MS/MS method was written by the authors listed below and submitted to the ASTM Forensics Committee for review and ballot.

In 2002 this ASTM committee recommended that this method should be a separate method from E-1618. The few negative ballots revolved around a concern for too much sensitivity and need for additional peer review. Data later referenced and discussed at the meeting showed that GC/MS/MS is still not as sensitive as the trained K9.

A larger sub-committee co-chaired by Dale Sutherland, Actlabs and Dr. Jose Almirall International Forensic Research Institute will review and embellish this method in 2002.
Fire Debris Analysis
GC/MS/MS
“Decisive Data”
Fire Debris Samples

Importance

• Assume all sample evidence will go to court
• Very important factual scientific evidence
• May be critical to the results of the case
Fire Debris Samples

Objectives

• Want to determine if the sample contains (positive) or does not contain (negative) an Ignitable Liquid
• Want to achieve the highest level of confidence in the result
• Want to be able to show the results clearly to both Judge and Jury
The Quality of the Laboratory Results Starts in the Initial Investigation!
Sample Extraction!

- Headspace
- Absorbent and solvent desorb
- Absorbent and thermal desorb
Compound Separation!

- Nearly all methods use Gas Chromatography
- Chromatography = “The art of separation”
- The analysis produces a “Chromatogram” that describes organic contents of the sample within the limits of the method.
- The use of narrow-bore fused silica capillary chromatography columns is common and usually the use of the term GC implies HRGC
Compound Detection

- FID, PID = Flame or Photo Ionization Detectors
- MS = Mass Spectrometry
- MS/MS = Mass Spectrometry/Mass Spectrometry
Combined Technologies

- GC/FID or GC/PID
- GC/MS
- GC/MS/MS

Significantly Different Capabilities
Interpretation by Pattern Recognition
Pattern Recognition in Fire Debris Analysis Rarely Yields a Perfect Match!
Due to Weathering

- Heat of fire
- Outside temperatures
- Ultra-Violet
- Water washing
- Bacterial action
- Time

and
**Matrix Effects**

- Natural components
- New components from combustion of carpet, plastic, wood, material, etc.

= Pyrolysates!
FIRE DEBRIS ANALYSIS METHODS

This presentation now compares the following methods that have been used to analyze fire debris samples.

GC/FID
GC/MS
GC/MS/MS
A Chromatogram of Gasoline

A Total Ion Chromatogram (TIC) of Gasoline
A Chromatogram of a Sample

Only one sample profile is available for comparison with GC/FID

A Chromatogram of Gasoline
A Chromatogram of a Sample

A Chromatogram of Gasoline
A Chromatogram of a Sample

A Chromatogram of Gasoline
A Chromatogram of a Baseboard Sample

A Chromatogram of Gasoline
A Chromatogram of a Baseboard Sample

A Chromatogram of Gasoline

Positive
A Chromatogram of a Sample

A Chromatogram of Gasoline
A Chromatogram of a Sample

A Chromatogram of Gasoline

Positive
ANALYSIS BY GC/FID IS INSUFFICIENT!

• Indefensible compared to other methods, except for strong ignitable liquids with simple profiles.

• Using GC/FID as a screening procedure prior to GC/MS has a high level of risk of missing the presence of an ignitable liquid (a false negative result).
“A calculation of error rates among over 200 laboratories participating in the last three CTS (Round Robin) tests revealed that users of E-1618 (GC/MS) had an error rate roughly half that of users of E-1387 (GC/FID). As a consequence, (ASTM committee) E30 is considering the withdrawal of E-1387.”

Chairman ASTM Committee E30
THE METHOD OF ANALYSIS IS AT A CROSSROADS!

