THE CSM APPROACH TO THE CALCULATION OF THE UNCERTAINTY IN XRF ANALYSIS OF LOW- AND HIGH-ALLOYED STEELS

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The CSM laboratories are, for some tests, accredited by SINAL (the Italian Laboratories Accreditation System) and must meet the specification of ISO/IEC 17025.
This standard states that "*Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement*".

The calculation of the uncertainty of XRF analysis of low and high-alloyed steel was made according to the "bottom-up" or "component-by-component" method suggested in the ISO 25 "Guide to the Expression of Uncertainty in Measurements" and in the Eurachem Guide "Quantifying Uncertainty in Analytical Methods".

<u>Repeatability</u>, <u>calibration standards</u> and <u>calibration curves</u> were individuated as the most important contributions to the total uncertainty.

In this work only Cr, Ni, Mo and Mn were considered.

The repeatability was calculated performing 10 measurements in different days with different operators on two reference samples:

sample **QC1**	**Cr** %	**Ni** %	**Mn** %	**Mo** %
average	17,4	8,4	1,8	0,30
std dev	0,14	0,13	0,04	0,002
QC8				
average	0,162	0,123	0,707	0,070
std dev	0,002	0,002	0,005	0,001

Being an unknown sample analysed usually only once, it was decided not to consider the standard deviation of the mean ($s/\sqrt{n}$), but only s.

The contribution, as standard uncertainty, of the uncertainty of the certified reference materials used for the calibration was calculated as follows:

If the limits ± *a* were given without any confidence level, it was assumed a rectangolar distribution with a standard deviation of *a/Ö3*.
If the limit ± *a* were given with a 95% confidence level, the standard deviation considered was *a/1.96.*

Being the calibration curve obtained with more than 15 points, and so with more than 15 reference materials, each of them with its uncertainty, it was decided to consider, for a given concentration of one element, the uncertainty of the reference material with the concentration closest to the value of interest.

The contribution of the calibration curve was calculated considering that in XRF the intensity (*I*) of the signal of a defined wavelenght is correlated to the element concentration (*C*)in the sample:

$$I = a + b * C$$

then

$$C = \left(\frac{I - a}{b} \right)$$

The standard errors of a and b were obtained from the linear least square regression, while the standard error of the intensity was derived from instrument resolution information.

All the standard uncertainties were combined and, to obtain the expanded uncertainty, the number of degrees of freedom was calculated by means of the Welch-Satterthwaite equation:

$$\nu_{eff} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}}$$

Then, the coverage factor was chosen using the Student's t-distribution

Being the degrees of freedom generally higher than 20, the coverage factors ranged from 2.0 to 2.1

Results

In the following table are shown the uncertainty and the uncertainty budget for the given elements and concentrations

element	conc %	uncertainty %	% of contribution *cal. Curve*	 *CRM*	 *repeatability*
low-alloyed steel					
Cr	0,16	0,03	48,9	44,1	7,1
Ni	0,12	0,02	73,7	5,3	21,0
Mn	0,71	0,05	20,1	63,9	16,0
Mo	0,070	0,007	37,2	38,3	24,5
high-alloyed steel					
Cr	17,4	0,4	62,5	4,6	32,8
Ni	8,4	0,3	28,0	9,3	62,7
Mn	1,8	0,1	21,4	26,6	52,0
Mo	0,30	0,08	74,3	25,4	0,3

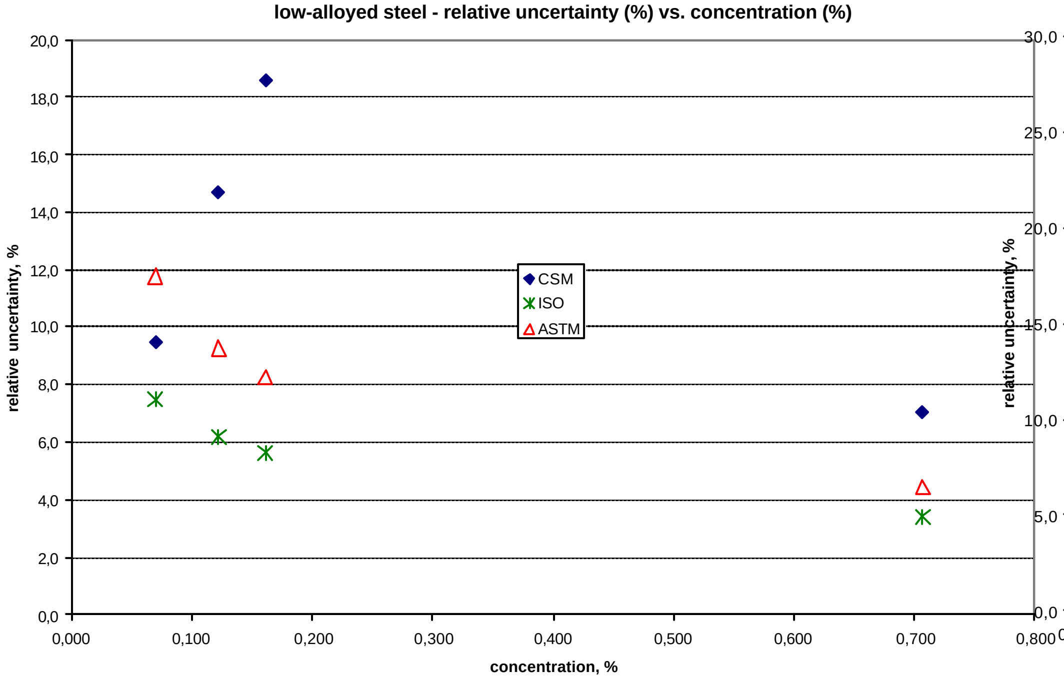
ASTM E2165-01 gives two experimental *Horwitz-like* equations obtained from ISO TC 17 SC 1 and from ASTM Proficiency Test Programs for plain carbon low alloyed and stainless steel.

