Application Note

Determination of Boron in Steel by On-line Matrix Simplification

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1 Introduction

Iron has a spectrum of more than 5,000 recorded lines. For this reason, when you determine trace elements in steel, you may encounter spectral interferences. To reduce the number of interferences, a very high-resolution spectrometer is needed. Even so, some elements such as As, B, Bi Pb, Sb, etc. are difficult to determine in steel samples. With such a matrix, three solutions are possible: 1) direct analysis using a line which has no interference, but which may be less sensitive, 2) using inter-element correction or 3) determination after eliminating the matrix. Here we will discuss the third approach using the example of boron in steel.

2 Principle

2.1 Technique used

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the "profile" function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

In the Figure 1, you will find the example of B (0.1 mg/L) at 249.773 nm in presence of Fe (1 g/L).

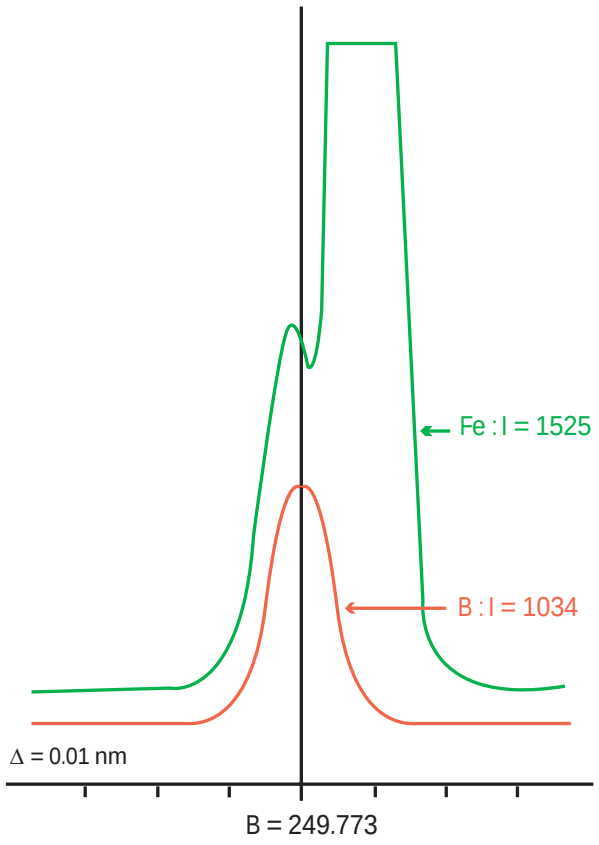

Figure 1: B in presence of Fe

3 Instrument specification

The work was done on a ULTIMA. The specifications of this instrument are listed in Tables 1 and 2.

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Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1 m
Thermoregulation	Yes
Nitrogen purge	Yes
Grating number of grooves	2400 gr/mm
1st order resolution	0.010 nm
2nd order resolution	0.005 nm
Order	2nd order

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

4 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1000 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer gas flowrate	1.2 L/min
Nebulizer flowrate	3 bars (45 psi)
Sample uptake	1 mL/min
Type of nebulizer	Concentric
Type of spray chamber	Cyclonic
Argon humidifier	Yes
Injector tube diameter	3.0 mm

The resin chosen is the following:
OnGuard - H from DIONEX (Ref: P/N 039596).
This is the anion-exchange column for strong cations on polystyrene, with a maximum flowrate of 2 mL/min.

The column is placed between the solution and the peristaltic pump, as shown in Figure 2 below.

