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Quality control procedure for fire debris analysis

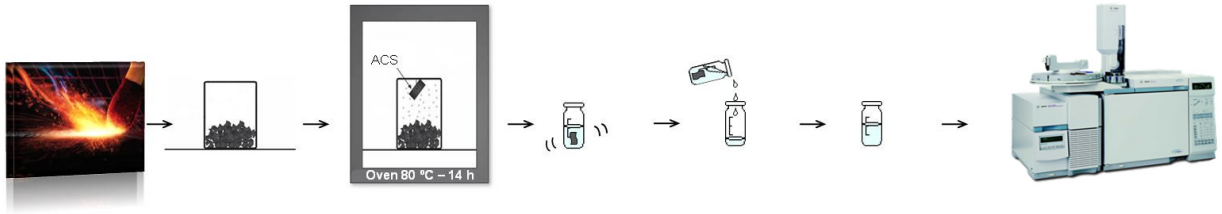
Introduction:

The qualitative evaluation of the use of accelerants in arson, by the ASTM E 1412-07 standard, involves the concentration of the volatile fraction of debris into activated charcoal strips (ACS) at defined temperature and time, the solvent extraction of the concentrated compounds from ACS and the evaluation of extracts by GC-MS according to ASTM E 1618-10 standard. The variability of the performance of the analysis of some microliters of extract by GC demands the monitoring of measurement performance by the internal standard technique. Hence, this work proposes an integrated strategy for controlling some of the most critical stages of arson detection individually, namely: sample conservation from sampling to laboratory, sample components extraction and GC-MS injection.

The ASTM methodology

The most widely used standards for the analysis of ignitable liquid residues (ILRs) are issued by the American Society for Testing and Materials (ASTM), namely:

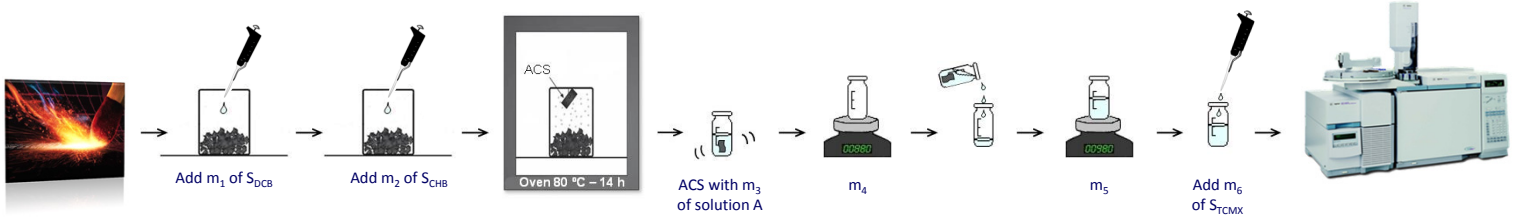
Sampling | Laboratory



Sample preservation – ASTM E 2451-08 | **Extraction and concentration of ILRs – ASTM E 1412-07** | **Identification and data analysis by GC-MS – ASTM E 1618-10**

The proposed internal standard technique

Sampling | Laboratory



m_1 – mass of S_{DCB}
S_{DCB} – Standard solution of Dichlorobenzene

m_2 – mass of S_{CHB}
S_{CHB} – Standard solution of Cyclohexylbenzene

m_3 – mass of Solution A (DCM:Pentane)
m_4 – mass of the empty vial

m_5 – mass of the vial with extract
S_{TCMX} – Standard solution of Tetrachloro-m-xylene (TCMX)
m_6 – mass of S_{TCMX}

Since the internal standard adsorption into ACS significantly varies with the amount of previously retained compounds, the TCMX standard has to be added after charcoal strips removing from the extracts. A strategy for the addition of TCMX to solvent extracts from debris, involving the gravimetric control of the volume of solvent mixtures with several composition using models of the volumetric mass variation with composition was developed. The adequacy of the developed strategy for the control of the repeatability of GC-MS measurements was metrologically checked using the numerical Kragten and the Monte Carlo methods for uncertainty components combination. The Kragten method successfully handled 21 input quantities since the linear assumption of the variation of the output quantity with the input quantities uncertainty is valid. The developed quality control strategy proved to be valid after performed adjustments in relevant analytical steps and further supported the control of the sample preparation performance and debris conservation by using two additional internal standards.

i. TCMX concentration: C_{TCMX} (mg L^{-1}) – estimated from:

