

Internal Quality Control of Explosive Substances - Identification by Ion Chromatography

Introduction

Many types of explosives have been used in terrorist attacks, however, the number of attacks using improvised explosives (IED) is increasing. In most cases, IEDs are inorganic explosives produced using commercially available materials and/or military explosives. The purpose of forensic analysis of explosives is to identify the used explosive that can link it to a suspect. The identification of inorganic explosives is supported on various composition data, from which relative concentration of major components is particularly relevant. For that, selective and sensitive analytical techniques are required, such as ion chromatography (IC). IC allows the identification and quantification of ionic species in water soluble fraction of explosives and consequently determination of their ionic and mass balance. These balances are supported on the uncertainty of estimated composition data. This study presents the used strategy to control performance of determination of ionic composition of water soluble fraction of explosives including estimated measurement uncertainty using the "bottom-up" approach.

The strategy used to the determination of ionic composition of water soluble fraction of explosives and for the internal quality control of tests are based on the results of the validation of the qualitative and quantitative performance of the procedure. The validation of the quantitative measurement procedure involves the assessment of the linearity and homoscedasticity of variance of the IC response, definition of the calibration range, evaluation of the measurement uncertainty and assessment of standard solutions stability.

Cation	r (min)
Lithium	0.086
Sodium	0.092
Ammonium	0.093
Potassium	0.099
Calcium	0.328
Magnesium	0.403
Strontium	0.465
Barium	0.697

Anion	r (min)
Fluoride	0.045
Chloride	0.079
Nitrite	0.071
Bromide and Chlorate	0.155
Nitrate	0.104
Sulfate	0.225
Carbonate	0.151

The internal quality control of the qualitative analysis is based on the repeatability limits (r) determined during the validation.

1st Step

Evaluation of the performance of the procedure, by comparing retention times (t_R) of the analyte in standard solutions analysed before and after samples: Criterion (1)

2nd Step

Check retention time of sample peaks using criterion (2)

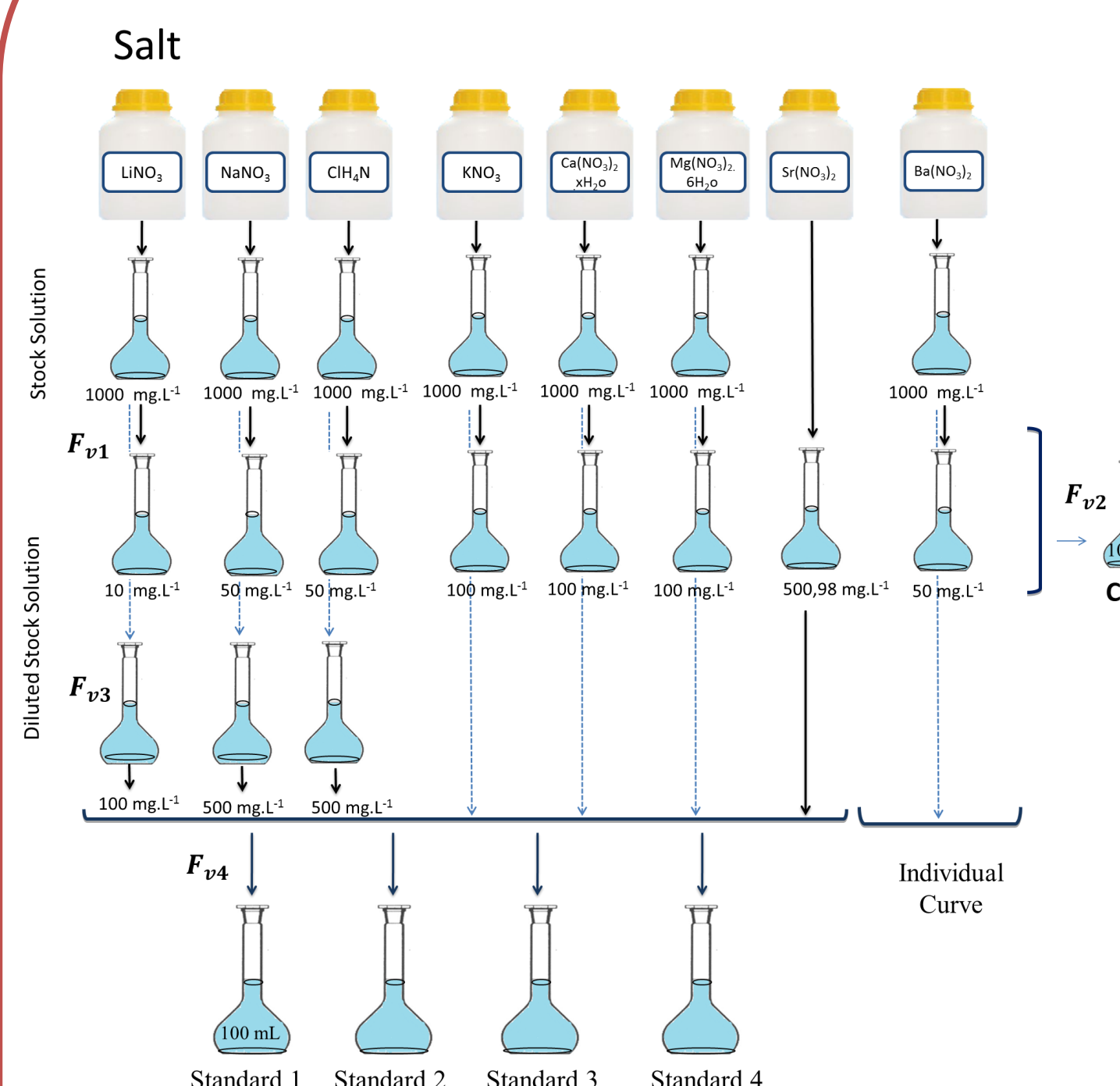
Internal quality control of quantitative analysis:

