LABORATÓRIO DE POLÍCIA CIENTÍFICA

ArsonCPU

FACULDADE DE CIÊNCIAS

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Metrological assessment of internal standard technique for quality control of GC-MS determinations for arson detection

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Overview

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1. Aim

This work aim at developing 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;
- GC-MS injection.

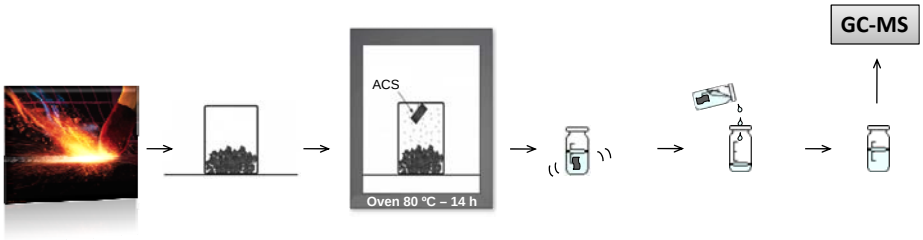
2. The analysis of ignitable liquid residues from fire debris samples using ASTM methodology

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

- Sample preservation – ASTM E 2451-08;
- Extraction and concentration of ILRs – ASTM E 1412-07;
- Instrumental analysis by GC-MS – ASTM E 1618-10.

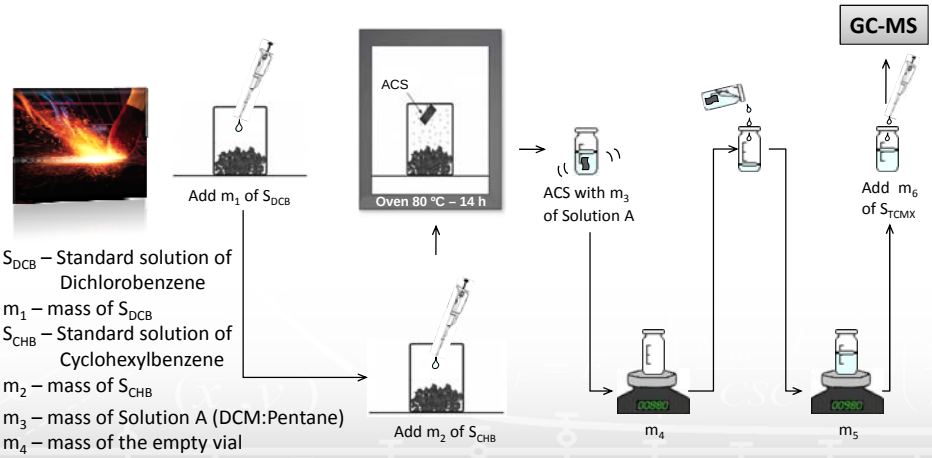
2. The analysis of ignitable liquid residues from fire debris samples using ASTM methodology

Sampling | Laboratory



3. The proposed internal standard technique

Sampling | Laboratory



S_{DCB} – Standard solution of Dichlorobenzene
m_1 – mass of S_{DCB}
S_{CHB} – Standard solution of Cyclohexylbenzene
m_2 – mass of S_{CHB}
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; m_6 – mass of S_{TCMX}

3. The proposed internal standard technique

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

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

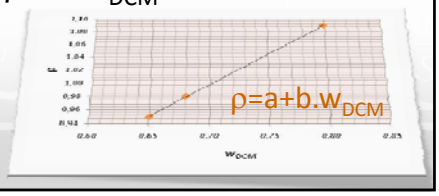
Total volume (V_E): $C_{TCMX}=\frac{m_{TCMX}}{V_E}$

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}

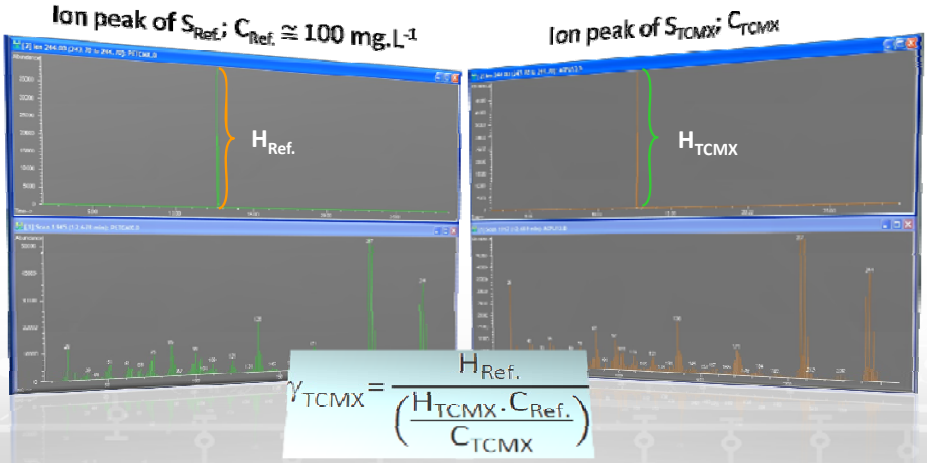
$$V_E=\frac{m_E}{\rho_E}$$



3. The proposed internal standard technique

ii. Quality control procedure:

