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BORON DETERMINATION IN STEELS BY INDUCTIVELY-COUPLED PLASMA SPECTOMETRY (ICP)

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16. Abstract

The sample is treated with $5N-H_2SO_4$ followed by conc. HNO_3 and the diluted mixture is filtered. Soluble B is determined in the filtrate by ICP spectrometry after addition HCl and extraction of Fe with ethyl ether. The residue is fused with Na_2CO_3 and, after treatment with HCl, the insoluble B is determined by ICP spectrometry as before. The method permits determination of ppm amounts of B in steel.

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Boron Determination in Steels by Inductively-Coupled Plasma Spectometry (ICP)[*]

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Abstract   A method is proposed for boron determination in steels at ppm levels by inductively-coupled plasma spectometry. Solutions equivalent to 5 g sample in 100 m were used, a previous separation of iron being performed, in HCL, with ethylic ether. The analytical line used for boron analysis was 2496.78 Å and the results were verified with standard samples from the British Chemical Standards.

1. INTRODUCTION

Boron steel alloys, known for several decades, have been reintroduced in the past few years, thanks to technological advances favoring their correct preparation, as well as various studies concerning their properties (1).

Boron steels have been specified by the various standardizing agencies: ISO, UNE, AISI, AFNOR, DIN, etc., and there are hundreds of varieties. The majority of boron steels are alloyed with manganese ($\approx$ 1%) and with chrome (<0.5%) and, in some cases, with nickel and molybdenum. Carbon content varies between 0.15 and 0.45%. Aluminum and titanium are routinely used respectively as deoxidizing and denitriding agents, with a

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consequent residual content of these elements in the order of 0.030%.

The considerable interest in these steels is based on the fact that small amounts of boron (in the order of ppm) improve tempering to a much higher degree than other alloy elements.

There are various theories to explain the effects of boron in improving the hardening of steels. This effect diminishes as the carbon content of the steel is increased, and is practically eliminated in eutectoid alloys.

Because of its high affinity for nitrogen and oxygen, and its readiness to substitute for the carbon in carbides, it is accepted that a large proportion of the total boron present in steel is made up of oxides, nitrides and/or borocarbides. By selective chemical attack, it is possible to distinguish the two types of boron present in steels: soluble and insoluble boron.

Although the complete separation of the various boron combinations is difficult, it is generally accepted that:

- the soluble boron component includes the boron of the solid solution, the borocarbides, $M_{2.3}(B,C)_6$ and $M_3(B,C)$, and the boron oxides. This boron component is placed in solution by acid attack.

- the insoluble boron component is made up of the boron nitrides, BN. This component is placed in solution by means of alcaline fusion of the acid-insoluble residue.

It is fully established that there is a direct relationship between the improved temperability produced by boron and the amount of the element present in the form of soluble boron. This

relationship goes through a maximum, in that there is an optimum soluble boron content at which temperability is highest, compared to an identical material without boron (2 and 2)(Fig. 1).

As can be observed in Figure 1, all the authors find an optimum soluble boron content, located between 5 and 30 ppm. The differencess among these values can be attributed both to variations in analytical methods and to different levels of oxidized boron, taken to be soluble boron, although it exerts no influence whatever on temperability.

There are certain clearly established facts with respect to insoluble boron:

- the content of insoluble boron increases as the content of nitrogen (BN) increases.
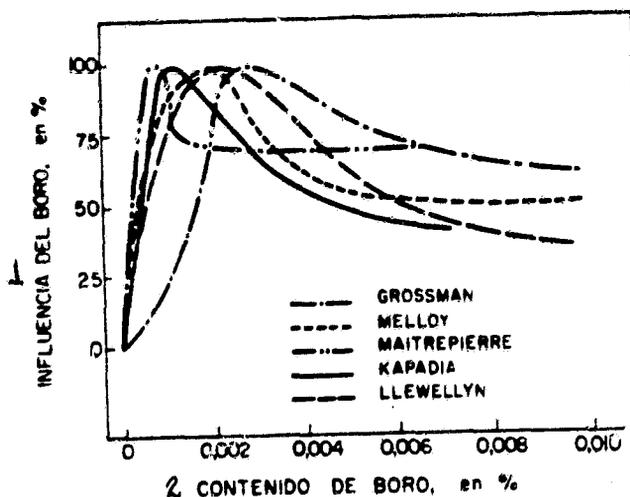
Fig. 1. Influence ol boron on temperability according to various authors. The maximum effect is set equal to 100%.
1- Influence of boron given as a %; 2- Boron content, %.