The reliability of the measurements is controlled through the analysis of a control standard (CS). The determination of CS composition, x_0 , in a daily calibration curve, is checked through the assessment of the metrological compatibility of measurement results with the estimated concentration (C_{CSPrep}) of CS based on their uncertainties (u_{x0} and $u_{CCSPrep}$).

Internal quality control of ionic balance:

After the quantification of the ionic composition of the aqueous extract of the explosive, the total concentrations of anions (C_A) and cations (C_C) are compared considering ions charge values. Ionic balance is supported on measurement results reported, with uncertainty, in mol.L⁻¹ units [criterion (4)]

Standards prepared from Pure Salts



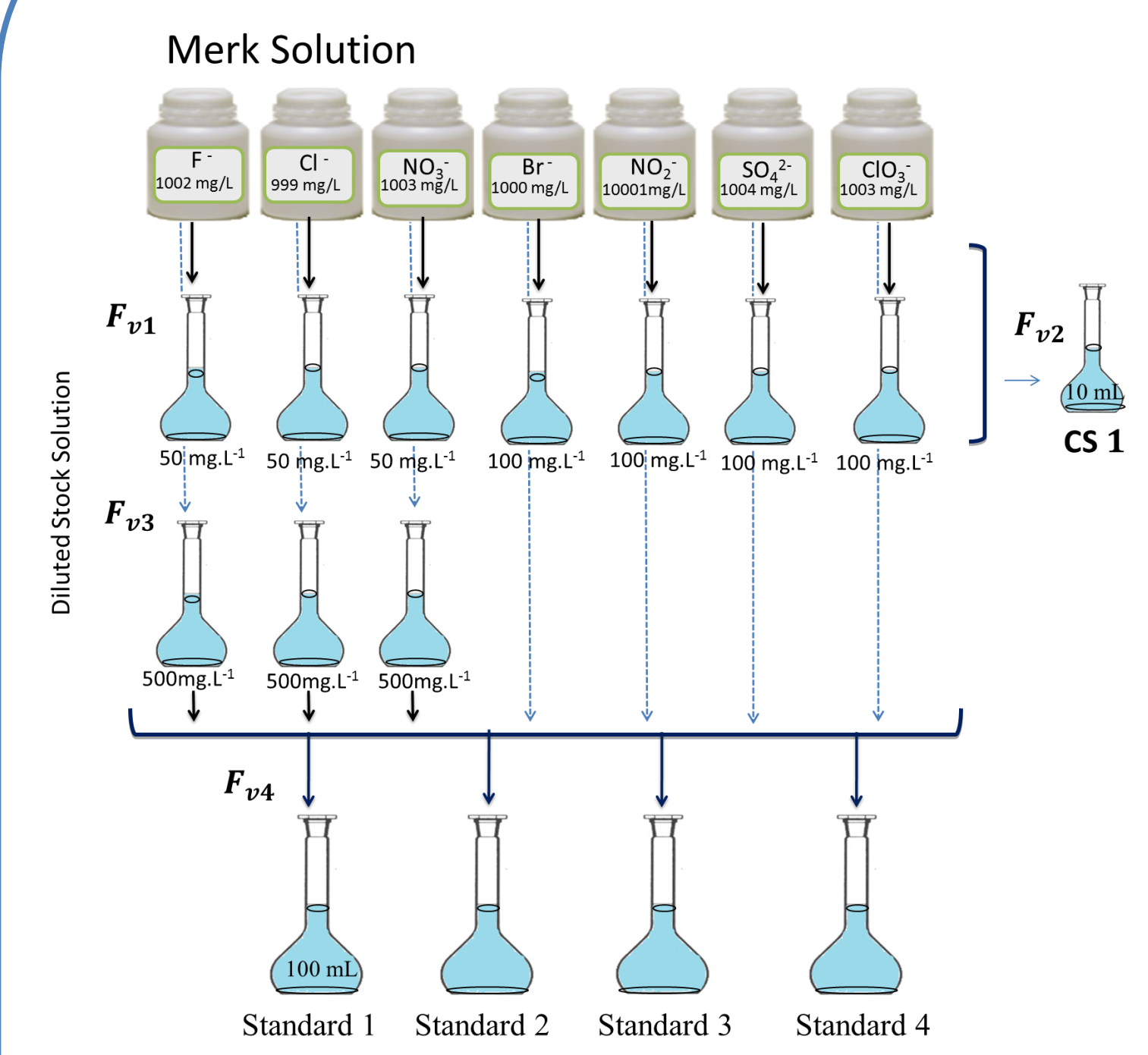
Uncertainty associated with estimated concentration of CS

