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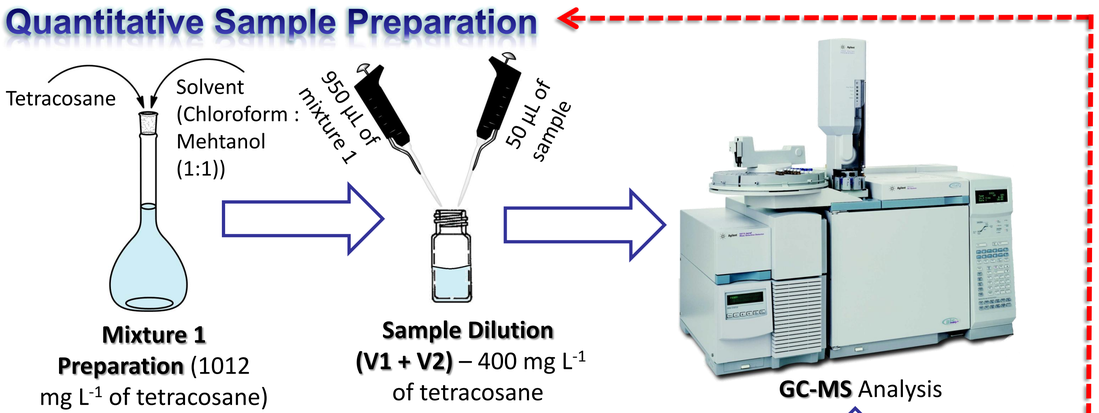
Development of metrological models for the quantitative or semi-quantitative GC-MS assessment of the compliance of self-defense weapons with legislation

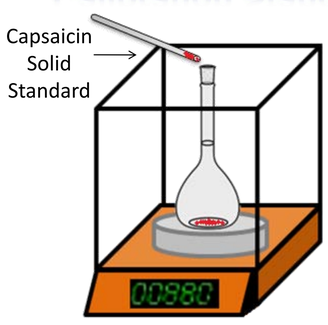
INTRODUCTION

Self-defense weapons based on Riot Control Agents (RCA) (like lachrymators) are worldwide used, but its use is are limited by national legislation. In Portugal self-defense aerosols can only use the active principle (RCA) Capsaicin or *Oleoresin Capsicum* (OC; extraction product from peppers and similar species) in a concentration lower than 5 (w/v) %. The juridical consequences of using illegal self-defense weapons demand the use of validated analytical methods and the assessment of the weapons compliance with legislation considering the reliability of measurements. In Portugal, these evaluations are performed in the Scientific Police Laboratory from Polícia Judiciária, in a two steps metrological procedure, divided on a qualitative (active principle identification) and quantitative analysis. The quantitative evaluation is further divided in two stages: a semi-quantitative (single-point calibration) and a quantitative analysis (multi-point calibration).

