

Australian Standard<sup>®</sup>

## Examination of ignitable liquids in fire debris



This Australian Standard® was prepared by Committee CH-041, Forensic Analysis. It was approved on behalf of the Council of Standards Australia on 23 November 2011. This Standard was published on 5 December 2011.

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- Australia New Zealand Policing Advisory Agency
  - Australian and New Zealand Forensic Science Society
  - Australian Federal Police
  - Consumer Action
  - Expertise, Evidence & Law Program, School of Law, University of New South Wales
  - National Association of Testing Authorities
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  - New South Wales Police Force
  - Queensland Police Service
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  - Victoria Police Forensic Services Department
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  - Western Australia Chemistry Centre
  - Western Australia Police
- 

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## Examination of ignitable liquids in fire debris

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## PREFACE

This Standard was prepared by the Australian members of joint Standards Australia/Standards New Zealand Committee CH-041, Forensic Analysis.

The objective of this Standard is to outline procedures that are designed to maximize the recovery and evidential value of ignitable liquid residues (ILR) that may be present in fire debris samples submitted for analysis.

This Standard provides requirements and information on methods for the determination of the presence of ILR in fire debris for forensic purposes and covers the following processes:

- (a) Packaging and storage of fire debris samples.
- (b) Extract of sample.
  - (i) Solvent extraction.
  - (ii) Steam distillation.
  - (iii) Headspace sampling.
  - (iv) Passive headspace sampling.
  - (v) Dynamic headspace sampling.
  - (vi) Passive headspace sampling with SPME.
- (c) Analysis of extract.
  - (i) Gas chromatography (GC).
  - (ii) Gas chromatography/mass spectrometry (GC/MS).
- (d) Interpretation of results.
- (e) Classification scheme for ignitable liquids.
- (f) Reporting of results.

Reference was made to the following ASTM Standards in the preparation of this Standard:

### ASTM

|       |                                                                                                                                                                                     |
|-------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| E1385 | Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Steam Distillation (historical standard)                                                 |
| E1386 | Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction                                                                        |
| E1388 | Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples                                                                                                         |
| E1412 | Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal                                   |
| E1618 | Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography—Mass Spectrometry                                                     |
| E2154 | Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME) |

The terms ‘normative’ and ‘informative’ have been used in this Standard to define the application of the appendix to which they apply. A ‘normative’ appendix is an integral part of a Standard, whereas an ‘informative’ appendix is only for information and guidance.

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## FOREWORD

In the investigation into the cause of any suspicious fire, the identification of any ignitable liquids that may be present is a key part of the process. The presence or absence of ignitable liquid residues can assist in reaching a conclusion on the cause of a suspicious fire. It is critically important that any information generated is reliable and based on accepted standards of scientific practice.

Because of the volatile nature of ignitable liquids, the procedures involved in packaging, storing, sampling and analysing samples from fire debris need to be defined and carefully controlled to ensure that potential evidence is not lost or altered.

A number of alternatives in sampling, extraction, analysis and interpretation are available. The methodology selected to collect, sample and analyse fire debris can be influenced by numerous factors. The type and amount of sample being analysed, requirements for re-analysis, analysis time and sensitivity are all factors that will influence methodology. It is critical that the methodology and equipment employed are fit for purpose and provide appropriate sensitivity and discrimination.

The utilization of accepted scientific practice in the interpretation and classification of results is also critically important to ensure that the conclusions reached are reliable and verifiable. Because of the nature of fire debris samples, the impact of matrix effects and evaporation can be significant and, for this reason, such factors must be considered when interpreting analytical results.

For reliable interpretation of results, it may be desirable for the analyst to know about relevant aspects of the case. Interpretation of results may be informed by observations regarding the scene from which material was collected. Recent research\* suggests the importance of blinding or sequential exposure for reliable interpretation, therefore information that does not directly inform the analysis should be avoided.

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\* Dror, Itiel E., Charlton, David, Péron, Ailsa E., 'Contextual information renders experts vulnerable to making erroneous identifications'. *Forensic Science International*; 6 January 2006; 156 (1): 74–78

## STANDARDS AUSTRALIA

## Australian Standard

## Examination of ignitable liquids in fire debris

**1 SCOPE**

This Standard specifies requirements and provides guidance for the analysis of fire debris on methods applicable to the determination of the presence of ignitable liquid residues (ILR) in fire debris for forensic purposes.