$$u'_{x0} = \sqrt{\left(\frac{s_{x0}}{x_0}\right)^2 + (u'_{Fv3})^2}$$

Uncertainty associated with the reference value of CS from its preparation

$$u'_{CCSPrep} = \sqrt{(u'_{Fv1})^2 + (u'_{Fv2})^2}$$

Standards prepared from Merk Solution

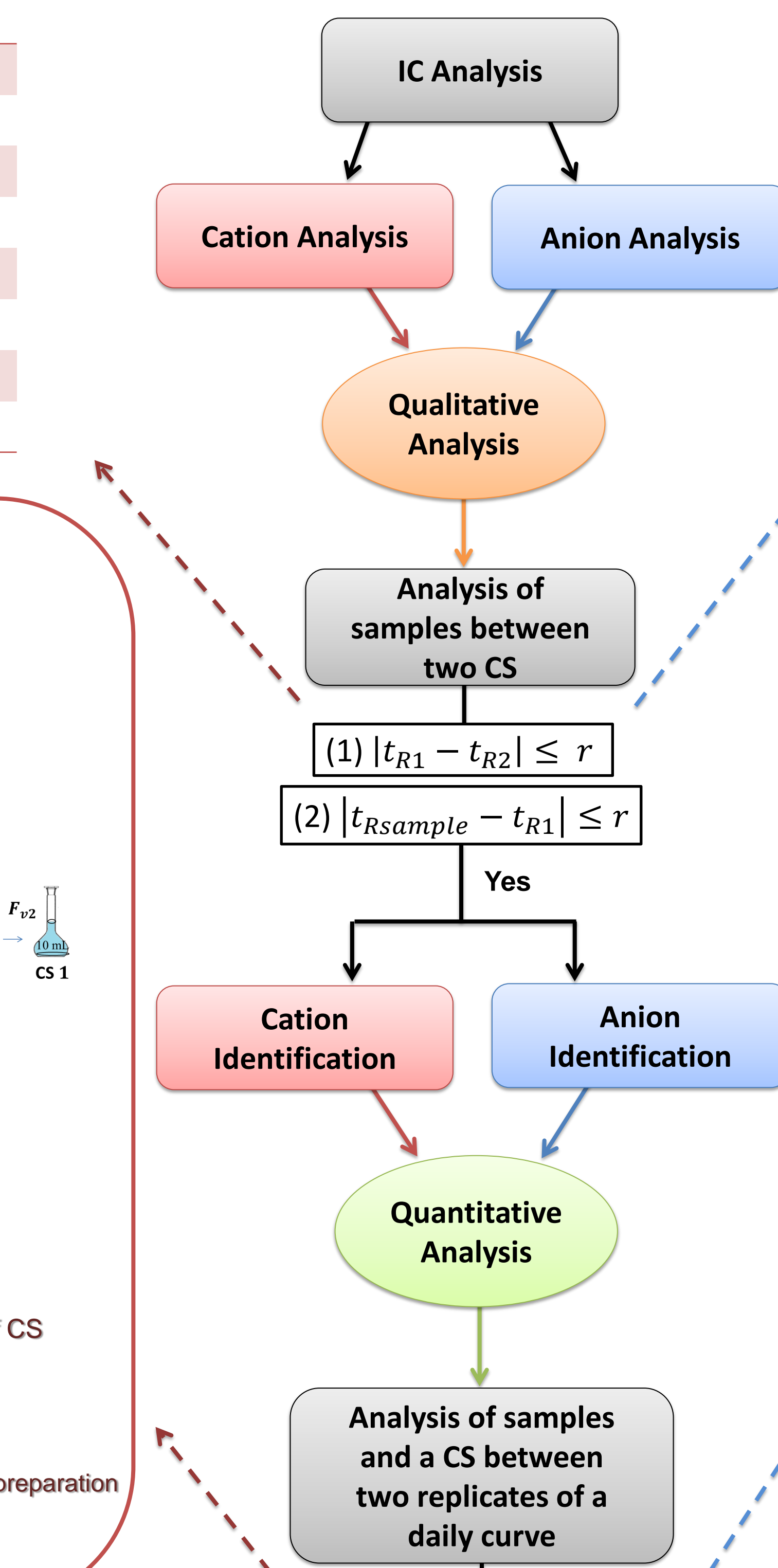


Uncertainty associated with estimated concentration of CS