- ASTM E-1387, GC-FID, considered for withdrawal!
- ASTM E-1618-97, GC/MS, new update in 2001
- ASTM E-*****, GC/MS/MS, next year
A Fire Debris Sample of Baseboard

GC/MS

Sample

Gasoline
Ion Chromatograms or Mass Chromatography

The Power of GC/MS

Methyl-Naphthalenes in Gasoline

Methyl-Naphthalenes in Sample
Ion Chromatograms or Mass Chromatography

The Power of GC/MS

- C3-Alkylbenzenes in Sample
- C4-Alkylbenzenes-Sample
- C3-Alkylbenzenes in Gasoline
- C4-Alkylbenzenes-Gasoline
Ion Chromatograms or Mass Chromatography

The Power of GC/MS

Alkanes in Sample

Alkanes in Gasoline
What is GC/MS/MS?

- Gas Chromatography - Separation
- Mass Spectrometry
  - 1st Stage - Isolation & Collision
- Mass Spectrometry
  - 2nd Stage - Daughter Ion Detection
When is GC/MS/MS used?

- Highly weathered samples
- Samples with trace (low) level concentrations
- Highly complex samples
**GC/MS/MS**

- Gas Chromatography - Same as for GC/MS
- Mass Spectrometry / Mass Spectrometry

"Tuned for Ignitable Liquids"
How is GC/MS/MS Currently Used?

Step 1: GC/MS analysis
GC/MS Result: More information required
Step 2: GC/MS/MS analysis

GC/MS/MS - A Second Analysis for Confirmation
GC/MS/MS
--A Review To This Point--

- The second MS is truly a second Mass Spectrometer scan
- In the first MS operation a set of “Parent Ions” are chosen that are important in the detection and identification of Ignitable Liquids.
- In this way we are “tuning” the method to be specific for Ignitable Liquids
- In-between the MS operations, the Parent Ions collide with Helium and undergo more fragmentation (CID - Collisionally Induced Dissociation)
- The second MS operation records the new fragmentation pattern obtained as a “Daughter Ion Spectrum”
- This Daughter Ion Spectra is thus “very specific” for the Ignitable Liquid components and has exceptionally little interference, if any, from other burnt components (pyrolysates) in the sample.

The next slides summarize that GC/MS/MS has more capability/confidence in fire debris analysis than GC/MS. GC/FID is a very distant third. Also the more sensitive GC/MS/MS works in conjunction with the ultra-specificity to deliver a very “Defensible” result.
Fire Debris Analysis
More information means more confidence!

- GC/FID
- GC/MS
- GC/MS/MS
GC/MS/MS

"DEFENSIBLE"

"DEFINITIVE" → "SENSITIVE"
MS/MS IS A PROVEN TECHNIQUE

FORENSIC USE OF MS/MS

- Confirmation of Unusually High Marijuana Levels in Postmortem Blood Samples
- Analysis of EDTA in Blood by the FBI Forensic Science Research Unit - O.J.Simpson Trial

USE OF MS/MS IN OTHER FIELDS

- Environmental - Dioxins
- Pharmaceutical - New Drug Development
Apr. 97 - Research and Library Development  
Dec. 97 - Journal of Canadian Society of Forensic Sciences  
Nov. 98 - National Underwriter Review  
May. 99 - Research - Extension of the Sampling Period  
Oct. 2000 - “GC/MS/MS - An Important Development In Fire Debris Analysis”

Other institutions conducting research during this time:  
CSIR - The Council of Scientific and Industrial Research  
South Africa  
Florida International University  
University of Alabama
"THE LATEST IN FIRE DEBRIS ANALYSIS - GC/MS/MS"

At this point it should be noted that GC/MS/MS

- Can be used in the target compound approach developing a much more specific Target Compound Chromatogram (TCC) than in GC/MS

- Can be used to target specific compound classes characteristic of Ignitable Liquids providing many new and unique daughter ion chromatograms used in pattern matching review

- Although GC/MS/MS can analyze fire debris as the sole method, the analyst is not able to view the amount of pyrolysates present and does not have the ability to investigated unknown responses as in GC/MS

- Actlabs currently uses GC/MS/MS as a second confirmatory analysis, if needed, after an initial GC/MS analysis. In essence we have been running these methods in parallel since 1997 for many samples.
GC/MS/MS
AN IMPORTANT DEVELOPMENT IN FIRE DEBRIS ANALYSIS

- Multiple samples of new carpet
- Spiked with Gasoline (5 drops)
- Completely burnt with propane torch
- Added water for dilution effect
- Left outside near loading dock
- Periodically collected
RESEARCH RESULTS
Gasoline Spiked Carpet (5 drops)

Note: The Small Quantity Used was to Accelerate Weathering

• Positive results by GC/MS for 3 days
• Positive results by GC/MS/MS to 17 days
GC/MS/MS
Extends the life-time of the sample
What have we said?