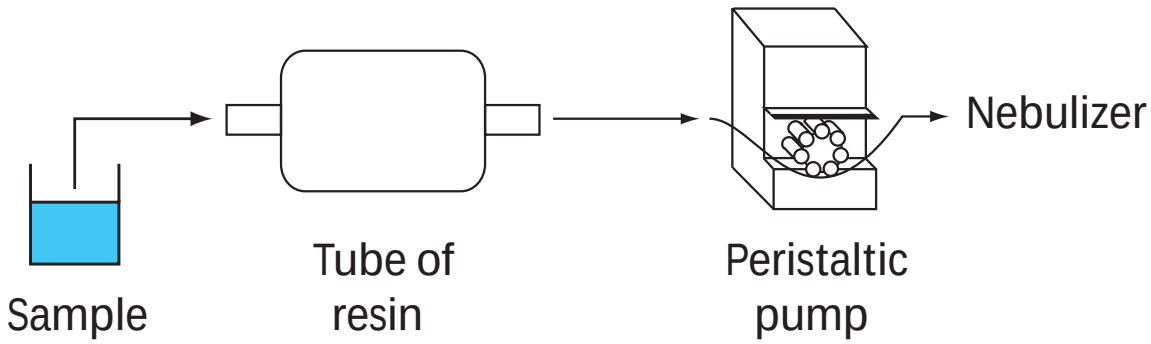


Figure 2: System installation

5 Optimization

All the optimization was made with normal standards.

5.1 Elements retained

Observing the following curve, one can see that some elements are retained, e.g., Si, Mo, while some are not e.g. Ni, Cr and some are retained for a time such as Fe. The elements retained are those forming cations. Si was used for tracing the rinse. If Si appears and is stable it means that the system is well rinsed. Because we want to eliminate the matrix, mainly Fe, the minimum rinse time will be determined for the retention of Fe. More than 90 % of the matrix is retained.

Table 4 summarizes the retention of the elements.

Table 4: Element retention

Elements retained	Elements not retained
Major	Major
Fe, Co, Cr, Cu,	Al, Mo, Nb, Si,
Mn, Ni, V	Sn, Ti, W
Traces	Traces
Be, Bi, Pb, Zn,	Ag, As, B, P,
Zr	Sb, Se, Ta

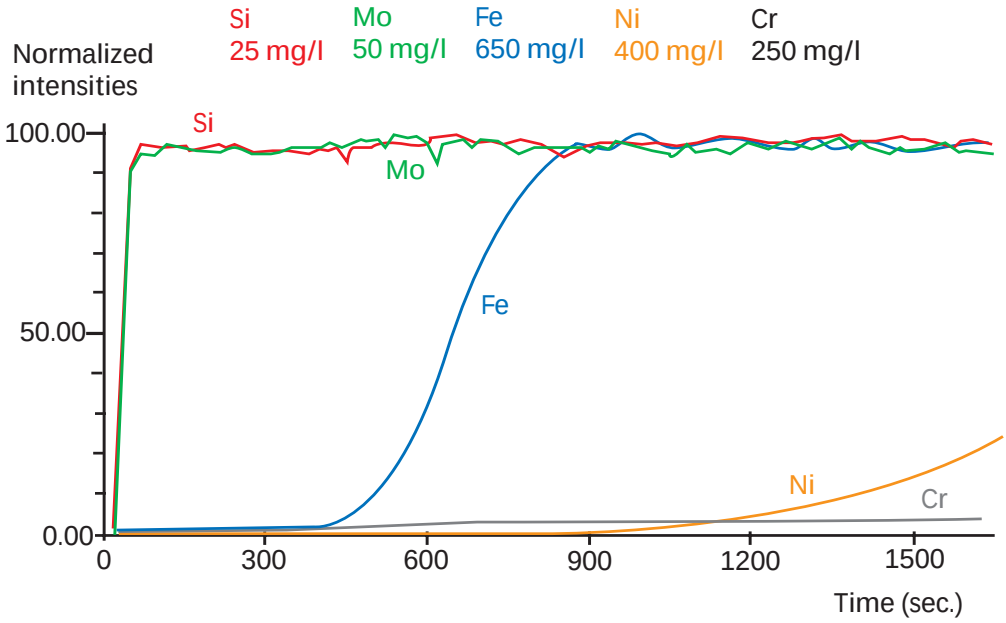


Figure 3: Retention of various elements

5.2 Influence of the pump flowrate

To determine the pump flowrate, i.e. the sample uptake, we must make a compromise between the sensitivity and the used time of the column. With the help of the two following curves (see Figures 4 and 5), a flowrate of 1.6 ml/min was determined to be optimum.