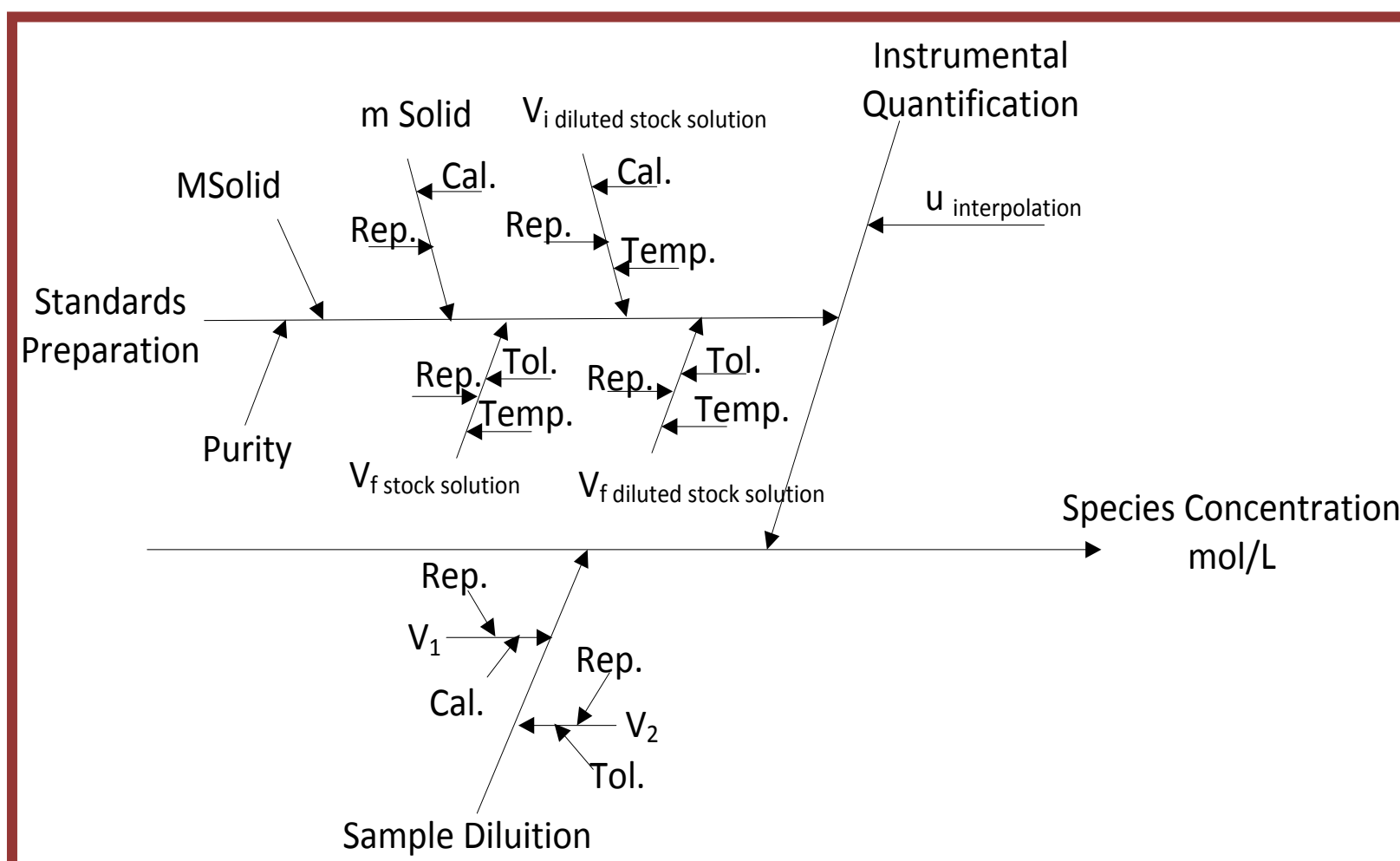
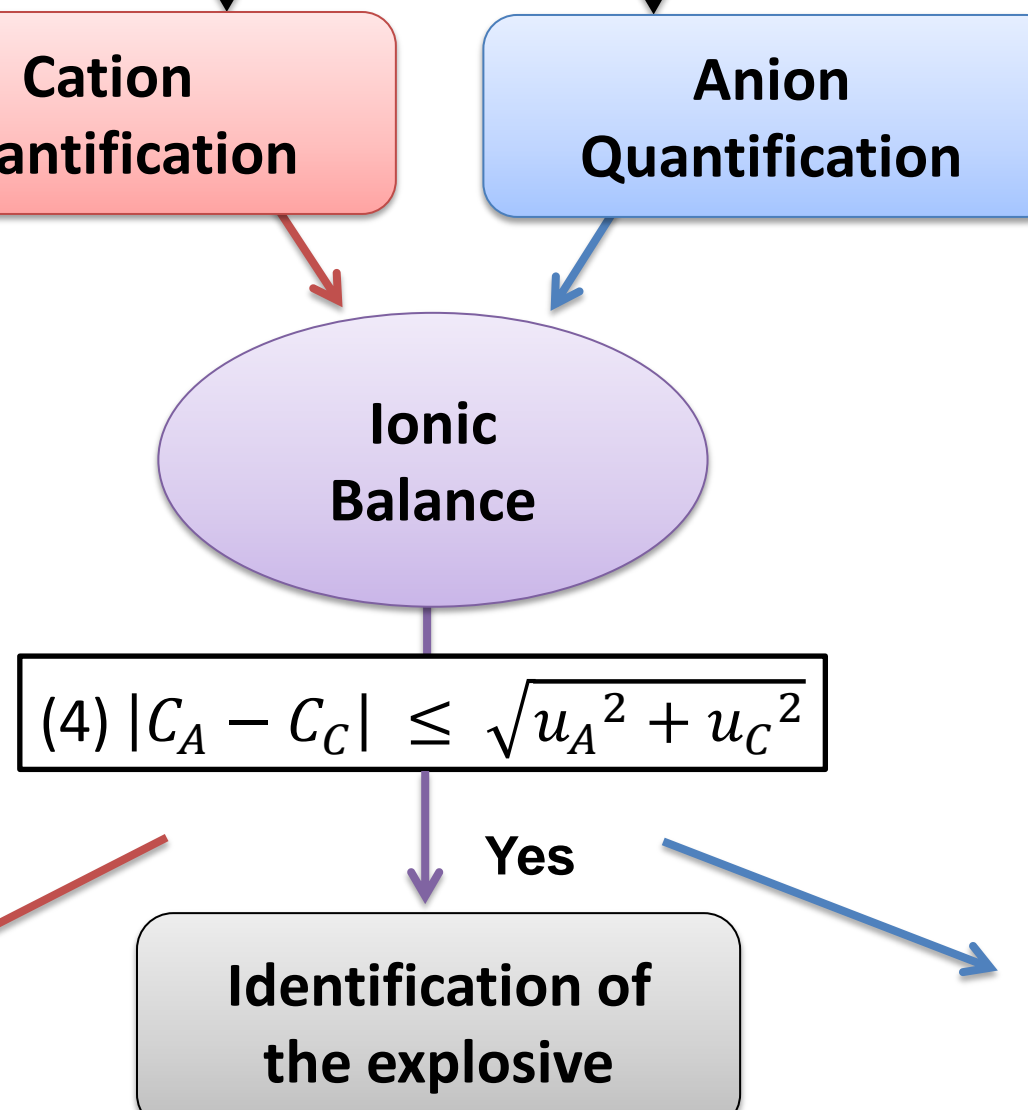
$$u'_{x0} = \sqrt{\left(\frac{s_{x0}}{x_0}\right)^2 + (u'_{Fv3})^2 + (u'_{tolip5mL})^2}$$

