

Semi-automatic analysis of fire debris

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Abstract

Automated analysis of fire residues involves a strategy which deals with the wide variety of received criminalistic samples. Because of unknown concentration of accelerant in a sample and the wide range of flammable products, full attention from the analyst is required. Primary detection with a photoionisator resolves the first problem, determining the right method to use: the less responsive classical head-space determination or absorption on active charcoal tube, a better fitted method more adapted to low concentrations can thus be chosen. The latter method is suitable for automatic thermal desorption (ATD400), to avoid any risk of cross contamination. A PONA column (50 m×0.2 mm i.d.) allows the separation of volatile hydrocarbons from C₁ to C₁₅ and the update of a database. A specific second column is used for heavy hydrocarbons. Heavy products (C₁₃ to C₄₀) were extracted from residues using a very small amount of pentane, concentrated to 1 ml at 50°C and then placed on an automatic carousel. Comparison of flammables with referenced chromatograms provided expected identification, possibly using mass spectrometry. This analytical strategy belongs to the IRCGN quality program, resulting in analysis of 1500 samples per year by two technicians. © 2000 Elsevier Science Ireland Ltd. All rights reserved.

Keywords: Arson; Accelerant; Automatic thermal desorption

1. Introduction

Arson is a willful destruction of property by fire which often involves the use of accelerants, usually flammable liquids, to increase the rate and the intensity of burning. A challenge for the analytical chemist is the examination of evidence collected from a

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fire scene. An accurate detection and identification of alcohol as well as wax or oil, in very low or very high concentrations have to be achieved.

Analytical methods based on capillary gas chromatography (CPG) and gas chromatography-mass spectrometry (GC-MS) have been successful in providing better identification of accelerants, thus decreasing the rate of wrong conclusions. Two major problems are: (1) the increase of requests from investigators for accelerant analysis, resulting in analysing 1500 samples by only two technicians last year; and (2) law enforcement doesn't suffer any miscarriage.

So, although quick results are required, the analysis must be comprehensive and responsive.

In France, in addition, all samples are packed in glass jars and closed with metallic screw. This package is the most convenient and most suitable for an automated process and the chosen analytical strategy.

An analytical strategy has been developed that takes the wide range of criminalistic samples received into account, introducing an automated process. This paper reports a semi-automatic process to analyse fire debris.

2. Materials and methods

2.1. Reagents — internal standard

Tetradecane olefine free grade was obtained from Fluka (99087139B). n-Pentan spectroscopic grade was obtained from Merck (99.5%–1.07179).

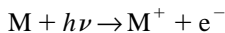
2.2. Apparatus

2.2.1. HNU detection

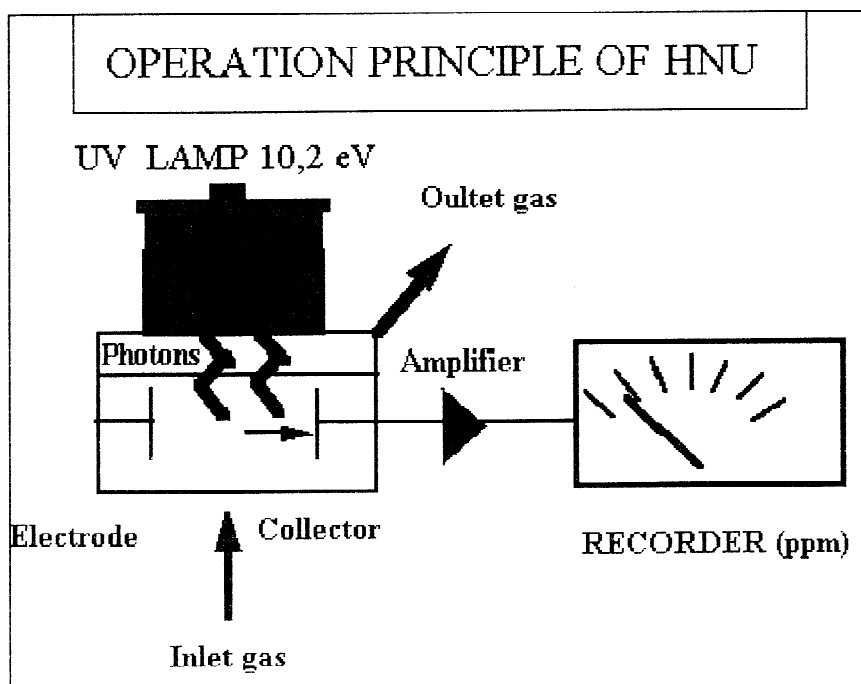
A HNU DL-101 portable photoionization analyzer (Autochim) was used to detect [1] and pre-estimate the amount of accelerant in a given sample. The sniffer was calibrated with 10 ppm benzene purchased from Autochim. The result determined the method to use in order to avoid any saturation of the ATD.

