



Valid internal standard technique for arson detection based on gas chromatography–mass spectrometry

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ABSTRACT

The most popular procedures for the detection of residues of accelerants in fire debris are the ones published by the American Society for Testing and Materials (ASTM E1412-07 and E1618-10). The most critical stages of these tests are the conservation of fire debris from the sampling to the laboratory, the extraction of residues of accelerants from the debris to the activated charcoal strips (ACS) and from those to the final solvent, as well as the analysis of sample extract by gas chromatography–mass spectrometry (GC–MS) and the interpretation of the instrumental signal. This work proposes a strategy for checking the quality of the sample conservation, the accelerant residues transference to final solvent and GC–MS analysis, using internal standard additions. It is used internal standards ranging from a highly volatile compound for checking debris conservation to low volatile compound for checking GC–MS repeatability. The developed quality control (QC) parameters are not affected by GC–MS sensitivity variation and, specifically, the GC–MS performance control is not affected by ACS adsorption saturation that may mask test performance deviations. The proposed QC procedure proved to be adequate to check GC–MS repeatability, ACS extraction and sample conservation since: (1) standard additions are affected by negligible uncertainty and (2) observed dispersion of QC parameters are fit for its intended use.

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1. Introduction

Arson is a crime difficult to investigate since evidences at the crime scene are frequently destroyed by fire. The cause of fire is investigated through the interpretation of the fire scenario and by the collection of chemical evidences of the presence of fire accelerants residues. Whenever accelerants finger-prints are observed in the deflagration point, it must be investigated possible criminal origin of fire.

Since accelerant residue detection affects decisively the course of fire investigation and constitutes major material evidences of the crime, the reliability of these tests are of utmost importance.

The most widely used standards for the detection of ignitable liquid residues (ILRs) in fire scenarios are the ones issued by the ASTM. These standards are divided into the involved pre-analytical and analytical steps. ASTM standards E 2451-08 [1], E 1412-07 [2] and E 1618-10 [3] describing sample preservation from sampling to laboratory, sample extraction and, GC–MS extract analysis

respectively, are within the most used standards. The ASTM E 1412-07 standard [2] describes a passive headspace concentration of volatile sample components in ACS followed by solvent extraction of ILR from ACS. The ASTM E 1618-10 standard [3] describes both GC–MS signals production and interpretation.

The ASTM E 1412-07 standard [2] suggests the addition of an internal standard to the sample to allow the ILR extraction control. Nevertheless, no standard addition procedure is proposed in this standard. Several authors [4–8] highlighted the merits of using internal standard techniques in arson detection but there were no detailed control procedures or performance data shown.

The stage where internal standard is added defines the controlled pre-analytical and/or analytical stages. The addition of internal standard, controls the combined performance of subsequent stages. A sequence of additions of several internal standards in different stages allows the identification of the cause of observed deviation by identifying the stage where deviation is observed first. This information is useful to decide adequate corrective measures that may vary from GC–MS analysis repetition to collected sample rejection due to its inadequate conservation. This control is particularly important to avoid false native results (e.g. the wrong conclusion about the absence of ILRs in fire debris).

The selected internal standard compound and the way it is introduced in the pre-analytical or analytical stage affects the adequacy of the control procedure. Thermolabile compounds are inadequate

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to be used as internal standards to GC analysis since the variability of their chromatography masks performance deviation. The internal standard addition must not be highly uncertain, for instance by the inadequate use of volumetric material, since it will affect the validity (e.g. adequacy for the intended use) of the quality control procedure.

Since GC–MS sensitivity can vary from one day to another, due to variations in uncontrolled experimental conditions, the assessment of the performance of the procedure must be able to compensate this effect. The performance of analytical steps controlled by the addition of internal standard after ACS sample extraction may be masked by the variability of internal standard adsorption to ACS saturated with sample compounds. The outcome of the competition between the adsorbed sample components and the internal standard is known to be extremely variable. This phenomenon can be overcome by adding internal standard after the removal of ACS from the extract.

This work presents a valid and user-friendly procedure for the control of most critical stages of arson detection individually, namely (1) sample conservation from sampling to laboratory; (2) sample components extraction and (3) GC–MS analysis. The validity of the procedure is supported by the ability to detect deviations of the performance not masked by standard addition uncertainty, by GC–MS sensitivity variations or by sample dependent effects. The test quality control is based on checking the value of defined parameters considering statistically and metrologically sound criteria.

2. Experimental

2.1. Reagents and standards

Chemicals of GC-grade purchased from Merck were used.