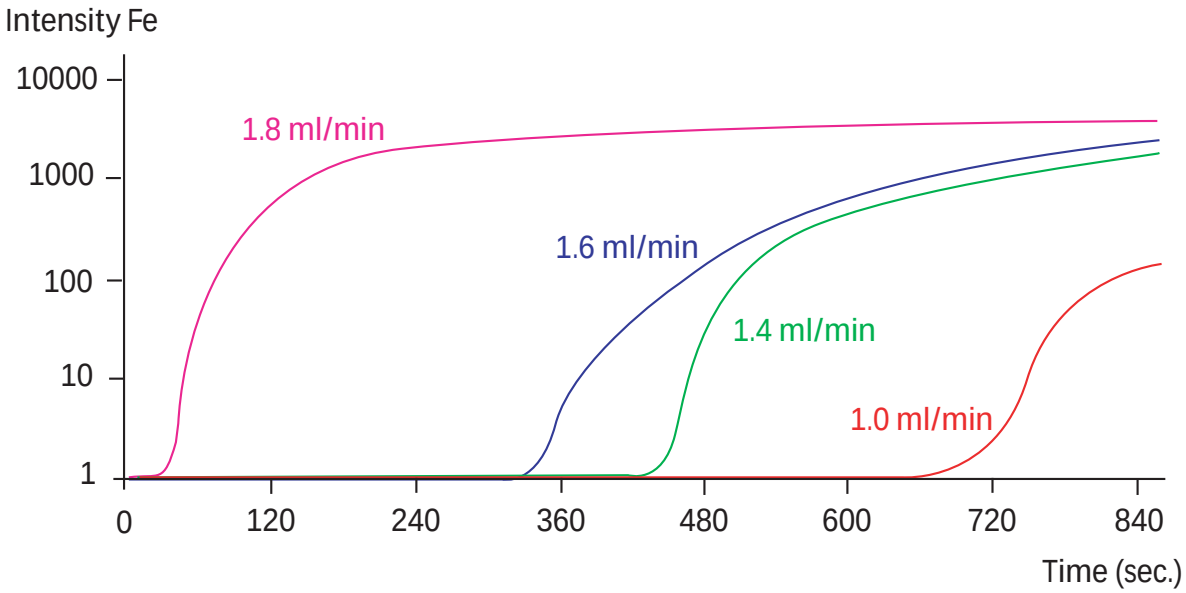


Figure 4: Influence of pump flowrate

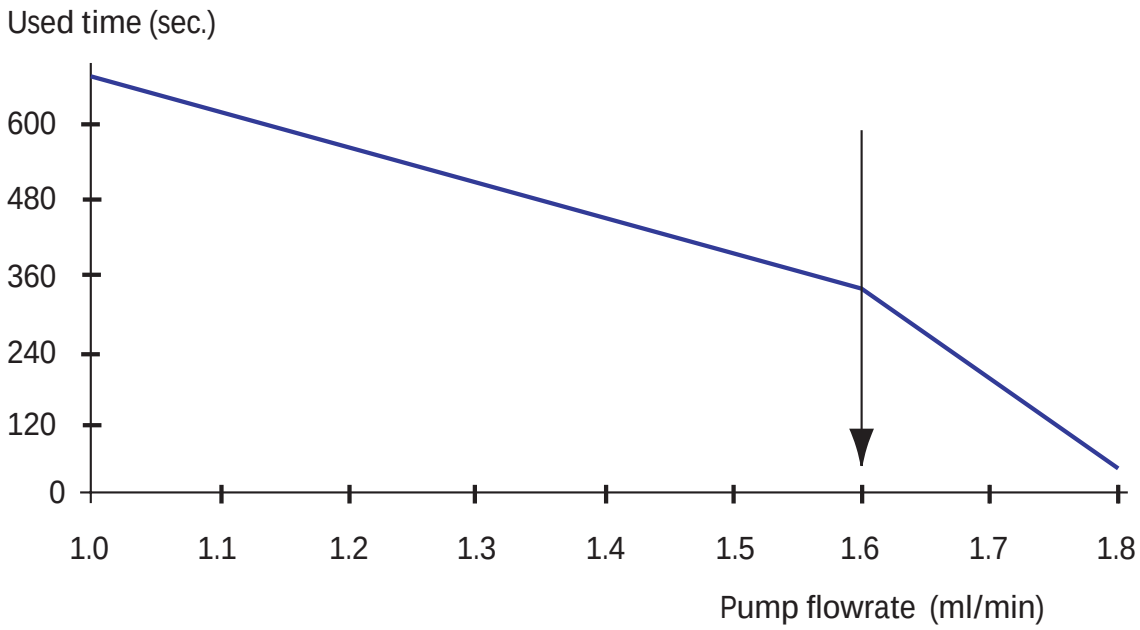


Figure 5: Influence of pump rate

The minimum time for rinsing with a flow rate of 1.6 ml/min was determined by the time where the signal of Si is stable. On inspection