Analysis of inorganic impurities in steel using the 7700x system

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Introduction

The analysis of inorganic impurities in steels is required in the process of their characterization. Issues related to such analysis are linked to the high presence of matrix following the sample preparation: up to 10g/L of total dissolved solid (TDS), mainly composed by iron.

Therefore, the conventional approach requires:
-The dilution of sample (down to 1g/L of TDS)
-Matrix-matching standards for the instrument calibration.

This methodology is time consuming due to the samples and standards preparation and performances are linked to the purity of the iron used for matching the matrix.

To overcome those issues, in the present work, we investigated the direct analysis of undiluted samples and the determination of their concentrations using standards only prepared in acid (without matrix reconstruction). This approach is possible thanks to the High Matrix Introduction (HMI) system available on the 7700x.

Results were compared with the conventional approach for the validation of the results and to underline the benefits of this new procedure.

Sample and standard preparation

4 certified reference materials (CRM) and 6 unknown samples were analyzed during the experiment.

500 mg of steel samples were digested in presence of HCL, HNO_3 and HF using a microwave device. Digested samples were completed till 50 mL with water.

➥ **Final sample contains up to 10 g/L of iron**

-Standards for calibration are simply prepared into acids

➥ **No matrix matching for standards**

Experimental

The Agilent 7700x system was used for the analysis. An inert kit, made from PFA, was employed to allow the introduction of HF into the system (presence of HF link to the sample preparation).

The CRMs were not certified on every elements of interest. So the first experiment consisted at the analysis of samples under the conventional approach for the determination of "reference" values. Therefore, samples were diluted ten times after their preparation and standards were prepared with the use of a high purity iron (NBS 365) dissolved at 1 g/L for matching the sample matrix.

In the second experiment, for the direct sample analysis, the configuration of the 7700x was modified before the analysis with the activation of the HMI system. Thanks to the MassHunter software, controlling the instrument, one click is sufficient for switching till the HMI configuration.

The table 1 summarizes parameters used for the analysis under the HMI conditions.

Plasma power	1600 W
Carrier gas	0.30 l min^{-1}
Dilution gas	0.75 l min^{-1}
Sample depth	10 mm