Uncertainty associated with the reference value of CS from its preparation

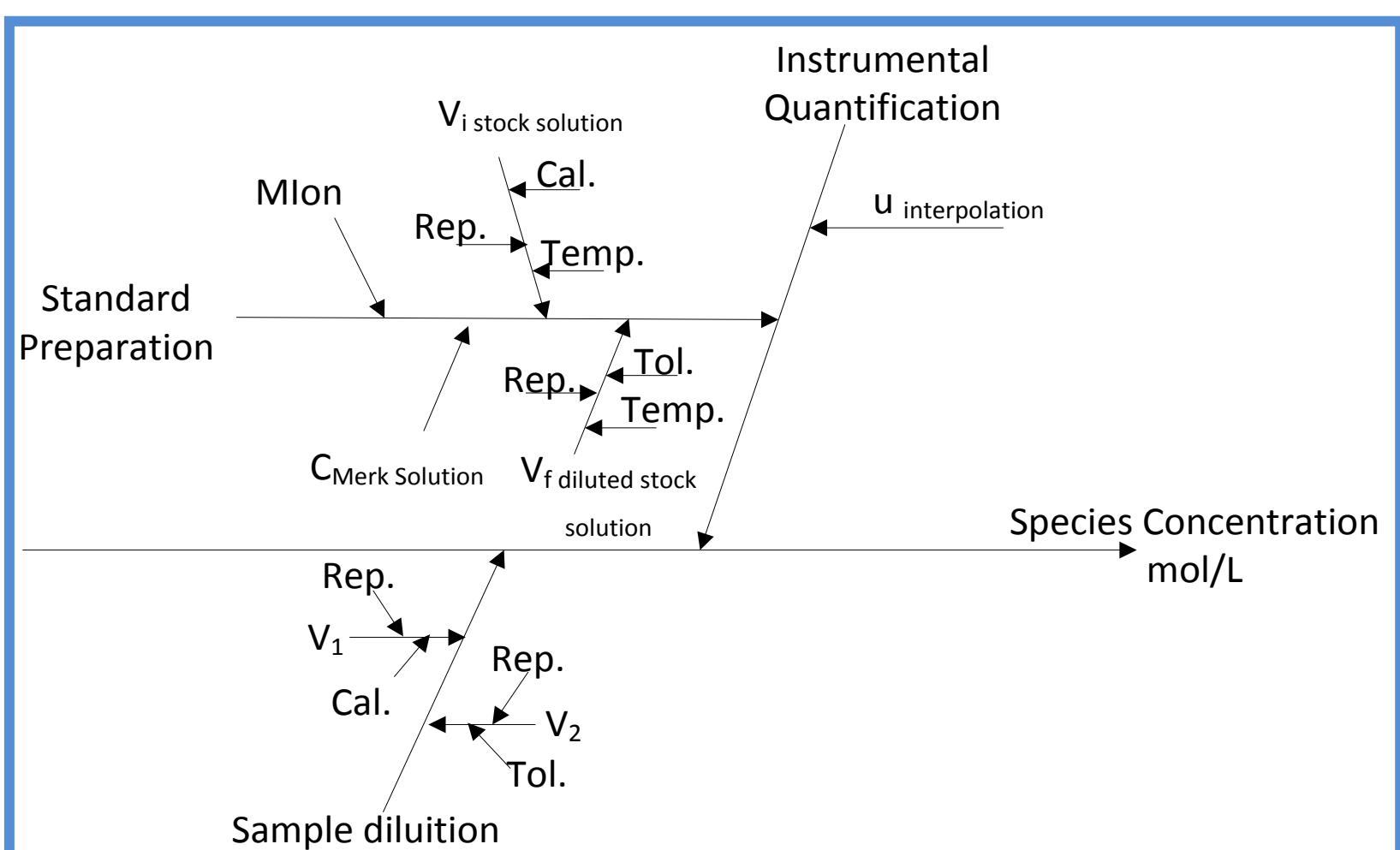
$$u'_{CCSPrep} = \sqrt{(u'_{Fv1})^2 + (u'_{Fv2})^2}$$



$$(3) |x_0 - C_{CSPrep}| \leq t(99; n-2) \times \sqrt{(u'_{x_0} \times x_0)^2 + (u'_{CCSPrep} \times C_{CCSPrep})^2}$$



$$u'_y = \sqrt{(s'_{x0})^2 + (u'_{Purity})^2 + (u'_m)^2 + (u'_{MSalt})^2 + (u'_V)^2 + (u'_{V1:2})^2 + (u'_{Fv})^2}$$



$$u'_y = \sqrt{(s'_{x0})^2 + (u'_{Merk})^2 + (u'_{Fv})^2 + (u'_{Mion})^2 + (u'_{V1:2})^2}$$

ANALYSIS OF REAL SAMPLES

Samples Identification of species and respective quality control

Samples	Identification of species and respective quality control		Ion
	$t_{RSample}$	t_{R1} t_{R2} (1) (2)	
	6.25	6.21 6.24	NO ₃ ⁻
	4.05	3.97 3.99	NH ₄ ⁺
	8.11	7.8 7.69	Ca ²⁺

Samples	Identification of species and respective quality control		Ion
	$t_{RSample}$	t_{R1} t_{R2} (1) (2)	
	6.22	6.21 6.22	NO ₃ ⁻
	4.02	3.97 3.99	NH ₄ ⁺