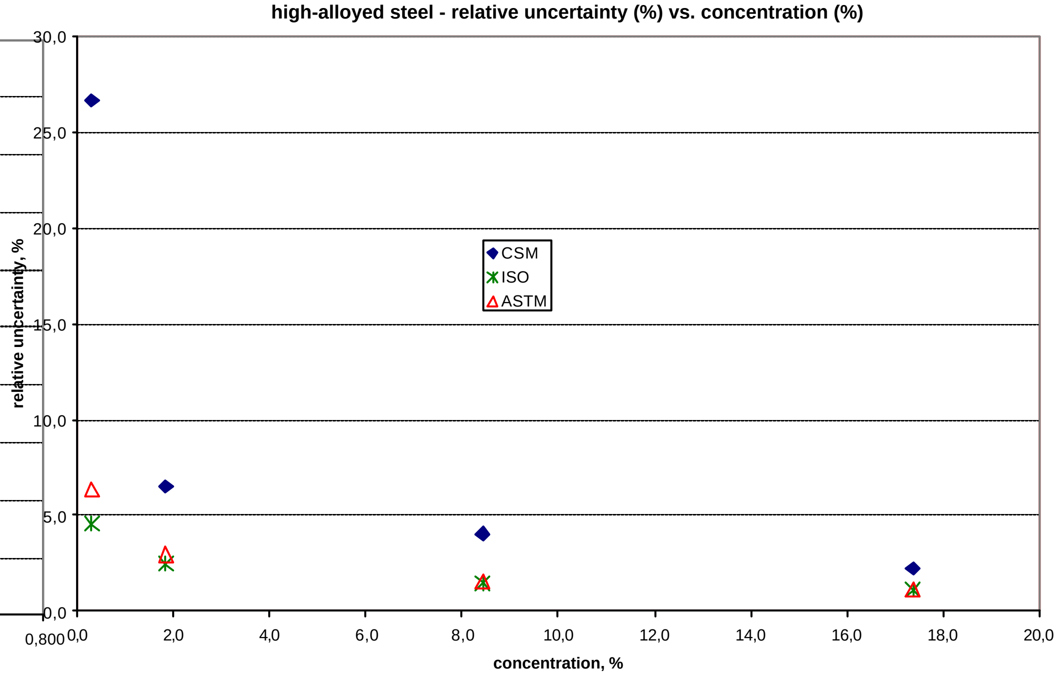
$$2s_{95\%} = 0.0303\, C^{0.6661} \quad \text{ISO}$$

$$2s_{95\%} = 0.0384\, C^{0.58} \quad \text{ASTM}$$

Where s is the interlaboratory standard deviation and C is the analyte concentration in m/m %

In the graphs are plotted the CSM uncertainty values together with those derived from the *Horwitz-like* equations





Conclusions

It can be said that:

The uncertainty values obtained at CSM using the bottom-up model are systematicaly greater than the 2s values derived from the experimental equations of ISO and ASTM proficiency tests.
In the high alloyed steels the trend of the 3 curves is similar (the higher the concentration, the lower the uncertainty), but in the low alloyed steels the CSM points are very scattered.

This could be explained looking at the uncertainty budget.
It is evident that at low concentrations the contributions to the uncertainty of the CRM and of the calibration curve are generally heavier than those at high concentrations.
The uncertainty in these cases depends strongly on the uncertainty of the CRMs used in the calibration.