The photoionisation analyser is composed of a 10.2 eV UV-lamp and an ionisation chamber like that shown in Scheme 1.

A photon absorbed by a molecule is sufficient to make a positive ion and an electron as it is described below:



All molecules having an ionisation potential lower or equal to 10.2 eV are ionised. This occurs for the most part of molecules we are looking for in arson. Moreover this analyser can be used to detect the presence of flammable products in fire scenes.



Scheme 1.

2.2.2. Gas chromatograph-flame ionisation detector

2.2.2.1. Analysis of light hydrocarbons Analyses were performed with a Hewlett-Packard model 5890-II gas chromatograph equipped with a Hewlett-Packard flame ionisation detector, using a 50 m PONA 0.25 μm capillary column (Hewlett-Packard) operating in split injection mode. Helium was used as carrier gas with an inlet pressure of 25.0 Psi and a linear flow rate of 0.8 ml/min at 35°C and a split ratio of approximately 25:1. The injector temperature was 290°C and the detector 300°C. After injection the column temperature was maintained at 35°C for 5 min followed by an increase from 35 to 100°C at 5°C/min, from 100°C to 250°C at 10°C/min and maintained for 5 min at 250°C. The instrument operated with HP chemstation 3365 software. The analytical time has been optimised to perform separation of compounds ranging from C_2 to C_{15} . The minimum time to get such a separation is 38 min.

Insert chromatograms number 1 and 2 (Figs. 1 and 2).

2.2.2.2. Analysis of heavy hydrocarbons A model HP 5890-II equipped with a Hewlett-Packard 7673 auto-sampler was used. The column was a 25 m HP-1 capillary column. Helium was used as carrier gas with an inlet pressure of 25.0 Psi and a linear flow rate of 0.8 ml/min at 35°C and a split ratio of approximately 25:1. The injector