of the curve, we see that 60 seconds is a good value.

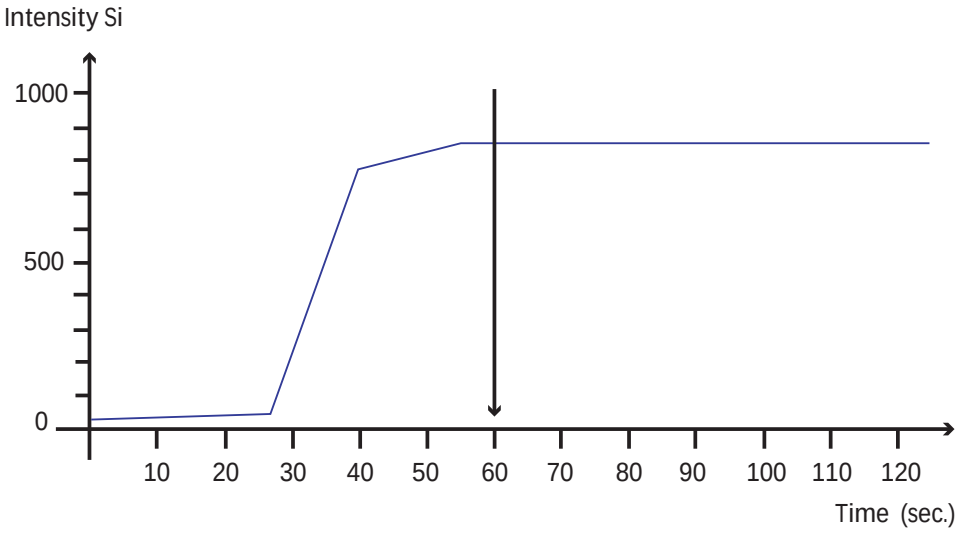


Figure 6: Rinsing time

5.3 Influence of the acidity of the sample

The previous curves were obtained with iron nitrate in a neutral solution. Next, we studied the effect of the acid molarity.