The overall processes involved in the analysis of ignitable liquids and covered in this Standard are—

- (a) packing and storage of fire debris samples;
- (b) extraction of sample;
- (c) analysis of extract;
- (d) interpretation of results;
- (e) classification of ignitable liquids; and
- (f) reporting of results.

The typical hydrocarbon classes that are normally present in ILR are illustrated in Appendix A.

**WARNING: THIS STANDARD CALLS FOR THE USE OF PROCEDURES THAT MAY BE A HEALTH HAZARD OR CAUSE INJURY IF ADEQUATE PROVISIONS ARE NOT TAKEN.**

NOTE: The provisions of this document are restricted to qualified scientists, with proven competence in the use of appropriate scientific instruments and techniques in a forensic context.

**2 REFERENCED AND RELATED DOCUMENTS****2.1 Referenced documents**

The following documents are referred to in this Standard:

AS

- 2162 Verification and use of volumetric apparatus
- 2162.1 Part 1: General—Volumetric glassware
- 2162.2 Part 2: Guide to the use of piston-operated volumetric apparatus (POVA)
- 2164 Laboratory glassware—One-mark volumetric flasks
- 2166 Laboratory glassware—One-mark pipettes
- 2167 Graduated straight pipettes

AS/ISO/IEC

- 17025 General requirements for the competence of testing and calibration laboratories

ISO

- 3696 Water for analytical laboratory use—Specification and test methods

## 2.2 Related documents

Further information may be found in the following Standards:

### AS

- 1470 Health and safety at work—Principles and practices
- 1940 The storage and handling of flammable and combustible liquids
- 2030 Gas cylinders
- 2030.1 Part 1: General requirements
- 2106 Methods for the determination of the flash point of flammable liquids (closed cup)
- 2106.0 Part 0: General
- 2134 Recommended practice for chemical analysis by atomic absorption spectrometry
- 2134.1 Part 1: Flame atomic absorption spectrometry
- 2134.2 Part 2: Graphite furnace spectrometry
- 2375 Guide to the selection, care and use of clothing for protection against heat and fire
- 2675 Portable first aid kits for use by consumers
- 2850 Chemical analysis—Interlaboratory test programs—For determining precision of analytical method(s)—Guide to the planning and conduct
- 2931 Selection and use of emergency procedure guides for the transport of dangerous goods
- 3765 Clothing for protection against hazardous chemicals
- 3765.1 Part 1: Protection against general or specific chemicals
- 3765.2 Part 2: Limited protection against specific chemicals

### AS/NZS

- 1336 Recommended practices for occupational eye protection
- 1337 Personal eye protection (series)
- 1715 Selection, use and maintenance of respiratory protective equipment
- 1716 Respiratory protective devices
- 2161 Occupational protective gloves (series)
- 2243 Safety in laboratories (series)
- 2865 Safe working in a confined space
- 4501 Occupational protective clothing
- 4501.1 Part 1: Guidelines on the selection, use, care and maintenance of protective clothing
- 4501.2 Part 2: General requirements

### AS/NZS ISO

- 31000 Risk management—Principles and guidelines

## 3 DEFINITIONS AND ABBREVIATIONS

For the purpose of this Standard, the definitions and abbreviations listed in Appendix B apply.

## 4 SAMPLE STORAGE

### 4.1 General

Due to the volatile nature of ILR, samples shall be stored in containers that preserve the integrity of the sample for subsequent analysis. Containers shall be airtight and non-reactive. Examples of appropriate packaging are given below.

### 4.2 Packaging of samples

#### 4.2.1 General

All packaging, whether bags, tins, or glass jars, shall be clean, new and unused.

When the fire debris being collected contains material with sharp edges, only containers that cannot be perforated should be used (e.g. friction-lid tins or glass preservative jars).

#### 4.2.2 Polymer bags

Commercially available bags, e.g. nylon bags, polyethylene/polyvinylidene dichloride (copolymer) bags or ethylene vinyl alcohol bags, are all effective in retaining volatile compounds when properly sealed. Polymer bags should not be used for packaging samples suspected of having low levels of ignitable liquid residue.