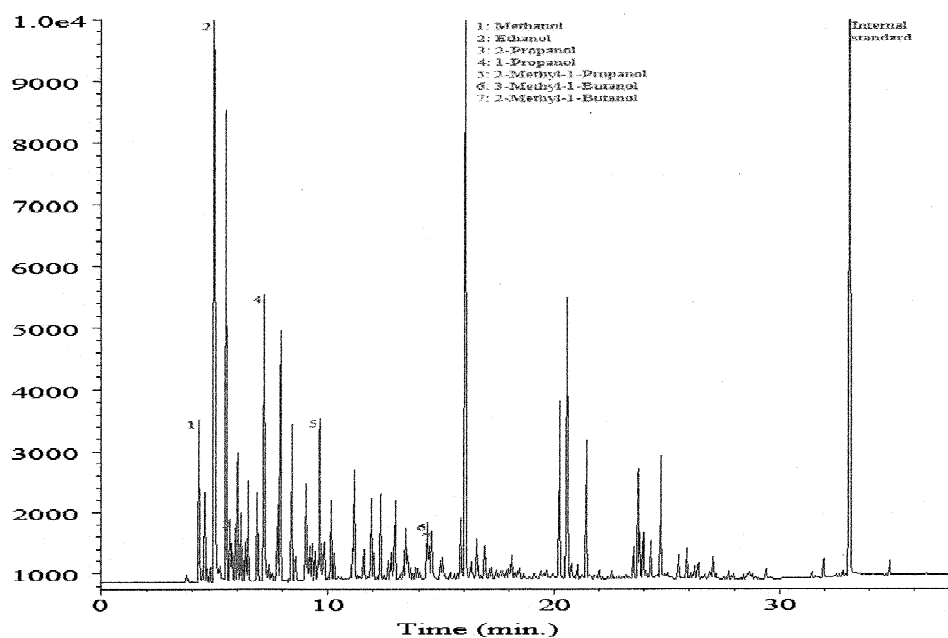


Fig. 1. Chromatogram number 1 (mixture of methylated spirit and gasoline).

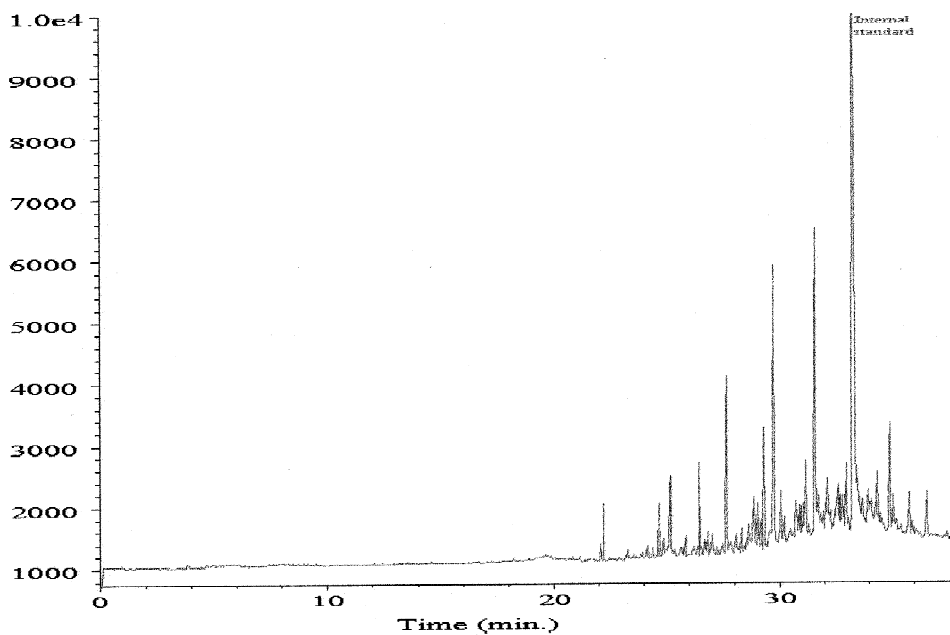


Fig. 2. Chromatogram number 2 (diesel fuel).

temperature was 290°C and the detector 320°C. After injection the column temperature was maintained at 100°C for 5 min followed by an increase from 100 to 200°C at 6°C/min, from 200°C to 310°C at 10°C/min and maintained for 15 min at 310°C. The instrument operated with HP chemstation 3365 software.

Insert chromatograms number 3 and 4 (Figs. 3 and 4).

2.2.3. Automatic desorption system-gas chromatograph

The analysis was performed with a Perkin Elmer Auto System gas chromatograph equipped with a Perkin Elmer ATD 400 suitable for analysis of 50 samples in one carousel loading [2]. The chromatograph with a 50 m PONA 0.25 µm capillary column was operating in the same conditions as for light hydrocarbon analysis. Interface temperature was maintained at 220°C. The automatic thermal desorption was used to perform a two staged desorption. In the first stage, sample tubes were desorbed at 300°C for 10 min with a desorption flow of 30 ml/min. In the second stage the cold trap was heated from –30 to 300°C where it was held for 20 min. The desorption flow was 30 ml/min and the outlet split of the cold trap was set to 25:1.

Insert chromatograms number 5 and 6 (Figs. 5 and 6).