From research conducted by Activation Laboratories, published in the October 2000 issue of the IAAI Fire & Arson Investigator journal, we showed that analysis by GC/MS/MS can detect the presence of an Ignitable Liquid a full two weeks past the point that the analysis by GC/MS fails.

We feel that this is important, especially in the private sector, when the investigator cannot collect the samples as soon as they would like to.

It also would be a distinct advantage in hot climates or when other forms of sample weathering is more active. GC/MS/MS thus extends the timeframe, or the lifetime, when a sample can still be defensibly shown to be positive.

GREAT! You’ve made it this far.

The next set of chromatograms again from real sample cases show the advantages of GC/MS/MS.

The next slide shows that GC/MS/MS has eliminated the pyrolysates observed in the GC/MS analysis. Now, after GC/MS/MS, the sample agrees very well with the same chromatogram from Gasoline, easily interpreted by Judge and Jury.
GC/MS/MS REMOVES PYROLYSATES

C2 - BENZENES

Sample by GC/MS

GC/MS of Sample

Sample by GC/MS/MS

GC/MS/MS of Sample

Gasoline Standard by GC/MS/MS

GC/MS/MS of Gasoline
GC/MS/MS CAN IMPROVE ALKANE CLARITY

ION 85

GC/MS of Gasoline

GC/MS/MS Gasoline
GC/MS/MS CAN IMPROVE ALKANE CLARITY

ION 85

GC/MS of 95% Weathered Gasoline

Clear Alkane profile by GC/MS/MS

GC/MS/MS of 95% Weathered Gasoline
WARNING!

The next set of five slides may be offensive to some viewers!
A fire ravaged “Porsche Boxster”!

GC/MS
"Porsche Boxster"

The Specificity of GC/MS/MS

Sample

Gasoline
The Specificity of GC/MS/MS

“Porsche Boxster”

Sample

Gasoline
The Specificity of GC/MS/MS

“Porsche Boxster”

Sample

Gasoline
“Porsche Boxster”

The Specificity of GC/MS/MS
STAIR TREADS - RN0391

GC/MS - Sample

Would be Negative

GC/MS/MS - Sample
The first reaction from looking at the Total Ion Chromatogram for this “Stair Tread” sample from the GC/MS analysis shown in the previous slide would lead the analyst to believe that this sample had some late eluting pyrolysates only, and appears to be negative for the presence of an Ignitable Liquid.

This is the same chromatogram as observed from a GC/FID (Flame Ionization Detector) or GC/PID (Photo-ionization Detector) and is a good example why these detectors are generally insufficient for Fire Debris analysis. They would most assuredly end up reporting a false negative result for this sample.
However, we can use the Mass Spectrometer to show only those classes of compounds used to identify Ignitable liquids. The top chromatograms on the next slide show that the GC/MS method has found traces of important C5-Benzences in this sample at the same elution/retention time as for Gasoline shown in the second chromatogram. However, the trace for the sample is very weak and is not very definitive evidence for presentation in court.

The second pair of chromatograms on the next slide shows the GC/MS/MS Daughter Ion chromatograms for C5-Benzences for the same sample and similarly a comparison to Gasoline. These GC/MS/MS chromatograms compare very well, and would be very easily interpreted by Judge and Jury.

What is also important is that these Daughter Ion chromatograms display a different pattern/fingerprint for the C5-Benzences than in GC/MS. These Daughter Ions are very specific and further enhance the confidence that we are truly detecting C5-Benzences in this sample.