#### 4.2.3 Friction-lid tins

Friction-lid tins may be used for the packaging of fire debris samples.

The use of adhesive tape to minimize the loss of volatile compounds should be considered if the samples are to be stored for a long period before analysis.

#### 4.2.4 Glass preservative jars

Glass preservative jars with a 'snap-lid' and retaining ring may be used for the packaging of fire debris samples as they provide an airtight seal. Other types of jars (e.g. jars with screw-top lids) do not provide an acceptable seal and should not be used for packaging of fire debris samples. When properly sealed, glass preservative jars minimize volatile sample loss and cross contamination.

#### 4.2.5 Other containers

Screw-top glass vials or crimp-top glass vials may be used for collecting solvent washings or liquid samples. Such containers shall have an appropriate seal to avoid sample loss or contamination.\*

#### 4.2.6 Inappropriate packaging

In cases where samples are provided for analysis in inadequately sealed or inappropriate packaging, any report produced shall include a description indicating the use of inappropriate packaging.

### 4.3 Storage of sample containers

In order to minimize volatile sample loss and degradation, sealed sample containers shall be stored appropriately until samples are ready for extraction and analysis\* †.

The storage environment shall be separate from possible sources of ignitable liquid contamination such as motor vehicles, bulk fuels, or solvents, and the area should be ventilated to avoid the build up of volatile compounds in the storage environment.

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\* Mann, D., 'In Search of the Perfect Container for Fire Debris Evidence'. *Fire & Arson Investigator*, 2000; 50 (3): 21–25.

† Kirkbride, K.P., Yap, S.M., Andrews, S., Pigou, P.E., Klass, G., Dinan, A.C. and Peddie, F.L., 'Microbial Degradation of Petroleum Hydrocarbons: Implications for Arson Residue Analysis', *Journal of Forensic Sciences*, 1992; 37(6), 1585–1599.

The use of refrigeration is recommended for medium to long-term storage of ILR samples.

Refrigerators used for forensic purposes should be on an electrical circuit with a suitable power supply backup and shall either be monitored by a temperature recorder or be equipped with a temperature alarm.

Laboratories should have a system in place to record the storage conditions and location of all samples.

Laboratories are advised that their jurisdiction may have legal requirements regarding retention of samples.

## 5 REAGENTS

All reagents shall be of analytical reagent grade, and Grade 1 water as defined in ISO 3696 shall be used in all cases.

## 6 APPARATUS

If quantitation is required, laboratory calibrated volumetric glassware shall be used throughout. Volumetric flasks shall comply with AS 2164 and pipettes shall comply with AS 2166 and AS 2167. The use of volumetric apparatus shall conform with AS 2162, Parts 1 and 2.

## 7 SAMPLE EXTRACTION

### 7.1 General

Fire debris samples may be wet, may contain pyrolysis and combustion products, may consist of a complex matrix, and may only contain very small quantities of ILR. To obtain a suitable ILR sample for analysis, the fire debris sample collected from a scene is subjected to an extraction process that separates volatile compounds from the sample matrix.

Where practicable, prior to extraction, the fire debris should be examined and notes made on factors that include, but are not limited to, the material present, the amount of charring, the degree of moisture present, and the approximate total volume of the debris sample. The severity of the burning may be compared to the degree of evaporation of any petroleum distillates subsequently detected.

All ignitable liquids are either hydrocarbons or volatile organic solvents and the type of extraction process chosen impacts on sample recovery. Solubility, oxygenation and hydrocarbon fraction (light or heavy) are some of the factors that need to be considered if the presence of a particular ignitable fluid is suspected.

The use of an internal reference compound may be considered as part of the sample preparation or solvent extraction process. When added to the organic solvent at an appropriate concentration, the internal reference compound can provide a measure of GC performance and facilitate proper interpretation of analytical results.

Results of any re-analysis of fire debris samples are limited by the fact that any extraction already carried out causes alterations to the initial sample.

The techniques that shall be used for ignitable liquid extraction from fire debris samples consist of at least one of the following:

- (a) Direct headspace sampling—Clause 7.2.
- (b) Direct solvent extraction—Clause 7.3.
- (c) Steam distillation—Clause 7.4.