2.2.4. Gas chromatograph-mass spectrometry

The analysis was performed with a Varian Star 3400CX gas chromatograph equipped with a Varian Saturn 3 mass selective detector, using a 50 m PONA 0.25 capillary column (Hewlett-Packard company) operating in a split injection mode. Helium was

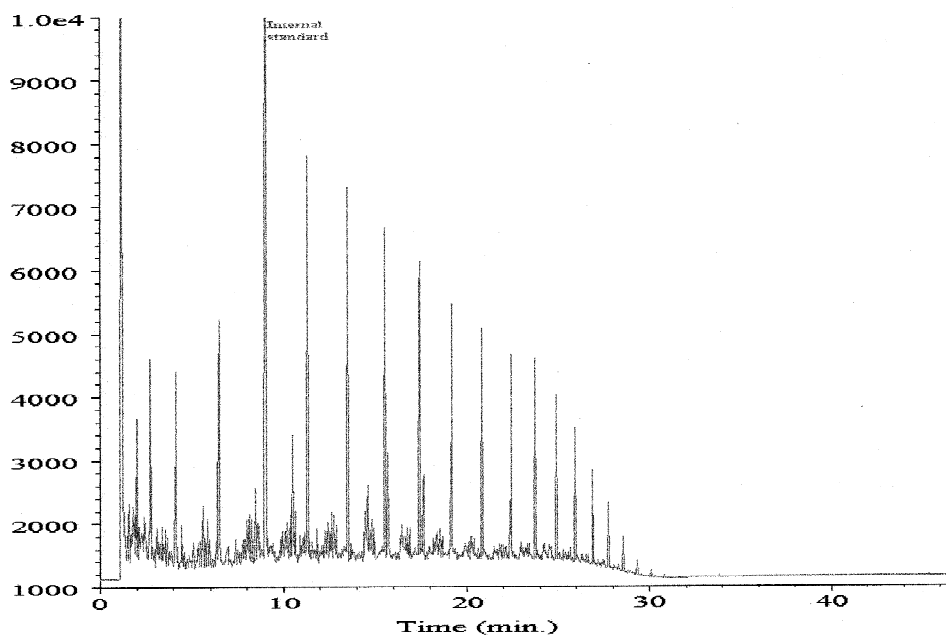


Fig. 3. Chromatogram number 3 (diesel fuel).

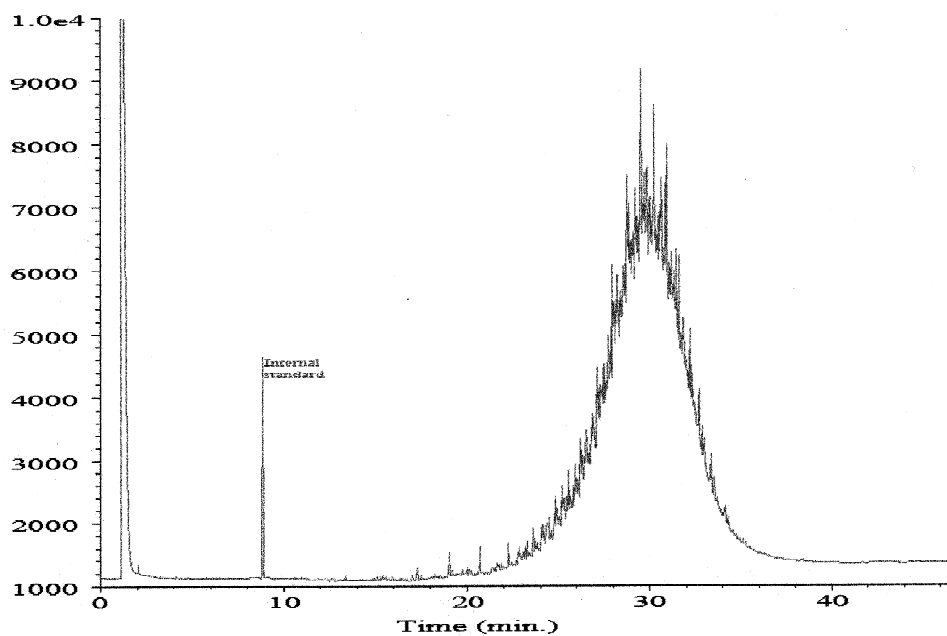


Fig. 4. Chromatogram number 4 (motor oil).