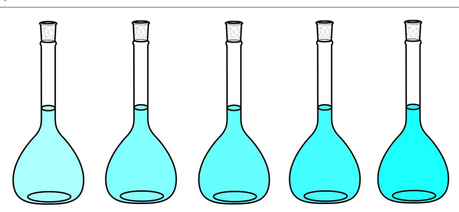
Quantitative Sample Preparation



Calibration Standards Preparation



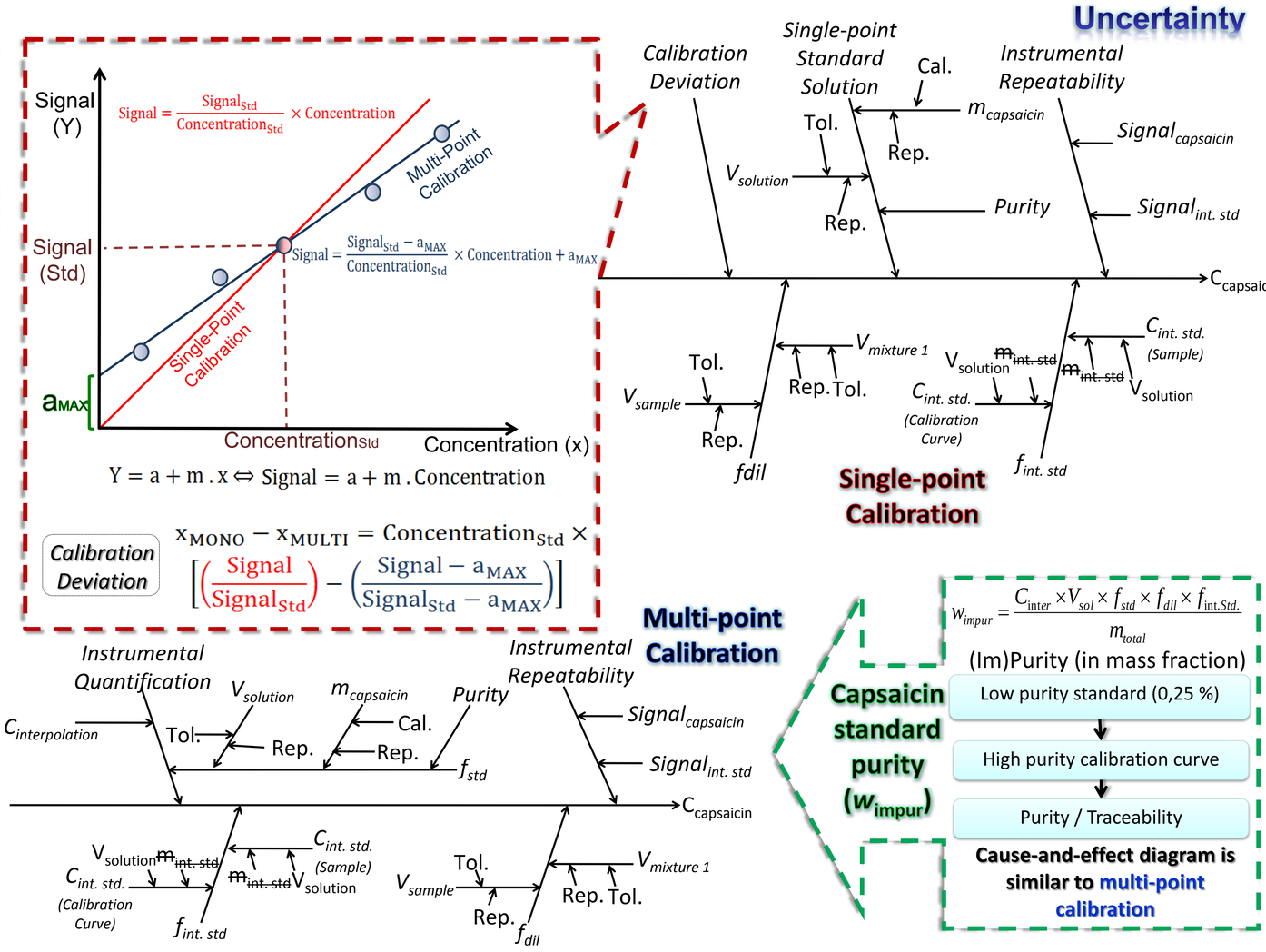
Capsaicin Concentration	0,15 %	0,20 %	0,25 %	0,30 %	0,35 %



Capsaicin Calibration Standards Preparation:
A capsaicin stock solution aliquot and 400 µL of tetracosane stock solution (internal standard) were diluted with chloroform:metanol (1:1) to a final volume of 1 mL using a volumetric flask.

Capsaicin standard *traceability*: It was used a highly pure capsaicin to determinate the purity of other standard.

Uncertainty



Capsaicin standard purity (w_{impur})

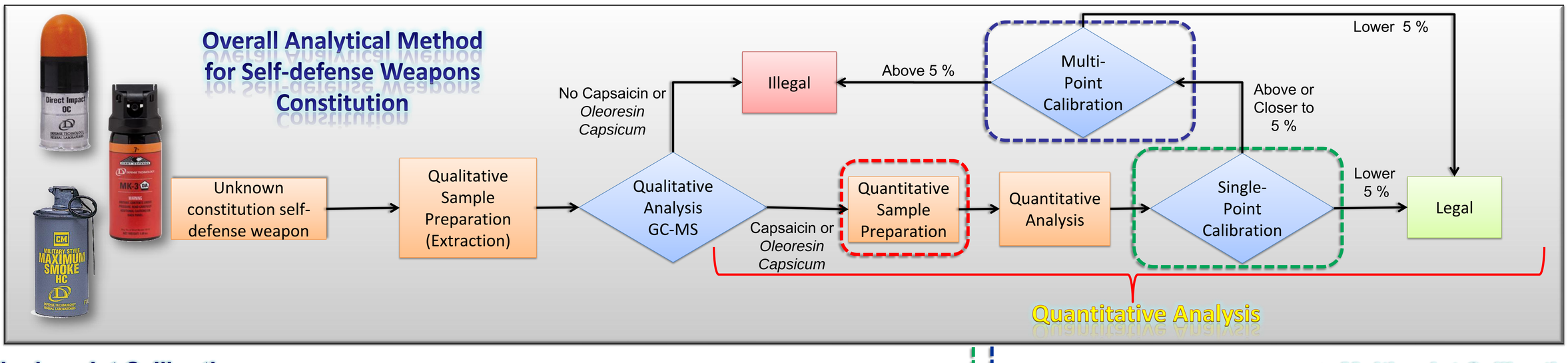
$$w_{impur} = \frac{C_{inter} \times V_{sol} \times f_{std} \times f_{dil} \times f_{int.Std.}}{m_{total}}$$