Lets also do the same investigation for the chemical class of Indans.
STAIR TREADS - RN0391

C5 - BENZENES

Stair Tread - GC/MS

Would be Negative

Gasoline - GC/MS

Stair Tread - GC/MS/MS

Now Positive

Gasoline - GC/MS/MS
STAIR TREADS - RN0391

INDANS

Stair Tread - GC/MS

Would be Negative

Poor comparability

Gasoline - GC/MS

Stair Tread - GC/MS/MS

Confirmed Positive

Gasoline - GC/MS/MS

Excellent comparison

GC/MS Spectra

Co-elutants

GC/MS/MS

Daughter Ion Spectra

Clean & Isomer Specific

New Spectra = Additional Identification Assurance
When we use GC/MS to look for the Indan class of compounds we again find a very weak response. When directly compared to Gasoline in the second chromatogram we discover that the response has some similarities to the Indans in Gasoline.

After analysis by GC/MS/MS a much more definitive response is obtained. A very good comparison can be made that would again be very easily interpreted by Judge and Jury.

Note that in this case the pattern obtained for Indans by GC/MS/MS is the same as that obtained by GC/MS. To look at this further we have compared the results for one compound as shown by arrows in the chromatograms of the two analyses. The top spectra on the left-hand side for GC/MS is the standard spectrum obtained for Indans. This spectrum can also be called the Parent Spectrum for the compound we are looking at. It’s most intense ion is 131. This is the ion we selected to be the Parent Ion for our GC/MS/MS analysis.
In GC/MS/MS, after isolating the Parent Ion 131 and after the subsequent Collisionally-Induced Dissociation, we obtain the Daughter Ion Spectrum. Note that this spectrum is significantly different than the GC/MS spectrum and thus this test is also very definitive for Indans.

We then selected the most intense Daughter Ion to reconstruct the ion chromatogram. This Daughter Ion is also 131 and thus the GC/MS/MS ion chromatogram is the same as for GC/MS.

By reviewing other classes of compounds in a similar way, we develop a set of chromatograms that describe this one sample that would be very easily interpreted by Judge and Jury. With this set of scientific evidence, we have definitively shown that this sample is positive for the presence of the Ignitable Liquid, Gasoline with a very high degree of confidence.

Note that this sample would have been negative using an analysis by GC/FID or GC/PID. The information obtained from GC/MS makes this sample suspect for the presence of an Ignitable Liquid. But, due to the weak response this information would be insufficient as conclusive evidence and the sample would also be reported as negative by GC/MS. However by using GC/MS/MS we can confirm our suspicions and conclusively present that this sample is positive for the presence of Gasoline.
TIN CAN - RN0414

GC/MS

Would be Negative

GC/MS/MS
OH BOY!

The analysis of this rectangular gallon tin can sure looks blank at first glance. This can had a very small portion of the label still attached but it was unreadable and gave no clue as to its contents. It did receive enough heat that the spout/cap was missing as the solder had melted.

This result would automatically be reported as negative by GC/FID or GC/PID. Unless a strict GC/MS interpretational program is in place, this sample would also be reported as negative.

Using the same systematic review as for the previous samples (and for all samples), the GC/MS analysis revealed some responses that could be linked to the presence of an Ignitable Liquid. The next slide shows the GC/MS comparison to Gasoline for C3- or Trimethyl-Benzene.

The subsequent analysis by GC/MS/MS confirms the presence of the C3-Benzenes. Again a set of Daughter Ion chromatograms describe this sample in a way that would be very easily interpreted by Judge and Jury. The rest of this scientific evidence (not shown) confirms the suspicions seen in the GC/MS analysis. This sample is positive for the presence of the Ignitable Liquid, Gasoline.
C3 - BENZENES

Sample - GC/MS
Would be Negative

Gasoline - GC/MS

Sample - GC/MS/MS
Now Positive

Gasoline - GC/MS/MS
The trace amount of Gasoline found in the tin can sample underlined the need to have very good control of the laboratory and method chemical background. Obviously similar traces cannot be found in an analysis having no sample. It also underlines the need for the best sample containers. Activation Laboratories has conducted research on sample containers for fire debris samples. We encourage the use of nylon evidence bags as having a much lower chemical background than tin cans or Mason jars. Other recent scientific publications concur. As not all nylon evidence bags are the same, we pre-analyze a representative portion of every batch of nylon evidence bags that we make available to our clients. In any submission of samples, it is important to submit an empty container for analysis.