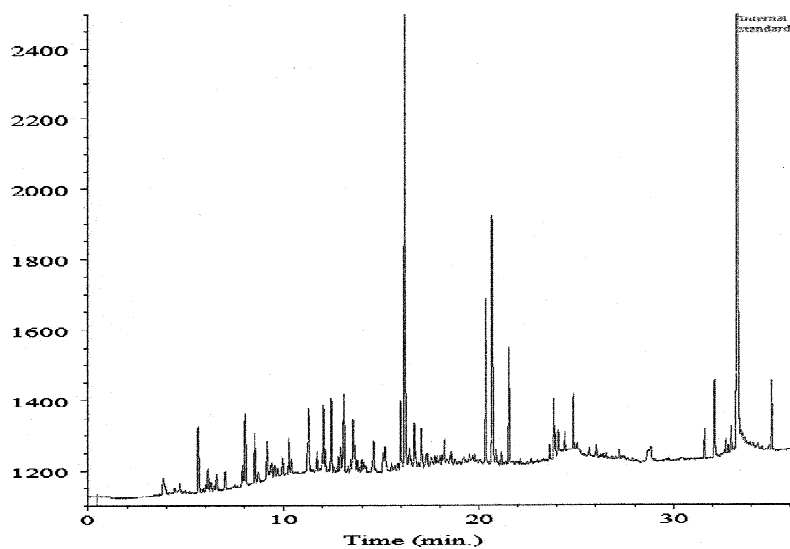


Fig. 5. Chromatogram number 5 (GC-FID 1.35 ppm).

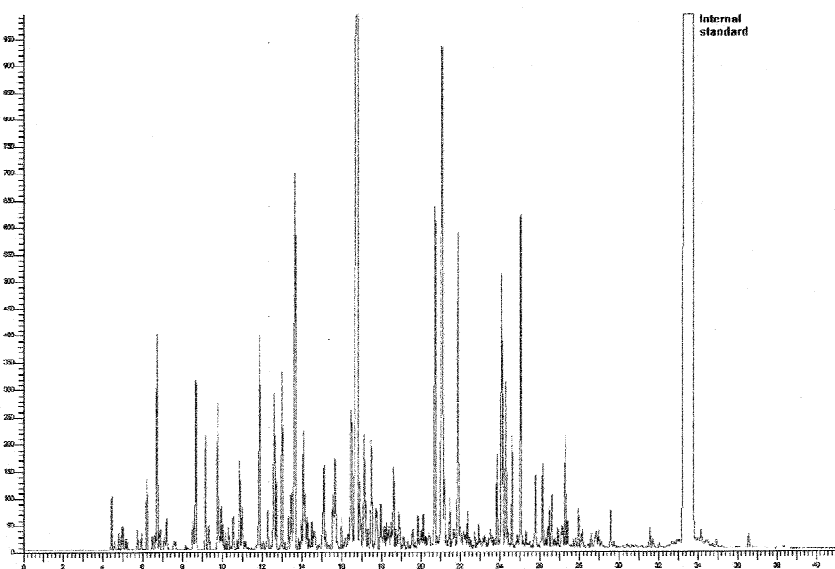


Fig. 6. Chromatogram number 6 (ATD 1.35 ppm).

used as the carrier gas with an inlet pressure of 20.0 Psi and a constant flow rate of 0.8 ml/min at 35°C and a split ratio of approximately 40:1. The injector temperature was 260°C and the detector 150°C. After injection the column temperature was maintained at 35°C for 5 min followed by temperature programming from 35 to 100°C at 5°C/min, from 100°C to 250°C at 10°C/min and maintained for 5 min at 250°C. The mass spectrometer was in the electron impact mode at 70 eV scanning from 29 to 270 AMU [3]. The data were analysed using the data system supplied with the mass selective detector [4].