Mass of TCMX: $m_{TCMX} = m_6.W_{TCMX}$

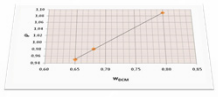
$$C_{TCMX} = \frac{m_{TCMX}}{V_E}$$

V_E is estimated from the mass fraction of DCM: w_{DCM}

$$w_{DCM} = \frac{(m_5-m_4).w_5+m_6(1-w_3)}{m_5-m_4+m_6} \cong \frac{(m_5-m_4).w_5+m_6}{m_E}$$

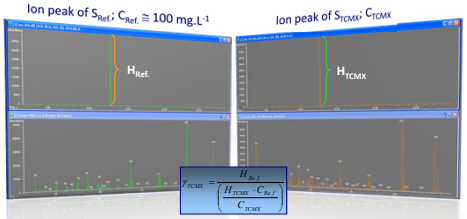
and a model of the variation of ρ vs. w_{DCM}

$$V_E = \frac{m_E}{\rho_E}$$



ii. Quality control procedure:

The GC-MS repeatability is checked by:



iii. Validation:

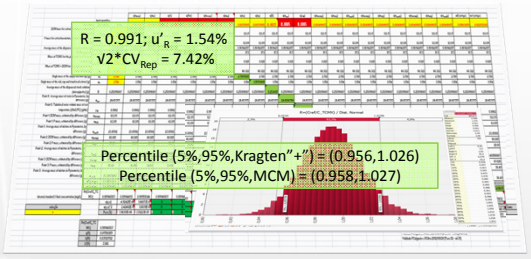
The validation of the proposed strategy for GC-MS repeatability check involves the evaluation of the uncertainty associated with the estimated ratio $R=(C_{Ref}/C_{TCMX})$ and the evaluation of the experimental variation of γ_{TCMX} values.
The GC-MS injection repeatability is estimated by the coefficient of variance, CV_{Rep}, of the height of TCMX molecular ion peaks from replicated injections of the same standard solution obtained in repeatability conditions.
The relative standard uncertainty associated with the calculated R must be negligible when compared with the relative repeatability of the ratio (H_{Ref}/H_{TCMX}), estimated by $(\sqrt{2}*CV_{Rep})$, to guarantee its fitness for the intended use.
The uncertainty associate with $R=C_{Ref}/C_{TCMX}$ was estimated from the algebraic relation used to calculate this concentration and the standard uncertainty associated with the input quantities.

Test Quality Control

The dispersion of γ_{TCMX} is characterised by the mean and standard deviation of results from various samples.
Test quality control is checked by assessing observed γ_{TCMX} values considering 95% confidence level interval.

This works illustrates the use of metrological tools in the development of test quality control strategies for qualitative assessments.

Sample	m_4	m_5	C_{TCMX}	H_{DCB}	H_{CHB}	H_{TCMX}	H_{Ref}	γ_{DCB}	γ_{CHB}	γ_{TCMX}
ACPU1	2.788	3.554	94.750	16235	36678	9962	10242	0.517	0.229	1.037
ACPU2	2.811	3.631	89.681	70387	87379	27178	26264	0.310	0.249	0.923
ACPU3	2.828	3.628	91.494	29909	63942	18792	19632	0.542	0.253	1.018
ACPU4	2.348	3.096	96.569	11607	22166	7040	7699	0.541	0.283	1.125
ACPU5	2.321	3.094	94.061	23503	68849	21980	24205	0.845	0.288	1.103
ACPU6	2.327	3.170	87.682	31068	121389	41100	39598	1.063	0.272	0.900
ACPU7	2.265	3.044	93.478	37944	181648	47655	35289	0.764	0.160	0.737
ACPU8	2.291	3.059	94.552	22955	72794	16989	19335	0.690	0.218	1.146
ACPU9	2.357	3.121	95.049	59999	59943	30857	28.125	0.384	0.384	0.922
ACPU10	2.250	3.032	93.190	13296	25427	9320	7287	0.451	0.236	0.776
ACPU11	2.816	3.587	94.257	25522	99041	28664	27681	0.889	0.229	0.969
			CV (%)	62	57	52	47	37	22	14
			QC criteria (Conf. level 95%)					0.620± 0.427	0.261± 0.128	0.979± 0.303



Conclusions:

It can be concluded from this work that developed procedure to control GC-MS repeatability, sample extraction and sample conservation, in the detection of ILR in fire debris, based on ASTM E1412-07 and E1618-10 standards, is fit for the intended use.
The proposed quality control procedure is easily implemented in routine since it just involves the addition of the internal standards, using an automatic pipette, and two weighing operations.

Bibliography:

- ASTM E 1412-07 – Standard Practices for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal, 2007.
- ASTM E 1618-10 – Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, 2010.
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