How to quantify the exact amount and establish metrological traceability of sulphur in biodiesel by ICP-IDMS and in copper samples by ICP-IDMS, GDMS, LA-ICP-MS, and LA-ICP-IDMS.

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BACKGROUND

This research had two main drivers being economic impact and metrological issues.

Economic Impact:

- Copper industry in 2014, 847,00 tonnes were produced by EU [1]
- Biodiesel Fuel: in 2010, 180 thousand barrels per day were produced by EU [2]
- Both industries have been important driver for the economy for the past decades.
- Keeping up the quality of the products continuous quality control is needed, which in turn requires suitable reference materials.

AIM FOR SULPHUR QUANTIFICATION

Metrological Issues:

- Lack of SI-traceability
- In-consistance results between laboratories
- Lack of suitable reference materials
- High relative measurement uncertainty
- Lack of reference procedure
- Challenge due to inaccurate/unreliable techniques

"Once measured, accepted everywhere"

METROLOGICAL TRACEABILITY

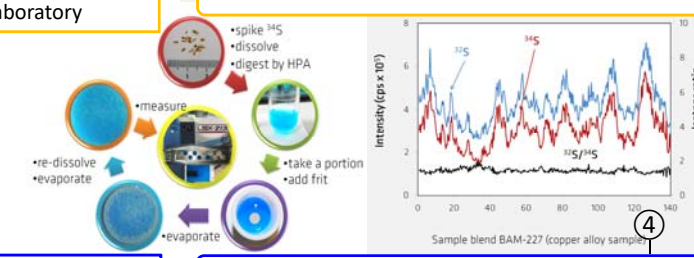
metrological reference of end-user's *measurement results*:
specification of *kind-of-quantity* amount-of-substance concentration and definition of the *measurement unit* μg g^{-1}

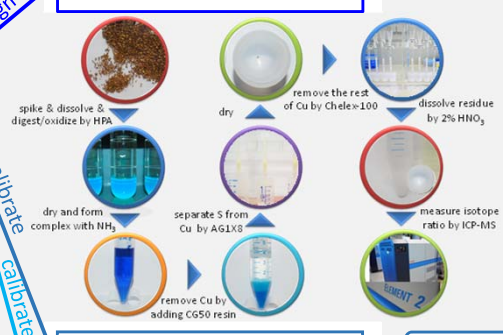
metrological reference for input quantities in a measurement model associated with metrological traceability side chains:

electric current : A (1) | mass : kg (1 2 3 4) | amount of substance : mol (1 2 3)

calibration hierarchy / *metrological traceability chain*

MEASUREMENT RESULT: MEASUREMENT UNCERTAINTY	MEASUREMENT RESULT: QUANTITY VALUE	CALIBRATOR or SAMPLE	ACTION	MEASURING SYSTEM	MEASUREMENT PROCEDURE
$u(w_1)/w_1$ = 2.9x10^{-3}	mass fraction of sulphur in primary calibrator 1 w_1 = 10.30 mg g^{-1}	*primary calibrator 1* NIST SRM3154	assign / calibrate	primary measuring system 1&2: gravimetric and coulometric titration system at NIST	*primary reference measurement procedure* 1 &2 governing gravimetric and coulometric titration and assignment of mass fraction value to sulphur solution
$u(w_2)/w_2$ = 3.3x10^{-3}	mass fraction of ^{34}S in secondary calibrator 2 w_2 = 92.21 μg g^{-1}	*secondary calibrator 2* sulphur in ^{34}S	assign / calibrate	measuring system 3: reverse IDMS at BAM laboratory	*measurement procedure 3 governing IDMS*
$u(w_3)/w_3$ = 6.22x10^{-3}	mass fraction of sulphur in biodiesel fuel sample w_3 = 7.39 μg g^{-1}	sulphur in biodiesel fuel (CCQM-K123)	assign / calibrate	measuring system 4a: **IDMS** at BAM laboratory	*measurement procedure 4a governing analysis by **ICP-IDMS*** [3]
$u(w_s)/w_s$ BAM-M376a = 1.3x10^{-1} BAM-228 = 5.2x10^{-2} BAM-227 = 8.0x10^{-2}	mass fraction of sulphur in metal (copper), μg g^{-1} BAM-M376a = 183.0 BAM-228 = 426.0 BAM-227 = 1374.0	sulphur in BAM-376a (copper pure), BAM-228 & BAM-227 (copper alloyed)	assign / calibrate	measuring system 4b: **IDMS** at BAM laboratory	*measurement procedure 4b governing analysis by **LA-ICP-IDMS*** [5]
$u(w_s)/w_s$ SRM494 = 6.7x10^{-3} BAM-M385 = 2.5x10^{-3} BAM-M376a = 3.2x10^{-3}	mass fraction of sulphur (w_s) SRM494 = 15.0 μg g^{-1} BAM-M385 = 37.7 μg g^{-1} BAM-376a = 133.7 μg g^{-1}	*third calibrator 3, 4, 5* SRM494, BAM-M385 & BAM-M376a (pure copper)	assign / calibrate	measuring system 4c: **IDMS** at BAM laboratory	*measurement procedure 4c governing analysis by ICP-IDMS* [4]
$u(w_s)/w_s$ = 2.8x10^{-2}	mass fraction of sulphur in metal (copper) w_s = 127 μg g^{-1}	sulphur in sample no. 422 (pure copper)	assign / calibrate	measuring system 5a: **GDMS** at BAM laboratory	*measurement procedure 5a governing analysis by external calibration*
$u(w_s)/w_s$ = 1.2x10^{-1}	mass fraction of sulphur in metal (copper) w_s = 139 μg g^{-1}	sulphur in sample no. 422 (pure copper)	assign / calibrate	measuring system 5b: **LA-ICP-MS** at BAM laboratory	*measurement procedure 5b governing analysis by external calibration*





Feature of ICP-IDMS

- Low procedure blank (0.54 μg g^{-1}) and low LOQs (0.20 μg g^{-1})
- High sulphur recovery > 80 %
- **High matrix removal efficiency**: 99.99 % for Cu
- **Wide working range**: from 1,500 μg g^{-1} down to 15 μg g^{-1} for Cu and 5 μg g^{-1} for biodiesel
- **Small relative measurement uncertainties**: < 1 %
- **Direct metrological traceability** to the SI
- Applicable to calibrate/validate GDMS and LA-ICP-MS method

CONCLUSION

- A **reliable procedure** was developed which enables SI traceable results and has the potential to be a reference method.
- **GDMS and LA-ICP-MS** were used as routine analytical techniques to quantify sulphur in the copper materials; the measurement results were traceable to SI through IDMS analysis.
- **LA-ICP-IDMS** was developed as universal technique with sufficient low measurement uncertainty.
- Every measurement result is accompanied by complete **uncertainty budget** and the **metrological traceability** chain is expressed clearly.
- Once measured sulphur (in copper sample), accepted everywhere (by these measurement procedures)

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