We also want to make clear that we use GC/MS/MS in conjunction with GC/MS. It is a second “confirmation” analysis and can clarify complex or trace responses seen in the GC/MS analysis. At this time we do not propose to use GC/MS/MS by itself. Together with the information found in the GC/MS analysis, GC/MS/MS results can be very definitive and have an associated level of confidence in the result that some scientists say is irrefutable.
DETAILED, COMPREHENSIVE, STANDARDIZED INTERPRETATIONAL REVIEW

• GC/FID - “One” Chromatogram
• GC/MS - Over 75 Mass Ion Chromatograms
• GC/MS/MS - Over 40 Mass “Daughter” Ion Chromatograms
The following four slides show four situations of varying amounts of the Ignitable Liquid Gasoline, pyrolysates and weathering. Each slide shows the GC/MS TIC of the sample as most scientists are used to seeing. The slide also shows the ability to detect in GC/MS/MS the alkane profiles. The third profile is a GC/MS/MS daughter ion observed for Indans that will be used to compare the four samples. Note that these are only two of the daughter ion profiles used in the determination of the presence of gasoline. Other criteria are also required to report a positive result.
95% Weathered Gasoline

Strong - No Pyrolysates

TIC - GC/MS

Ion 85 - MS/MS
Alkanes

ION 145 - MS/MS
Indans
Concrete & Debris From Floor

- Mixture-Few Pyrolysates
- TIC - GC/MS
- Ion 85 - MS/MS
  - Alkanes
- ION 145 - MS/MS
  - Indans
Debris In Footwell

Many Pyrolysates

TIC - GC/MS

Ion 85 - MS/MS
Alkanes

ION 145 - MS/MS
Indans
Footwell & Under Seat - Passenger Side

Weak Sample & Pyrolysates

TIC - GC/MS

Ion 85 - MS/MS
Alkanes

ION 145 - MS/MS
Indans
Footwell & Under Seat - Passenger Side

Ion 145 - MS/MS Indans
Footwell & Under Seat - Passenger Side

Ion 145 - MS/MS Indans

Strong - No Pyrolysates

Mixture - Few Pyrolysates

Many Pyrolysates

Weak Sample & Pyrolysates
In this presentation we have focused on the analysis of gasoline as a recent study indicated that over 65% of the samples determined to be positive for an ignitable liquid contained gasoline (1). GC/MS/MS is also capable of detecting the vast majority of other ignitable liquids.

(1) Fire Debris Analysis: Statistics and the Use of the Latest Analytical Tools - Canadian Association of Fire Investigators, September 1999
Medium Petroleum Distillates

Mineral Spirit - GC/MS

Mineral Spirit - GC/MS/MS

Alkanes Ion85 - GC/MS/MS
Heavy Petroleum Distillates

Fuel Oil - GC/MS

Fuel Oil - GC/MS/MS

Alkanes Ion 85 - GC/MS/MS
SENSITIVITY!

Analysis by GC/MS/MS is somewhat more sensitive primarily due to the increase in selectivity. In informal testing in 1998 using dilute concentrations of gasoline it is very close to the capabilities of the K9. New testing in 2001 indicated that the analysis by GC/MS/MS still does not exceed the capabilities of the K9 (separate presentation).
"...the improvement in analysis also saved the life of a hard working dog... Most of the time when the dog gave a positive indication at a fire scene the follow-up lab findings were negative. After working with GC/MS/MS the results are coming back with a majority of positive samples when the dog hits on them."

*National Underwriter  November 1998*

**NOTE:** This K9 handler was venting his frustration only. The dog was never in any danger of being put down due to a lack of performance.
GC/MS/MS LIMITATIONS!