- (d) Adsorption procedures—Clause 7.5:
  - (i) Passive headspace sampling:
    - (A) Activated carbon strips.
    - (B) Activated carbon tubes.
    - (C) Activated carbon ‘C-Bags’.
    - (D) Porous resin.
    - (E) Porous polymer adsorbent.
    - (F) Passive headspace sampling with SPME.
  - (ii) Dynamic headspace sampling.
- (e) Desorption procedures—Clause 7.6:
  - (i) Solvent desorption.
  - (ii) Thermal desorption.

## 7.2 Direct headspace sampling

Direct headspace sampling is the least sensitive extraction technique, but provides a means of detecting volatile compounds associated with a sample material without the use of solvent extraction. A sample of the atmosphere surrounding the material may be withdrawn using a gas-tight syringe and injected into a GC/FID or GC/MS. Prior to sampling, the vessel containing the material may be warmed.

Direct headspace sampling is also used as a screening technique to determine the presence of a particular class of ignitable liquid and its relative concentration, prior to extraction using other techniques.\*

## 7.3 Direct solvent extraction

### 7.3.1 General

Solvent extraction may be used and is useful with small samples consisting of material with non-porous surfaces (e.g. glass) or low volatility ILR.

Solvent extraction may be used to extract ILR that is present in aqueous solutions collected from fire scenes.

### 7.3.2 Procedure

For aqueous solutions the procedure shall be as follows:

- (a) Salt out a sample of the solution.
- (b) Add a suitable solvent and shake the sample.
- (c) Collect the solvent fraction.

NOTE: Direct solvent extraction may be used to extract ILR that is not in an aqueous solution.

This technique should not be used for water soluble liquids that may not extract (depending on polarity). Nor should it be used for more volatile ignitable liquids (e.g. ketones, alcohols) as they may evaporate during the concentration step.

NOTE: Solvent extraction is considered destructive; a sample subjected to this technique extraction may not be suitable for re-analysis.

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\* Lennard, C., ‘Fire (Determination of Cause)—A Review: 1992 to 1995’. Presented at the 11th INTERPOL Forensic Science Symposium, Lyon, Nov 1995.

There are a number of solvents that may be used for the direct extraction of ILR from fire debris. All solvent extractions shall be performed in a fume cupboard meeting the appropriate Australian Standard. Measures shall be taken to minimize the risk of accidental exposure to organic solvents.

**WARNING: ALWAYS WEAR SOLVENT-RESISTANT GLOVES, EYE PROTECTION AND LABORATORY COATS WHEN CONDUCTING DIRECT SOLVENT EXTRACTION.**

See Appendix C for examples of solvents, other than hexane, that may be used for solvent extraction from fire debris and for desorption of ignitable fluids.

#### 7.4 Steam distillation

Steam distillation provides a means of estimating the quantity of ILR present in a fire debris sample\*.

Steam distillation should not be used for water soluble ignitable liquids such as alcohols or ketones†.

CAUTION: CARE MUST BE TAKEN TO ENSURE THAT GLASSWARE IS THOROUGHLY CLEANED TO AVOID CONTAMINATION FROM REUSE OF GLASSWARE.

#### 7.5 Adsorption procedures

##### 7.5.1 General

Passive and dynamic headspace sampling provide a range of techniques to the analyst for collection of an extract of volatile compounds from fire debris samples onto an adsorbent matrix material for later desorption (see Clause 7.6). This Clause (7.5) provides guidance on such techniques.

##### 7.5.2 Passive headspace sampling

###### 7.5.2.1 General

Passive headspace sampling of ILR from fire debris samples can be achieved by using activated carbon.

As an adsorption matrix, commercially available materials such as activated carbon strips (see Clause 7.5.2.2), activated carbon-filled glass tubes (see Clause 7.5.2.3) or 'C-bags' (see Clause 7.5.2.4) may be used.

Passive headspace sampling of ILR from fire debris samples using activated carbon membranes (also known as activated carbon strips) has been widely adopted since its introduction in 1991 because of its sensitivity, simplicity and reproducibility‡.

CAUTION: WHEN APPLYING ANY PASSIVE HEADSPACE TECHNIQUE WHICH USES ACTIVATED CHARCOAL, THE ADSORBANT SHOULD NOT BE EXPOSED TO DIRECT CONTACT WITH THE FIRE DEBRIS OR MOISTURE AS THIS WILL LIMIT THE EFFECTIVENESS OF THE ADSORPTION.