Table 1 7700x parameters with the HMI configuration

High Matrix Introduction (HMI) System

The 7700x includes the unique HMI system which dilutes the aerosol stream from the spray chamber, thereby reducing the aerosol and matrix loading on the plasma. The result is a significant increase in the effective plasma temperature, which effectively eliminates matrix suppression, and also allows samples containing % levels of TDS to be analyzed routinely, without the need for time consuming dilutions of over-range samples. Therefore samples at 10 g/L were directly injected into the system without prior dilution. The principle of the HMI system is detailed in the figure 1.
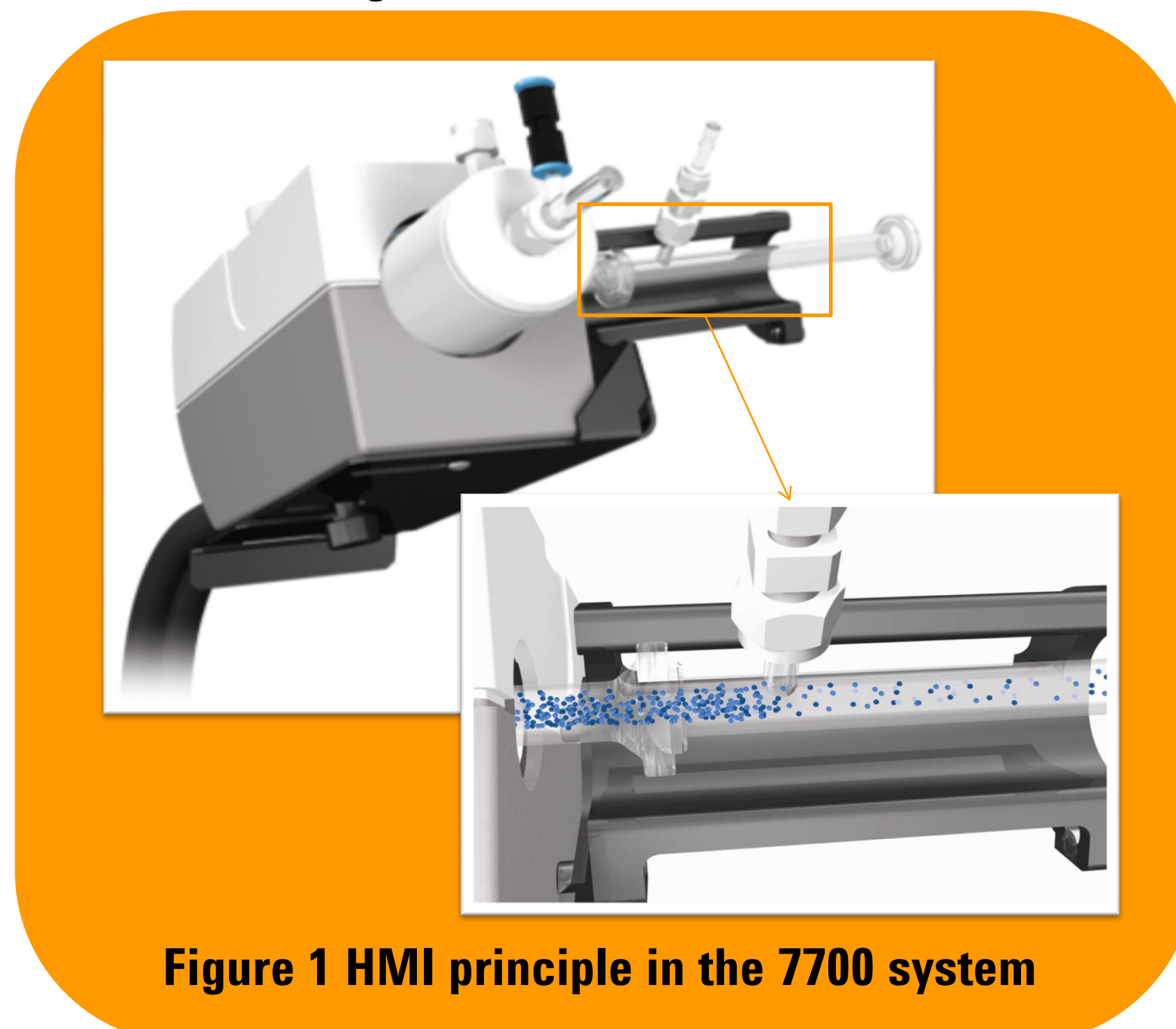

Figure 1 HMI principle in the 7700 system

Results and Discussion

The comparison of the Method Detection Limits (MDL) is a first evaluation of the new procedure proposed. The table 2 summarized the MDLs obtained with the two procedures. Data are taking into account the dilution factor link to each sample preparation.

Mass	Name	conventional	HMI
11	B	0.0983	0.072
31	P	10.55	2.695
34	S	593.37	75.907
75	As	0.2315	0.015
111	Cd	0.0382	0.004
115	In	0.0037	0.002
118	Sn	0.1126	0.027
121	Sb	0.0459	0.004
201	Hg	0.0307	0.038
205	Tl	0.0035	0.007
208	Pb	0.0309	0.002
209	Bi	0.0014	2.02E-05

Table 2 Comparison of Method Detection Limits in the steel samples (unit: mg/kg)

Thanks to the use of the HMI system, MDLs are 10 times improved for almost all the elements in comparison with the conventional methodology. Those improvements are mainly coming from the standards only prepared in acids. As there is no more reconstruction of the matrix, no impurities are introduced during the calibration of the instrument.