(Im)Purity (in mass fraction)

- Low purity standard (0,25 %)
- High purity calibration curve
- Purity / Traceability

Cause-and-effect diagram is similar to multi-point calibration

Overall Analytical Method for Self-defense Weapons Constitution



Single-point Calibration ⟵ ⟶ Multi-point Calibration

Acceptation criteria for single-point standard (*First*)

Criterion Interval for **Area Ratio** of single-point standard

$$\overline{R} \pm t \times s_R$$

Criterion interval for **Retention Time** of single-point standard (**Capsaicin**)

$$\overline{T_r} \pm t \times s_{T_r}$$

(*First*) Single-point Standard Analysis

Obtained Data
- Chromatographic Area Ratio (R_1)
- Retention Time (Tr_1) (Capsaicin)

Acceptation criteria for sample replicates

Criterion Interval for **Retention Time** of sample replicates (**Capsaicin**)

$$|T_{r1} - T_{rS}| \le 3 \times \sqrt{2} \times s_{rTr}$$

Sample Analysis (*Replicated*)

Obtained Data
- Chromatographic Area Ratio (R_S)
- Retention Time (Tr_S) (Capsaicin)

Acceptation criteria for single-point standards (repeatability)

Criterion Interval for **Area Ratio** of single-point standard replicates

$$|R_1 - R_2| \le 3 \times \sqrt{2} \times s_{rR}$$

Criterion Interval for **Retention Time** of single-point standard replicates

$$|T_{r1} - T_{r2}| \le 3 \times \sqrt{2} \times s_{rTr}$$

(*Second*) Single-point Standard Analysis

Obtained Data
- Chromatographic Area Ratio (R_2)
- Retention Time (Tr_2) (Capsaicin)

Decision criteria for single-point calibration

If

$$C_{caps-SP} + 2 \times u_{caps-SP} < 5\%$$

Then the self-defense weapon is **legal**

Or

$$C_{caps-SP} + 2 \times u_{caps-SP} \ge 5\%$$

Then quantification is required (**Mutli-point calibration**)

Criteria Data
- Single-point calibration uncertainty (u_{caps}-*SP*)

Sample Results (*Single*)

≥ 5 %

< 5 %

Obtained Data
- Single-point Capsaicin Concentration (C_{caps}-*SP*)

Acceptation criteria for multi-point calibration

Calibration Curve **Linearity**

$$r \ge 0{,}99$$

Calibration Curve **Control** – Standard *3*

$$|C_{CS3-CC} - C_{CS3-QP}| \le 2 \times \sqrt{\left(u_{C_{CS3-CC}}\right)^2 + \left(u_{C_{CS3-QP}}\right)^2}$$

Multi-point Calibration Curve

Obtained Data
- Retention Time of standard 2500 mgL^{-1} (Tr_3)

Criteria Data
- Concentration and uncertainties for standard *3* (*CC* and *QP*)

Legal

Decision criteria for multi-point calibration

Criterion Interval for **Retention Time** of samples(Capsaicin)

$$|T_{r4} - T_{rS}| \le 3 \times \sqrt{2} \times s_{rTr}$$

If

$$C_{caps-MP} + 2 \times u_{caps-MP} < 5\%$$

The self-defense weapon is **legal**

Or

$$C_{caps-MP} + 2 \times u_{caps-MP} \ge 5\%$$

The self-defense weapon is **illegal**

Sample Results (*Multi*)

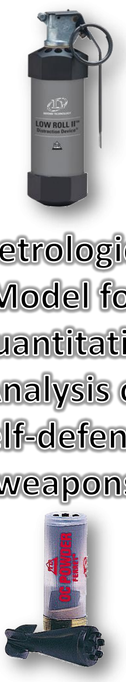
Obtained Data
- Multi-point Capsaicin Concentration (C_{caps}-*MP*)

< 5 %

Criteria Data
- Multi-point calibration uncertainty (u_{caps}-*MP*)

≥ 5 %

Illegal



Metrological Model for Quantitative Analysis of self-defense weapons

CONCLUSIONS:

The developed analytical method and metrological models allow the reliable identification of the active principles in self-defense weapons and the quantification of capsaicin in it.
This was accomplished by a detailed method validation, that allowed the determination of used quantitative and qualitative metrological criteria.

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ACKNOWLEDGEMENTS:

To the Biotoxicology Area Direction of the Scientific Police Laboratory of Polícia Judiciária (Dr. Sandra Santos and Dr. Joana Alegre).