An alternative to using a charcoal adsorption matrix is to use a commercial polymer such as a porous resin (see Clause 7.5.2.5) or a porous polymer adsorbent (see Clause 7.5.2.6). These products consist of a porous polymer or resin that adsorbs (or traps) volatile organic vapours. Once trapped, the vapours may be thermally desorbed from the matrix and analysed.

\* Lennard, C., 'Fire (Determination of Cause)—A Review: 1992 to 1995'. Presented at the 11th INTERPOL Forensic Science Symposium, Lyon, Nov 1995.

† American Society for Testing and Materials, ASTM E1385, *Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Steam Distillation*.

‡ Dietz, W.R., 'Improved Charcoal Packaging for Accelerant Recovery by Passive Diffusion,' *Journal of Forensic Sciences* Jan 1991; 36 (1), 1991, 111–121.

### 7.5.2.2 *Activated carbon strips*

Activated carbon strips consists of a thin layer of activated carbon particles immobilized on an inert polymer substrate.

### 7.5.2.3 *Activated carbon tubes*

Activated carbon tubes contain activated coconut carbon inside a sealed glass vial.

### 7.5.2.4 *Activated carbon 'C-bags'*

Activated carbon 'C-bags' are prepared by enclosing activated carbon in a folded sheet of high strength, lightweight, high porosity tissue paper.

### 7.5.2.5 *Porous resin*

Commercially available porous resin is based on 2,6-diphenyl-p-phenylene oxide. It has been specifically designed for the trapping of volatiles and semi-volatiles from air or which have been purged from liquid or solid sample matrices. Porous resin can be applied both as a column packing material and for trapping organic volatile and semi-volatile compounds. Using thermal desorption techniques, detection of volatile organics in the  $\mu\text{g}/\text{m}^3$  and  $\text{ng}/\text{m}^3$  level is feasible. Due to its low affinity for water, porous resin is especially useful for the purging and trapping of volatiles from high moisture content samples including the analysis of volatile organic compounds in water.

Because of their greater thermal stability and lower binding power, higher boiling hydrocarbons are more easily eluted compared to other polymers, although they are a relatively poor adsorbent for polar compounds such as alcohols and ketones.

### 7.5.2.6 *Porous polymer adsorbent*

Commercially available porous polymer adsorbents consist of ethylvinylbenzene-divinylbenzene copolymer. It has a low affinity for water and a high affinity for organic compounds. Trapped volatiles can be recovered by solvent elution.

### 7.5.2.7 *Passive headspace sampling with SPME*

Passive headspace sampling using solid phase microextraction (SPME) is a non-destructive sampling technique that can be employed at the fire scene as well as in the laboratory. It is a simple technique where the use of solvents is not necessary.

SPME is a fibre that is coated with a polymer phase that can be used to extract volatile analytes from the headspace of a fire debris sample. The quantity of analyte extracted by the fibre is proportional to its concentration in the sample, as long as equilibrium is reached. After extraction, the SPME fibre is transferred to the injection port of a GC where thermal desorption of the analyte takes place and analysis is carried out\*.

The advantages of SPME are that the extraction is fast and simple, and can be done without solvents. Detection limits can reach  $\text{ng}/\text{m}^3$  levels for certain compounds. SPME also has great potential for field applications: onsite sampling can be performed without specialist technical knowledge and without the need to have a GC/MS at each location. When properly stored, samples may be able to be analysed days later in the laboratory without significant loss of volatiles.\*

The type of SPME fibre selected for use will impact on the extraction process. For example, ILR in the C10–C25 range extract well using a 100- $\mu\text{m}$  polydimethylsiloxane (PDMS) coated fibre, while residues in the C1–C10 range extract well using an 85  $\mu\text{m}$  polyacrylate (PA) and combined 75  $\mu\text{m}$  carboxen/PDMS coated fibre†.

\* For additional information, see Pawliszyn, J., Handbook of Solid Phase Microextraction, Chemical Industry Press of China, 2009.

† American Society for Testing and Materials, ASTM E2154, *Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME)*.