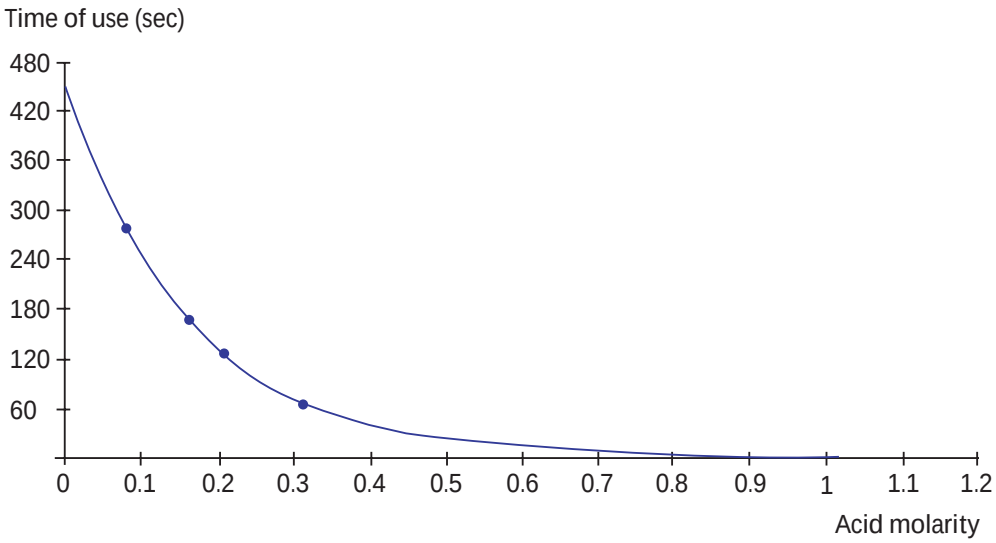


Figure 7: Effect of acid molarity

5.4 Analytical conditions

The profile of B in Figure 8 shows that major elements like Mo and W did not interfere with the analysis if we choose the correct slits (20/10 µm).

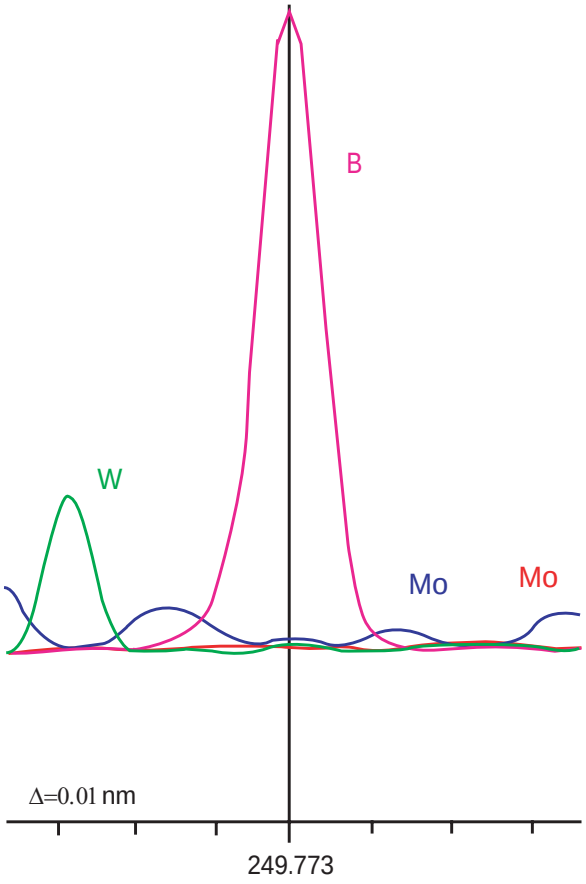


Figure 8: Profiles of B, Mo and W

Table 5: Analysis conditions

Element	Wavelength (nm)	Slits (µm)	Analysis mode	Integration time (sec)
B	249.773	20/10	Direct Peaking	20

Pump flowrate: 1.6 mL/min.
Rinse time: 60 seconds.

6 Results

The limit of detection obtained for B is 0.3 µg/L at 3 s. The interference effect of a 1 mg/L iron solution is 0.18 µg/L B. Fe becomes a problem at 1 mg/l.To determine B we also determine Fe to be sure that the remaining concentration is below 1 mg/L.

Conversion µg/L to µg/g:

The time necessary for analysis requires low molarity (Volume of acid minimum/Volume of flask maximum). The relation of µg/L to µg/g implies maximizing the weight of the sample a flask volume as small as possible. Therefore, the sample preparation is as follows, using a closed-vessel microwave system.

- 0.5 g of sample
- 2.5 mL HCl
- 1 mL HNO3
- 1.5 mL HF
- diluted with water in a 500 mL flask.

The limit of detection of Boron 0.3 µg/L becomes 0.3 µg/g.