To evaluate the matrix effect during the analysis of undiluted samples (experiment 2), the recovery of internal standards (scandium, rhodium and iridium) during the full sequence was measured. The figure 2 shows its evolution during the analysis of the sequence.
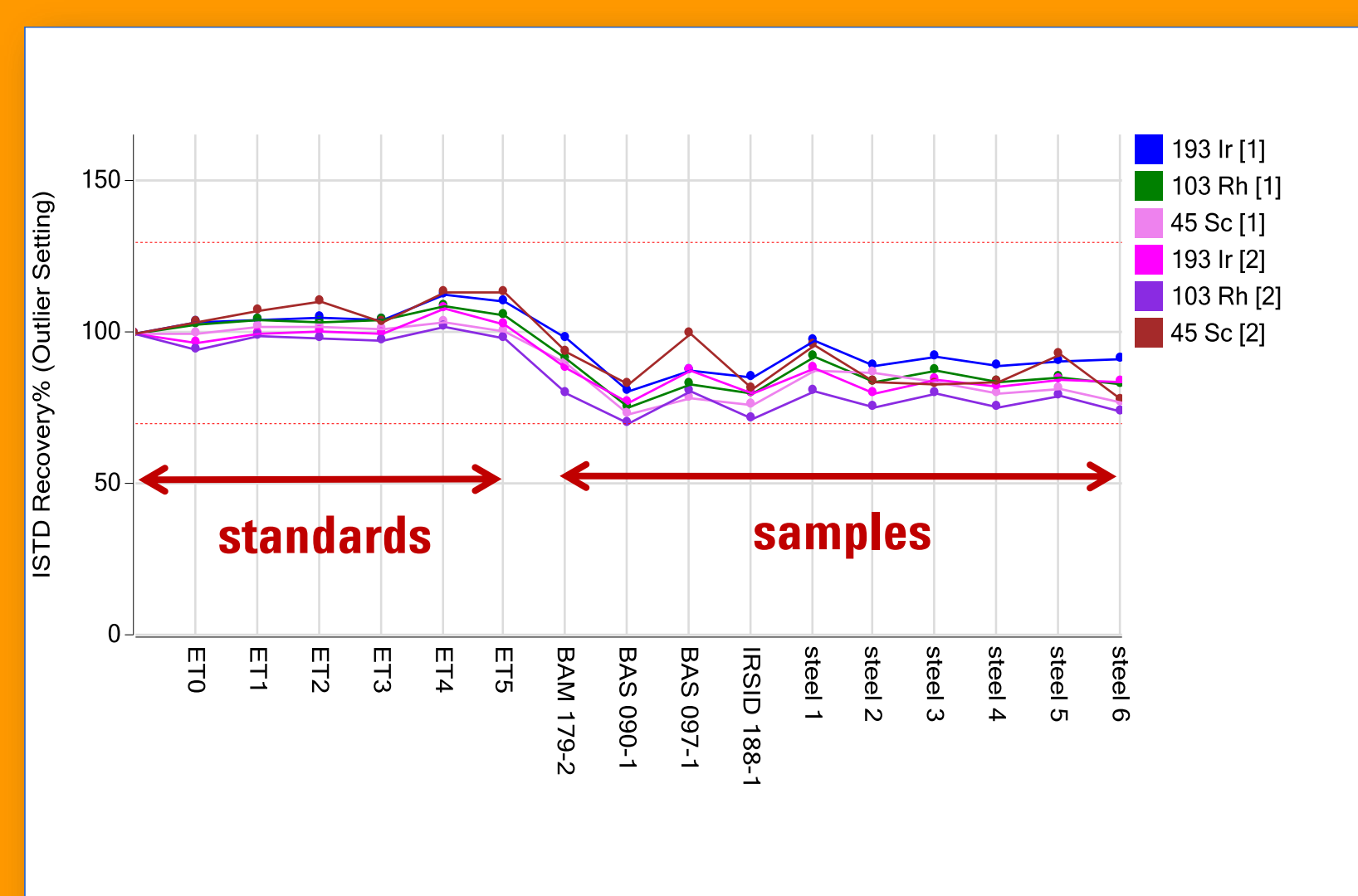

Figure 2 Internal standard evolution during the analysis of undiluted samples

As can be seen from fig.2, the recovery of the internal standards for the samples (containing 10 g/L of the matrix) are superior to 70% (the reference is the first point of calibration only prepared in 2% of HNO_3). In consequence, **the matrix effect is relatively low** and will be corrected by the internal standards. It's also interesting to see that along the sequence the recovery is stable: **no matrix deposits nor drift are observed during the analysis of samples containing 10 g/L of iron**.

