

TRACEABILITY STATEMENT FOR THE DETERMINATION OF TOTAL CHROMIUM MASS FRACTION IN SERPENTINE SOILS BY ATOMIC ABSORPTION SPECTROMETRY

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Abstract – The purpose of this work is to contribute for the metrological traceability statement of chemical measurements. Traceability statement for total chromium mass fraction in serpentine soils was developed. Accordingly, the quantity values requiring a high degree of control are calibration and quality control standard solutions, matrix certified reference material and the calibration curve model fit.

Keywords: Traceability; uncertainty; soils; chromium

1. INTRODUCTION

Measurement uncertainty and metrological traceability are properties of the measurement results closely linked. Measurement uncertainty characterizes the dispersion of the quantity values being attributed to a measurand and metrological traceability allows relating the result to a reference through a documented unbroken chain of calibrations [1]. Each link of the chain contributes to the measurement uncertainty showing the relationship between both concepts [2].

In this work the metrological traceability statement for total chromium determination in serpentine soils was developed, following the interrelated steps [3, 4]:

- i) Selection of a suitably validated method and identification of the acceptable uncertainty for the analytical result;
- ii) Writing and understanding the measurement function;
- iii) Identification of any reagents or equipment with specified values and fixed experimental conditions used in the procedure;
- iv) Establishment of appropriated stated references for the influence quantities, identified according to the degree of control needed;
- v) Measurement uncertainty evaluation.

2. MEASURAND AND ACCEPTABLE UNCERTAINTY

Our measurand of interest is the mass fraction of total chromium in soils, w (mg kg^{-1}), which was determined by flame atomic absorption spectrometry after soil digestion with HF, HNO₃ and HClO₄ acid mixture [5], following a quality assurance programme [5, 6]. Before analysis the soil samples were air dried, sieved through a 2-mm aperture sieve and crushed with an agate mortar and pestle (particle size < 150 μm). The analytical procedure is summarised in Fig 1.

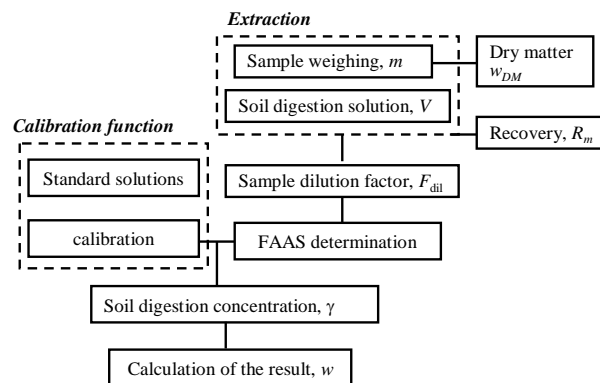


Fig. 1 - Analytical Procedure.

Target relative combined standard uncertainty, $u_c^{rel}(w)$, close to 0,1 was considered, based on in house criteria, since no standard measurement uncertainty was required by legislation [5].

All the results were expressed on an oven-dry mass basis at 105 °C. Since a non-dry sample was used for the chemical analysis the chromium mass fraction was corrected by the degree of moisture, at the end.

3. MEASUREMENT FUNCTION

Chromium mass fraction, w (mg kg^{-1}) was calculated and reported on a dry matter basis using equation 1:

$$w = \gamma \times \frac{V}{m} \times F_{dil} \times \frac{1}{R_m} \times \frac{1}{w_{DM}} \quad (1)$$

where γ is the concentration of Cr in the soil digestion solution estimated from the calibration curve (mg L^{-1}), V the volume of the soil digested solution (mL), m the mass of sample used for analysis (g), F_{dil} the dilution factor, R_m the mean recovery of the Certified Reference Material (CRM) and w_{DM} (g g^{-1}) the dry matter mass fraction, determined by drying an independent aliquot of the sample at $(105 \pm 5)^\circ\text{C}$.

4. STATED REFERENCES

The traceability of all influence quantity values reported in equation (1), with adequate uncertainty, should be known, since all of them require a high degree of control.

The metrological traceability of γ values are related to the uncertainty of the calibration standards and the uncertainty associated to the regression line. The calibration standards were obtained by diluting a $(1000 \pm 5) \text{ mg L}^{-1}$ Cr standard solution (Merck, Darmstadt, Germany). The calibration function was metrological controlled as previously described [5, 6]. Since the dilution steps influence the uncertainty of the measurement results all volumetric glassware used was of class A, with H conformity. The measurement uncertainty of the volumetric flasks was estimated from their volume tolerance assuming a triangular distribution [7]. In the case of automatic pipettes, they were calibrated by accredited calibration laboratory equipments which results are traceable to national standards. For example in case of Eppendorf 100 μl micropipette, the calibration error was 0,22 μl (SOQUILAB certificate n° 06.10.11A7).

The m values were determined using a Mettler AT 200 analytical balance (Mettler Toledo, Switzerland) with 200 mg capacity and 0,0001 g readability (resolution), calibrated by an accredited calibration laboratory using E2 class weights traceable to national standards.

The bias of the method was evaluated as recovery, R_m , obtained using the reference material river clay sediment LGC 6139, with Cr concentration of $(126 \pm 18) \text{ mg kg}^{-1}$.

Dry matter mass fraction, w_{DM} , was determined by gravimetry [8] using a MEMMERT UM 400 oven, thermostatically controlled and calibrated at $(105 \pm 5)^\circ\text{C}$, by an accredited calibration laboratory using Pt 100's thermometer which results are traceable to national standards. According to the ISQ calibration report n° ETEM 1274/06, the expanded uncertainty for each temperature measurement was $\pm 0,2^\circ\text{C}$. The measurement uncertainty of w_{DM} , was estimated using the procedure described in [9].