2.3. Preparation of standards and samples

2.3.1. Standards

Tetradecane was used as the internal standard and prepared weekly by dilution of 1 μ l into 50 μ l of pentane.

2.3.2. Samples

2.3.2.1. Packaging control Arson residues have to be stored in glass jars with a metallic screw. Samples are collected from fire scenes by Gendarmes, exercising all over the country, and sent to the laboratory for analysis.

2.3.2.2. Sampling for identification by headspace, GC-FID In order to extract hydrocarbons up to C₁₅, arson residues are stored in suitable packaging and 10 μ l of tetradecane are added. A little hole is made on the top and closed by a polyamide tape

rubber. The sample is allowed to stay at 90°C for approximately 1 h. One milliliter of vapour is directly injected using a 2.5 ml gas-syringe at 90°C.

Hydrocarbons from C₁₃ to C₄₀ are collected by addition of 20 ml of pentane, the jar is shaken and pentane extracts are transferred to a haemolysis tube which is then centrifuged for 5 min. The organic layer is extracted and concentrated to 1 ml by heating at 50°C. Five microliters are diluted in 1 ml of pentane and 10 µl of standard solution was added. Automatic injection of 1 µl is supplied by the automatic sampler.

2.3.2.3. Sampling for identification by passive diffusion, ATD While packaging arson residues as described above, a carbotrap 300 (Supelco) tube placed on a filter paper wetted by 1 µl of tetradecane is added and the container is allowed to stay 14 h in an oven set at 80°C. After removing the sample at room temperature, the tube is set on the rack.

2.3.2.4. Sampling for identification by GC-MS The process used for light hydrocarbons is the same as previously described for the GC-FID sampling, while for heavy hydrocarbons identification, the sample already prepared is used again.

2.4. Semi-automatic analysis of fire debris

Scheme 2 shows the strategy used to analyse fire debris, this results from the investigator's request for a quick and comprehensive answer.

Containers for fire debris have been chosen according to literature [5].