The following standards were used (CAS number/producer/purity): 1,4-dichlorobenzene, DCB (CAS 106-46-7/Alfa Aesar/99%), cyclohexylbenzene, CHB (CAS 827-52-1/Alfa Aesar/98%) and tetrachloro-m-xylene, TCMX (CAS 877-09-8/Supleco Analytical/97.5%). Individual standard solutions of DCB (S_{DCB}), CHB (S_{CHB}) and TCMX (S_{TCMX}), with mass fractions of 3.77×10^{-3} for DCB (w_{DCB}) and 3.77×10^{-4} (w_{CHB} and w_{TCMX}) for CHB and TCMX, were prepared by diluting 250 mg or 25 mg of pure substance in 66.322 g of dichloromethane (DCM).

Activated charcoal strips (ACS) (9 mm \times 20 mm each) were purchased from Albrayco Technologies, Inc. (Cromwell, CT).

A mixture of DCM and pentane (P) with a mass fraction, w_{DCM-P} , of DCM of 0.679 (mixture of similar volumes of both solvents), solution A, was prepared to extract adsorbed compounds from ACS.

A standard solution, S_{Ref} , with a concentration, C_{Ref} , of 93.9 mg L^{-1} of TCMX was prepared by diluting m_A mass of S_{TCMX} (measured with pipette P1 adjusted for 200 μL) through addition of m_B mass of solution A (measured with pipette P1 adjusted for 800 μL). C_{Ref} was estimated from w_{TCMX} , m_A , m_B and a model of the variation of solution density with DCM mass fraction (Section 2.6.1).

2.2. Equipment

The following equipment was used:

The analytical balance Mettler AE100 was purchased from Mettler-Toledo International (Greifensee, Zürich, Switzerland);

The oven Hereaus model KT500 was purchased from Thermo-Scientific (Waltham, MA, USA);

The micropipette (P1) VWR volume 100–1000 μL was purchased from VWR International, LLC (Radnor, PA, USA);

Table 1
Sample codification and description.

Code	Accelerant	Burned fraction (%)	Delay between the burning and the analysis (h)
ACPU1	Gasoline 95	75	24
ACPU2	Gasoline 95	50	24
ACPU3	Gasoline 95	25	24
ACPU4	Gasoline 95	100	0
ACPU5	Gasoline 98	75	24
ACPU6	Gasoline 98	75	72
ACPU7	Gasoline 98	50	24
ACPU8	Gasoline 98	50	72
ACPU9	Gasoline 98	25	24
ACPU10	Paint thinner	100	0
ACPU11	Solid charcoal starter	100	0
ACPU12	White spirit	100	0

The dispenser (D1) BrandTech, model Dispensette III Bottletop Dispenser 0.5–5 mL was purchased from BrandTech Scientific, Inc. (Essex, CT, USA);

Details of GC–MS equipment are provided in Section 2.5.

2.3. Samples

Five types of accelerants, often detected in arson scenes, were studied, namely: 95 octane gasoline, 98 octane gasoline, paint thinner, solid charcoal starter and white spirits. These accelerants were purchased from a local petrol station and drugstore.

Defined portions of the different accelerants were burned and recovered in a glass jar, equivalent to the ones used to collect real samples, to different extensions producing 12 simulated fire debris samples. The internal standard for sample conservation control was added to glass jar after fire extinction and cooling to room temperature. The jar was capped after internal standard addition. Different delays between combustion and ILR extraction were considered to simulate different delays between sample collection and laboratory analysis. Table 1 details the burning test conditions and the delay from first internal standard addition and ILR detection. The burned portion of liquid accelerants was 5 mL. A mass of 4.5 g of solid charcoal starter, the only solid accelerant, was burned in glass jar coded “ACPU11”.

2.4. Procedure

Fig. 1 describes the pre-analytical and analytical procedure.

For each sample, a mass m_1 of solution S_{DCB} , measured with pipette P1 adjusted to 500 μL , is added before jar capping. Since the used volumetric material is calibrated for measuring water volumes, the delivered solutions were measured gravimetrically as its performance may vary significantly for organic solvents. The mass of delivered solution estimated in an occasion is considered in subsequent routine tests and verified every six months to detect equipment malfunction.

At the laboratory and immediately before analysis, the glass jar is uncapped, mass m_2 of solution S_{CHB} (measured with pipette P1 adjusted to 500 μL) added to debris, ACS is positioned in the head space of the glass jar using an inert support and the capped jar is warmed up to $80 \pm 1^\circ\text{C}$ for $14.0 \pm 0.5 \text{ h}$ in the oven. Subsequently, the glass jar is cooled at room temperature for about 4 h, the ACS is transferred from the glass jar to vial 1 (2.0 mL) and immersed in a mass, m_3 , of solution A (added through dispenser D1 adjusted to 1 mL). The immersed ACS is subjected to occasional hand mixing for $30 \pm 5 \text{ min}$. The ACS extract is transferred to another previously weighed vial 2 (2.0 mL) (m_4 -mass of the vial and cap) and the mass

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