5. PERFORMANCE CHARACTERISTICS OF THE METHOD

In table 1 the performance characteristics of the method used for the determination of total Cr mass fraction in soils are shown.

Table 1 - Performance characteristics of the method used for the determination of total Cr mass fraction in soils.

Selectivity / Interference	Free from interferences
Linearity, working range	Linear range 0,05 – 2,0 mg L^{-1}
Limit of quantification	7 mg kg^{-1}
Repeatability	$RSD_r = 0,04$ at 3000 mg kg^{-1}
Within-lab reproducibility	$RSD_{Rw} = 0,04$ at 3000 mg kg^{-1}
Recovery (tolerance)	$(1,00 \pm 0,10)$ using CRM

RSD_r – Relative standard deviation in repeatability conditions; RSD_{Rw} - Relative standard deviation in within laboratory reproducibility conditions; CRM – certified reference material.

6. MEASUREMENT UNCERTAINTY

The combined standard uncertainty for w , $u_c(w)$, was estimated using an intralaboratory approach. Each measurement uncertainty associated with individual input parameters (eq. 1) was quantified and combined following the law of propagation of uncertainties for independent input quantities [7]. Fig. 2 shows the cause and effect diagram for w , summarizing all the input influence quantities. A branch combining all the individual repeatability contributions ($f_{precision}$), given by the standard deviation of replicate analysis, was added. The requirements for the digestion procedure are included in the recovery branch.

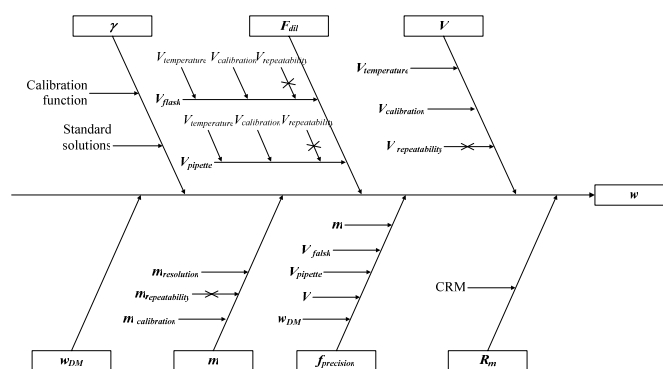


Fig. 2 - Cause and effect diagram.

In table 2 the input quantities values and associated standard uncertainties, $u(x_i)$, for total chromium mass fraction are shown. For a soil sample with $w = 3,05 \text{ g kg}^{-1}$ the $u_c(w)$ was $0,49 \text{ g kg}^{-1}$. The target measurement uncertainty was fulfilled since $u_c^{rel}(w) = 0,08$ which is lower than 0,1.

Table 2 - Input quantities values, X_i , and associated standard uncertainties, $u(x_i)$, for total chromium mass fraction, w , in serpentine soils.

X_i	x_i	$u(x_i)$
γ	0,419 mg L ⁻¹	0,017 mg L ⁻¹
V	100 mL	0,084 mL
F_{dil}	50	0,068
m	0,7518 g	0,0001 g
w_{DM}	0,913 mg kg ⁻¹	0,015 mg kg ⁻¹
R_m	1	0,06
$f_{precision}$	1	65 mg kg ⁻¹
$w = 3,05 \text{ g kg}^{-1}$		
$u_c(w) = 0,49 \text{ g kg}^{-1}$		

x_i is the best estimate of the i^{th} input quantity X_i

The assessment of each input quantity contribution into $u_c(w)$ value was carried out using the relative variance, as shown in Fig. 3. Precision ($f_{precision}$), γ and recovery (R_m) are the contributions that control $u_c(w)$ values.

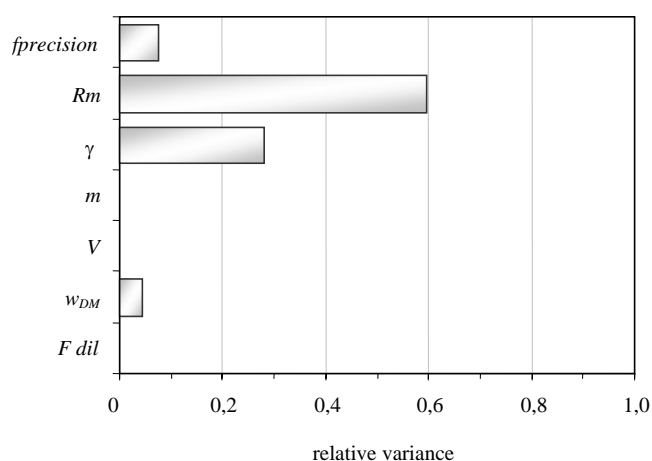


Fig. 3 - Relative variances.

7. CONCLUSIONS

Evaluation of traceability requirements for the determination of total chromium mass fraction in soils identified five property values requiring a high significant degree of control, which means that “special” stated references should be selected:

- Chromium standard solution
- Working calibration standard solutions
- Matrix certified reference material for chromium in soils
- Calibration curve model fit

Significant degree of control for mass and volume measurements, minerals acids, ultrapure water, temperature of the drying oven and the wavelength of the instrument are also needed. They are guaranteed by the quality assurance

system of the laboratory that provides appropriate stated references.

8. REFERENCES

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