The CRMs were only certified on few values. The table below shows the comparison between certified values and the one measured using the HMI system.

	BAM 179-2		BAS 097-1		BAS 090-1		IRSID 188-1	
	certified	measure	certified	measure	certified	measure	certified	measure
11 B	-	-	3 +/- 2	2.36	-	-	-	-
31 P	267 +/- 48	244.71	-	-	130 +/- 20	114.25	-	-
34 S	(6)	< LQ	-	-	95 +/- 14	103.82	113 +/- 12	98.09
75 As	-	-	51	44.11	-	-	-	-
111 Cd	< 0.3	0.13	-	-	-	-	-	-
118 Sn	-	-	< 25	7.33	-	-	-	-
121 Sb	17.5 +/- 1	17.06	< 10	9.66	-	-	-	-
205 Tl	< 0.35	0.008	-	-	-	-	-	-
208 Pb	1.3 +/- 0.2	1.19	< 5	0.39	24 +/- 1.2	22.11	-	-
209 Bi	< 0.3	0.05	-	-	-	-	-	-

Table 3 Comparison between certified and measured data using the HMI (unit: mg/kg)

The analysis of the CRMs underlines the method performances as excellent agreement can be observed between certified and measured values. Therefore those results confirm the **possibility of measuring the samples containing up to 10 g/L of matrix when calibrating the instrument only with standards prepared in acids**.

To improve the validity of the new HMI method, the results obtained for unknown samples were compared with the conventional procedure (results shown in the table 4).

		steel 1	steel 2	steel 3	steel 4	steel 5	steel 6
11 B	Conv.	< LQ	< LQ	33.24	12.83	5.89	7.61
	HMI	< LQ	29.82	11.80	5.65	7.49	
31 P	Conv.	52.32	193.83	120.67	88.57	53.02	59.70
	HMI	91.15	209.22	158.73	106.45	93.75	79.12
34 S	Conv.	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
	HMI	131.75	117.15	115.12	27.11	129.18	101.83
75 As	Conv.	143.76	132.85	132.46	130.05	51.25	49.01
	HMI	138.95	131.38	140.76	134.19	51.09	53.58
111 Cd	Conv.	0.24	0.08	0.08	0.14	0.04	0.04
	HMI	0.11	0.06	0.06	0.09	0.06	0.04
115 In	Conv.	0.035	< LQ	< LQ	0.003	< LQ	< LQ
	HMI	0.052	0.007	0.010	0.008	0.003	
118 Sn	Conv.	85.01	145.71	169.58	119.95	54.10	47.49
	HMI	82.03	136.90	161.51	115.37	55.27	48.85
121 Sb	Conv.	23.22	25.14	31.86	23.65	16.83	17.51
	HMI	23.29	24.75	31.91	23.87	17.23	17.84
201 Hg	Conv.	0.06	0.10	0.05	0.04	< LQ	< LQ
	HMI	0.12	0.14	0.12	0.09	0.10	0.09
205 Tl	Conv.	0.015	0.006	0.004	0.002	0.001	0.001
	HMI	0.005	0.005	0.003	0.003	0.002	0.001
208 Pb	Conv.	4.63	1.86	6.13	1.31	0.36	0.86
	HMI	4.54	1.91	5.76	1.37	0.42	0.88
209 Bi	Conv.	0.009	0.008	0.020	0.030	0.020	0.017
	HMI	0.006	0.009	0.020	0.029	0.017	0.022

Table 4 Comparison of measurements between conventional and HMI procedures (unit: mg/kg)

Excellent agreements between the two procedures are obtained for most of the elements. It can also be notify the interest of the HMI procedure on difficult elements such as sulfur (only measured with HMI).

Conclusion

The new procedure developed here allows the simple and reliable analysis of samples containing high TDS (up to 10 g/L). The methodology is time efficient as the best results were obtained with the direct analysis of steel samples and with standards only prepared in acids (no need for matrix matching approach). Therefore **the use of the HMI opens new possibilities for the direct analysis of high concentrated matrices with a 7700x ICP-MS**.