3. Results and discussion

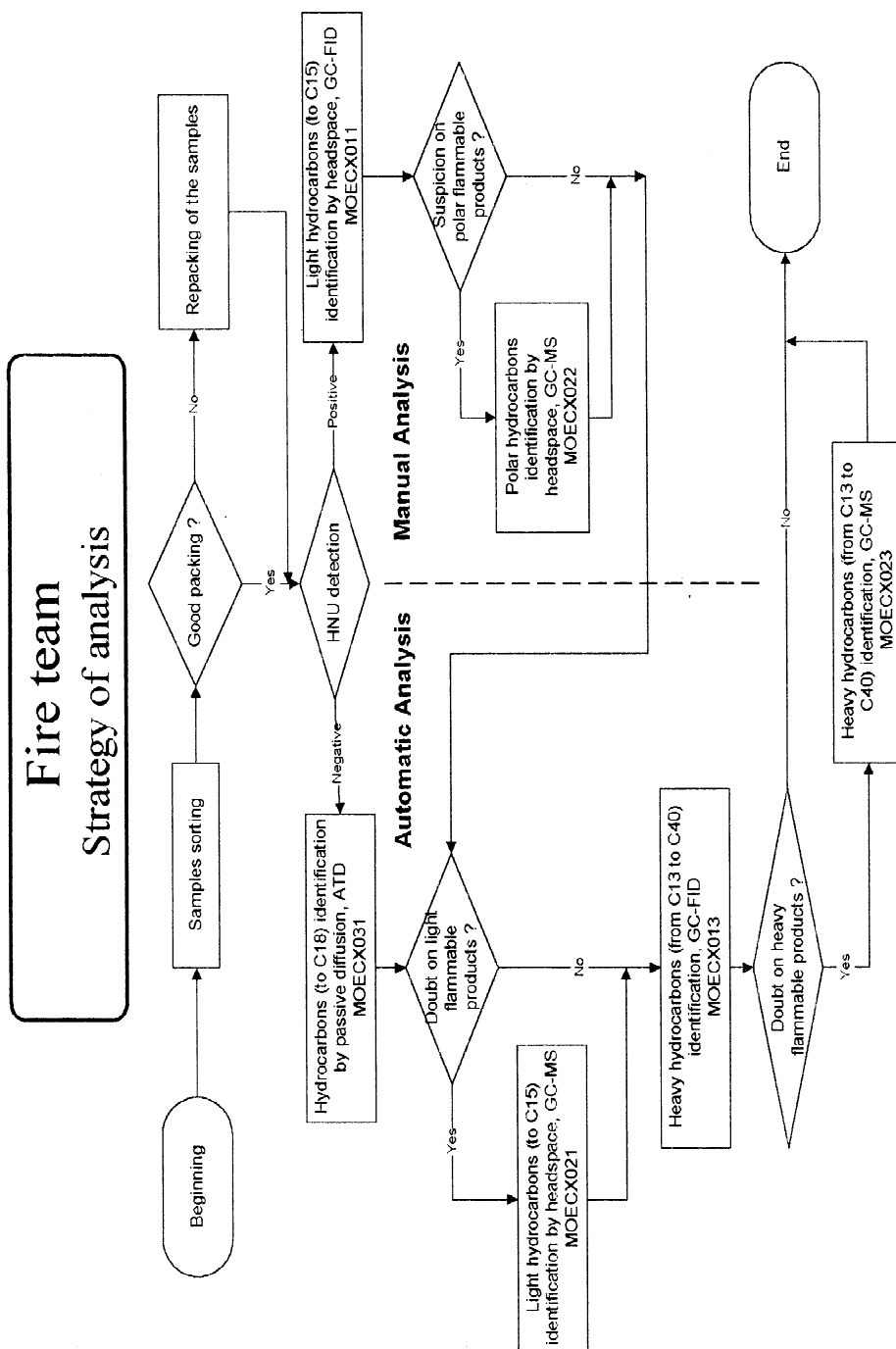
3.1. Initial screening by sniffer

The choice of the most suitable method depends on the particular conditions encountered. The HNU DL-101 photoionization analyzer was used to check the presence of flammable products and to estimate their concentrations in the sample. A debris sample containing more than 10 ppm of highly volatile accelerant was best studied directly by headspace method avoiding overloading the ATD system. A low accelerant concentration or no accelerant would lead to weak profiles or no answer using this technique, thus using HNU DL-101 before analyzer leads to choose the adequate process.

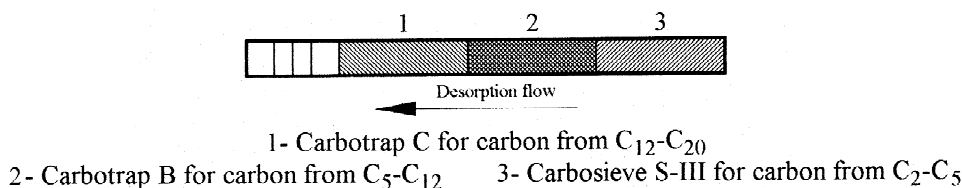
3.2. Light hydrocarbons identification

If the primary detection was higher than 10 ppm, headspace method is used with capillary gas chromatography. As ATD is the most accurate method [6], it is used to provide the analyst an easy identification of accelerants profile.

Charcoal type absorbents retain most of the organic compounds and have a low affinity for water. We used stainless steel tubes packed with carbotrap 300 (Supelco)



Scheme 2.



Scheme 3. Pre-packed sample tube: CARBOTRAP 300. (1) Carbotrap C for carbon from C_{12} to C_{20} . (2) Carbotrap B for carbon from C_5 to C_{12} . (3) Carbosieve S-III for carbon from C_2 to C_5 .

which is composed of three different absorbents (see Scheme 3). Thus the range of trapped volatile organic compounds (up to C_{18}) usually found in arson is increased [7].