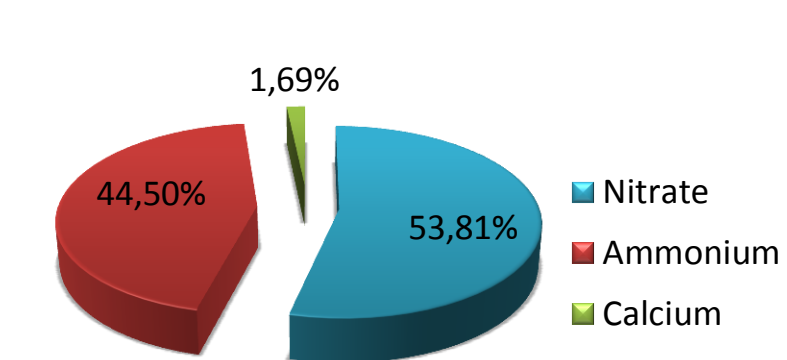
Quality control of the quantification

x_0 (mol.L ⁻¹)	C_{CSPrep} (mol.L ⁻¹)	u'_{x_0}	$u'_{CCSPrep}$	(3)
3.30×10^{-5}	3.23×10^{-5}	7.91×10^{-2}	6.78×10^{-3}	Yes
5.26×10^{-5}	5.48×10^{-5}	1.48×10^{-2}	6.75×10^{-3}	Yes
5.40×10^{-5}	4.94×10^{-5}	1.30×10^{-2}	6.78×10^{-3}	Yes

x_0 (mol.L ⁻¹)	C_{CSPrep} (mol.L ⁻¹)	u'_{x_0}	$u'_{CCSPrep}$	(3)
2.93×10^{-5}	3.23×10^{-5}	7.45×10^{-2}	6.78×10^{-3}	Yes
5.26×10^{-5}	5.48×10^{-5}	1.48×10^{-2}	6.75×10^{-3}	Yes

Sample results

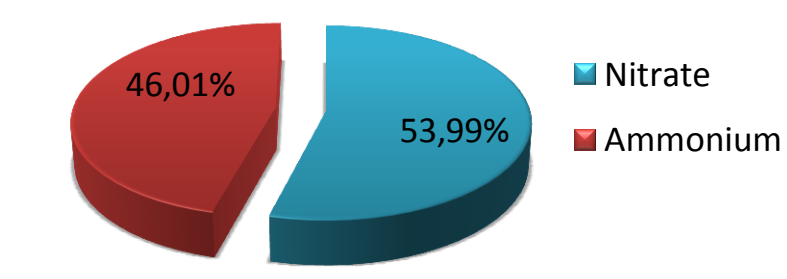
Ion	mol.L ⁻¹
NO ₃ ⁻	(0.030±0.001)
NH ₄ ⁺	(0.0248±0.0007)
Ca ²⁺	(0.00189±0.00003)



$$|C_{NO_3} - (C_{NH_4} + \frac{C_{Ca}}{2})| \leq \sqrt{u_{NO_3}^2 + u_{(NH_4 + \frac{Ca}{2})}^2}$$

Explosive based on ammonium nitrate and calcium nitrate

Ion	mol.L ⁻¹
NO ₃ ⁻	(0.0552±0.0025)
NH ₄ ⁺	(0.0470±0.0015)



$$|C_{NO_3} - C_{NH_4}| \leq \sqrt{u_{NO_3}^2 + u_{NH_4}^2}$$

Explosive based on ammonium nitrate

CONCLUSION:

The developed test quality control strategy ensures the reliable identification and quantification of the ionic composition of the water soluble fraction of explosives, including the estimated measurement uncertainty needed for ionic balance assessment.

BIBLIOGRAPHY:

- (1) Eurachem, CITAC (2000) Quantifying uncertainty in analytical measurement, Guide CG4, 2nd edn, Eurachem.
- (2) International Vocabulary of Metrology – Basic and General Concepts and Associated Terms VIM, 3rd edition, JCGM 200:2008