- GC/MS/MS is a target compound class analysis, cannot investigate unexpected compounds. Need GC/MS to review unknown components.
- Less knowledge of the amount or type of pyrolysates in the sample
- Two libraries of Ignitable Liquids and Substances are required. One for GC/MS, one for GC/MS/MS
“Without question, GC/MS/MS can be a very selective and sensitive analytical technique. Being more selective than other techniques such as GC/MS, GC/MS/MS improves the ability of the analyst to detect and identify ignitable liquids by reducing the effect of interferences.”

Duchesne
“His Additional Comment”

“Detecting increasingly lower quantities of ignitable liquids...puts a greater responsibility on the scene investigator to properly interpret the laboratory results.”

Duchesne

= A greater responsibility to thoroughly observe and make notes of the scene. Determine whether there could have been other "incidental" sources of an ignitable liquid.
REMEMBER!

“A positive result does not necessarily indicate that an arson has taken place. And a negative result does not preclude the possibility that an ignitable liquid is present at a concentration lower than the method can detect, or that an ignitable liquid may have been present in the sample at some point in time.”
GC/MS/MS

Benefits the Investigator!

- Reduction of “false negative” results
- Extends time for the Investigator to obtain the sample
- Improves confidence in the laboratory result
- More defensible in court
Why hasn’t GC/MS/MS been used on Fire Debris Before!

• High instrumentation costs (> $150,000 +)
• Sophisticated technique
• Higher level of training required
• Availability
What Other People Have to Say!

Our use of GC/MS/MS for Fire Debris analysis has been externally reviewed for publication in several journals & by the National Underwriter. Their review was published in the November 9, 1998 Property & Casualty/Risk & Benefits Management Edition. Comments obtained by the National Underwriter from other experts in our field included: “...there was a danger in pushing detection limits lower and lower because tiny traces of petroleum products could be found that had nothing to do with arson.” and “We live in a hydrocarbon world”

Another expert commented “I think it’s overkill”

The use of GC/MS/MS on samples that have suspect responses in the GC/MS analysis is in no way a guarantee that a positive result will be found. As we use GC/MS/MS more and more to ensure that we know the true content of these samples, there is a significant percentage of samples that are confirmed to be negative. These negative results prove that the GC/MS/MS sensitivity does not result in a positive for trace hydrocarbons commonly found in our environment. This is due to the specificity of GC/MS/MS. Our GC/MS/MS method is very specific, as it is in effect “tuned” to the detection of Ignitable Liquids.

We will continue to research, learn and improve our methods. We believe that better understanding the true content of a sample through an additional analysis and thorough interpretation programs to obtain the correct result with high confidence is not overkill.
What Other People Have to Say!

Activation Laboratories Ltd. published an article entitled “Fire Debris Analysis Statistics and the Use of the Latest Analytical Tools” in the September 1999 issue of the Journal of the Canadian Association of Fire Investigators. Among the information presented, this article showed that a significant number of analyses by GC/MS that would have been reported as “negative” for the presence of an Ignitable Liquid, but had some chemical response suspected to be from an Ignitable Liquid, were definitively proven to be “positive” after a second, confirmatory analysis, by GC/MS/MS.

Comments in reply to our article, from a Forensic Scientist, included, “Without question, GC/MS/MS can be a very selective and sensitive analytical technique. Being more selective than other techniques such as GC/MS, GC/MS/MS improves the ability of the analyst to detect and identify ignitable liquids by reducing the effect of interferences.” He also correctly pointed out that “detecting increasingly lower quantities of ignitable liquids...puts a greater responsibility on the scene investigator to properly interpret the laboratory results”. It is vital to any case that the investigator must make excellent notes and observations of the area where the samples are taken and the potential for any incidental occurrence of an ignitable liquid. We work closely with our clients to try and ensure that they have the correct understanding of the reported results.
GC/MS/MS

"DEFENSIBLE"

"DEFINITIVE"

"SENSITIVE"
GC/MS/MS

“There is one thing even more vital to science than intelligent methods; and that is, the sincere desire to find out the truth, whatever it may be.”

- Charles Sanders Pierce