Charcoal absorbents are preferred to polymer absorbents because the latter undergoes [8] alteration with time, moreover low affinity for water decreases the flame extinction risk and the freezing risk while cryogenic refocusing. Commercial prepacked tubes guarantee easy and reproducible analyses.

Another advantage of ATD is that the whole sample extract can be injected in the chromatographic column. The same chromatographic parameters, using a PONA capillary column, are established to separate light hydrocarbons up to kerosene and compounds such as methanol, ethanol, acetone, and are useful for both methods [9]. Differences between them relates to low concentration of accelerant as shown in Fig. 3.

Loading a carousel with 50 samples makes ATD more efficient for routine accelerant analysis, automation is a time-saving method for the analyst.

3.3. Heavy hydrocarbons identification

After headspace or ATD analysis, classical solvent extraction [10] is done using pentane in order to extract hydrocarbons from C_{13} to C_{40} . Using pentane instead of highly toxic carbon disulfide improves operator safety. Time is saved when using an automatic sampler HP7673 (Hewlett Packard) allowing the carousel to be loaded with up to 100 samples.

3.4. Mass spectrometry confirmation

When it is impossible to give an unambiguous conclusion, mass spectrometry is used. A higher responsive ion trap mass spectrometer [11,12] is used rather than a quadrupolar one. Application of this strategy gives the advantage that no mass spectrometer pollution will occur, because all samples have been analysed by GC/FID before. And any risk of ATD saturation will be avoided because of too high concentration.

3.5. Analysis strategy

At first glance, this strategy looks simple enough but its elaboration is not so easy because it is the result of continuous choices. These choices help optimise equipment

abilities in the laboratory and permit unambiguous identification of all accelerants than can be used by arsonists.

HNU primary detection avoids charcoal trap saturation, optimising ATD use since it is only used when accelerant is present at low concentration. This choice is therefore obvious.

Our strategy allows both identification of hydrocarbons from C_2 to C_{40} and identification of light oxygenated derivatives such as alcohols, ethers, ketones and esters. In order to get unambiguous chromatograms, and according to the column separating power, the separation of compounds from C_2 to C_{15} than from C_{13} to C_{40} is performed. Chromatographic parameters are specially optimised for each series.

Solvents are not required for light hydrocarbons extraction. So all light hydrocarbons may be characterised, avoiding interferences, especially with alcohols, and any risk of cross contamination and health hazards related to manipulation of these chemicals.

Automatic thermal desorption could be used for either light or heavy hydrocarbons identification, by programming particular analytical conditions. We have chosen to optimise ATD parameters for light compounds identification because automatic analysis of heavy hydrocarbons is already ensured by an automatic sampler.

Using charcoal prepacked stainless steel tubes instead of charcoal strips avoids loss of light hydrocarbons occurring when the trap is saturated by pyrolysis and the use of this solvent. In order to ensure best operators' care we do not use carbon disulfide any more, however excellent an extracting solvent, to collect light compounds. We replaced it by pentane for heavy hydrocarbons recovery.

Heavy compounds analysis is now automatic thanks to an automatic sampler and fast because separation has been optimised on a 25 m column. Reconcentration of the pentane extracts allows to keep a higher sensibility. Improving it is very important because it can show the use of a candle or other petroleum products like oil, gas-oil, etc. For example 'twin engine mixtures', containing oil and gasoline, are commercially available in France. So identifying oil in a sample already containing gasoline may reveal the use of such a mixture to the investigator.

Finally, comparing the result with chromatograms from our own databank checking all flammable products and interfering matrices is the last step of our strategy, avoiding dubious conclusions.

All our sampling and analytical techniques have been validated according to our Institute's programme: 'Analysis quality and control', ensuring reliable and reproducible results.

4. Conclusion and recommendations

Our strategy and quality organisation has resulted from increasing requests for accelerant analysis in suspected arson cases in France. It provides our experts with a good tool to inform investigators quickly and accurately. When investigators have to defend their reports in court, magistrates trust them because other experts are always in compliance with our results.

This strategy will evolve with new technologies, using more automatic qualitative analysis software, which will in turn provide more comfort to the analysts.

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