Time of analysis:

Rinse time: 60 sec
Boron 3 replicates of 20 sec
Fe 3 replicates of 5 sec

Total time of analysis is about 160 sec.
The profiles shown in Figure 9 are of real samples:
- High standard with 0.1 mg/L of B
- Fe blank with no B
- BAM 295-1 without column
- BAM 295-1 with column

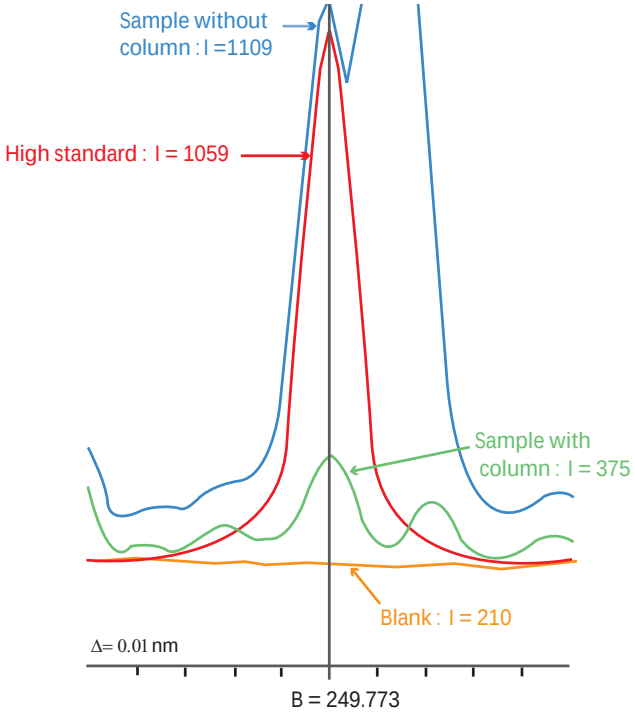
In sample BAM 295-1, the concentration of Fe is 480 mg/L (48 %), the concentration of Mo is 40 mg/L (4 %) and the concentration of B is 18 µg/L (18 µg/g).We see that the iron is not a problem.

We determined B in four quite different certified steel materials: BAM 285-1, BAS 295-1, BCS 456-1, BCS 457-1.

In the Table 5, the concentrations of the major elements are given by the certificate. The actual determination of boron is shown compared to the certified value.

Table 5: Analytical results

Major Elements (% in mass)	BAM 258-1	BAS 295-1	BCS 456-1	BCS 457-1
Fe	~ 66	48.36	~ 99	~99
Co	9.22	0.045	0.052	0.023
Cr	0.034	19.51		
Cu		1.481		
Mn	0.013	1.758	0.20	0.30
Ni	18.46	24.40		
V	0.046	0.022	0.166	
Mo	5.07	3.996		
Nb		0.006	0.022	
Si	0.418	0.24	0.051	
Ti	0.74			
W				
B (µg/g) certified	6	18	15	25
Standard deviation	1.5	1	2	2
B (µg/g) measured	5.8	18.8	15.0	25.8
Reproducibility (5 preparations and meas.)	Mean	18.8		
	Standard deviation	0.1		



Figures 9: B profiles

The column is only used for one sample, after that it has to be regenerated. Until recently, the column had to be regenerated off line by soaking it in acid for several hours. To exchange the column takes only a few seconds without stopping the plasma.

7 Conclusion

There are two possibilities to determine B in steel:

1. Direct analysis using the 182.529 nm line with a limit of detection of 3 µg/g. A background correction is needed because of iron. An inter-element correction is necessary when Mn is present (3 µg/g for 1 % Mn).

2. Analysis with "On-line" matrix elimination at 249.773 nm. The limit of detection is 0.3 µg/g.

Much work on the subject remains. The following lists some of the questions which should be investigated:

- Could we work in a neutral medium, like aluminia hydroxide?
- Is there a way to quickly regenerate the column "On-line", between two analyses?
- Alternatively, during one analysis, could a switching valve with several columns be used to regenerate the column?
- Is it possible to use this technique for other trace elements, and if possible without HF acid?
- Could we use this technique to suppress elements, which inhibit the hydride formation like Ni, Cu, Co?

It may be possible to use for decreasing the salt content, which would make the ultrasonic nebulizer easier use.

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