The GC-MS repeatability is checked by:



$$\gamma_{TCMX}=\frac{H_{Ref.}}{\left(\frac{H_{TCMX}\cdot C_{Ref.}}{C_{TCMX}}\right)}$$

3. The proposed internal standard technique

iii. Validation:

The validation of the proposed strategy for GC-MS repeatability involves the evaluation of the uncertainty associated with the estimated 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 uncertainty associated with the calculated C_{TCMX} must be negligible when compared with the GC-MS injection repeatability to guarantee its fitness for the intended use.

4. Evaluation of the measurement uncertainty using the numerical Kragten method

The uncertainty associate with C_{TCMX} was estimated from the algebraic relation used to calculate this concentration and the standard uncertainty associated with the input quantities.

The standard uncertainties associated with the input quantities were combined using the Kragten numerical method [1,2].

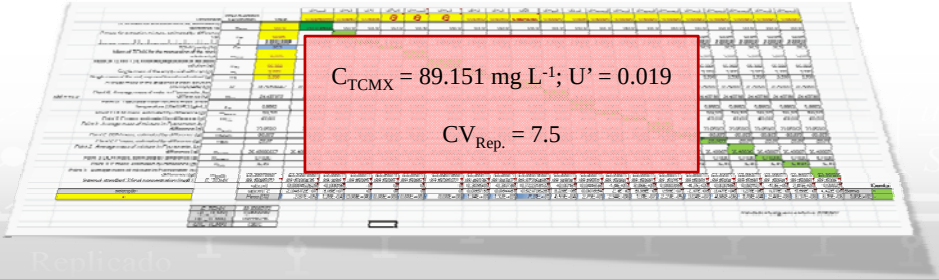
1 – J. Kragten, *Analyst,* **119**, 2161-2166 (1994).
2 – Eurachem/CITAC Guide Quantifying Uncertainty in Analytical Measurement, Draft 3rd ed. (2011).

4. Evaluation of the measurement uncertainty using the numerical Kragten method

Sample	m_4	m_5	C_{TCMX}	H_{DCB}	H_{CHB}	H_{TCMX}	H_{Ref}	γ_{DCB}	γ_{CHB}	γ_{TCMX}
ACPU1	2.772	3.598	89.151	20663	44207	40852	40708	1.637	0.765	0.888
ACPU2	2.808	3.654	87.428	28811	56372	40688	40708	1.180	0.603	0.875
ACPU3	2.801	3.632	88.714	22222	47873	48788	40708	1.524	0.707	0.740
ACPU4	2.794	3.610	90.038	21682	485549	43601	40708	1.556	0.659	0.841
ACPU5	2.743	3.546	91.218	17546	142264	57346	40708	1.917	0.236	0.648
ACPU6	2.786	3.610	89.327	15814	18686	42587	40708	2.138	1.809	0.854
ACPU7	2.797	3.598	91.102	15672	17378	40990	40708	2.146	1.935	0.908
ACPU8	2.318	3.139	89.592	6588	46746	42054	40708	5.128	0.723	0.867
ACPU9	2.308	3.120	90.398	12496	86025	39409	40708	2.698	0.392	0.934
ACPU10	2.771	3.530	95.450	16330	19901	41712	40708	2.038	1.672	0.931
ACPU11	2.851	3.535	103.642	23083	91092	155354	99427	3.445	0.873	0.663
ACPU12	2.809	3.587	93.575	24407	81481	142604	99427	3.346	1.002	0.652
ACPU13	2.843	3.610	94.651	13135	65056	140812	99427	6.200	1.252	0.668
ACPU14	2.812	3.611	91.587	9845	55150	135497	99427	8.338	1.488	0.672
ACPU15	2.846	3.664	89.860	13063	69311	134360	99427	6.312	1.189	0.665
ACPU16	2.850	3.655	91.034	20128	72846	178191	99427	4.084	1.128	0.508
ACPU17	2.756	3.557	91.402	14912	60807	163303	99427	5.507	1.351	0.557
ACPU18	2.781	3.563	93.190	13064	92415	102201	99427	6.257	0.885	0.907

4. Evaluation of the measurement uncertainty using the numerical Kragten method

The suitability of the measurement uncertainty for controlling GC-MS repeatability is checked by comparing the relative expanded measurements uncertainty, U', with the GC-MS injection repeatability quantified by CV_{Rep}. The U' should be approximately five times smaller that CV_{Rep} to be negligible and consequently adequate for this control.



5. Conclusion

The proposed internal standard technique is fitness for the intended use, because the uncertainty associated with the calculated C_{TCMX} is negligible when compared with the GC-MS injection repeatability.