- the effect upon temperability will decrease to the point of disappearance if the insoluble boron component is increased at the cost of a diminished component of soluble boron.

- the presence of a certain amount of insoluble boron (from 10 to 15 ppm, for example, seems to improve the tensile strength of steel (3).

From the foregoing considerations it can be deduced that the content of soluble and insoluble boron can be used to improve both temperability and tensile strength.

It is clear that the soluble boron/insoluble boron ratio is a function of the content of free nitrogen in the metal, and therefore, of the content of elements, such as titanium and aluminum, which can form nitrides.

It is of utmost importance to achieve a homogeneous distribution of the boron, as gaps can create local irregularities, such as sizeable oxide or eutectic formations (Fe-C-B).

The difficulties encountered by the first manufacturers of boron steel are now history; modern production methods make it possible to ensure an even distribution. This leaves us free to focus on the problem of providing analytic methods which will, in turn, guarantee the actual content of this element.

The most widespread methods for this type of analysis are included within two categories: spectrophotocolorimetry and emission spectroscopy (arc or spark). The former methods (4-14) present major difficulties because of the extremely critical working conditions under which they must be carried out, and the latter, in addition to being subject to the availability of suitable master samples, do not offer sufficient precision for the boron content levels we are concerned with.

In this paper, the problem is studied using the Inductively-Coupled Plasma emission source technique (ICP-AES)(15-20). An operating procedure is established to permit precise, exact determination of ppm levels of boron (soluble and insoluble) in steels.

2. EXPERIMENTAL METHOD

2.1. Selection of analytical lines

2.1.1. Sensitivity

The study was made using conventional ultraviolet boron analitical lines.

$$\lambda, \text{\AA}$$

2497.73
2496.76
2089.59
2088.93

Since the equipment utilized has no vacuum system (it merely permits purging of the monochromator with inert gas), the remote ultraviolet boron lines (λ = 1826.4 Å and 1825.9 Å) are not sufficiently sensitive for the boron levels we are concerned with. On the other hand, it is of interest to note that these lines are clearly interfered with by the 1826.3 Å line of sulphur.

Table I shows the peak/baseline ratio of the lines considered (calculated with emission values corresponding to 0.1 ppm of boron and to water), the equivalent baseline concentration (concentration of the element which gives an emission intensity over the baseline of the same order as the baseline itself) and the minimum determinable ppm. The Relative Standard Deviations(RSD) calculated on 20 determinations of these minimum ppm are below 1%.

The working parameters of the equipment employed (JY 38 P),
were selected with the purpose of obtaining, for each line,
baseline values (considering as baseline the emission
corresponding to water) of less than 1,000 mV.

λ Å	Relación pico/fondo $\perp$ 0,1 ppm B/H_2O	C.E.F (ppm)	ppm mínima determinable 2 (DSR 1%)
2497,73	2,5	0,060	0,05
2496,78	2,3	0,080	0,05
2089,59	1,8	0,12	0,10
2088,93	1,6	0,15	0,10

Table 1.   Sensitivity study of selected boron lines:
peak/baseline ratio, equivalent baseline concentration (C.E.F) and
minimum determinable ppm.
1- Peak/baseline ratio, 0.1 ppm B/H_2O;   2- Minimum determinable
ppm (RSD 1%).

2.1.2.   Interferences

Next, a study of spectral interferences was made, in order to
verify the analytic value of each of the lines considered in the
determination of boron in steels.   This study included not only
those interferences caused by the base element (iron), but also by
the other elements usually present in this type of material.

2.1.2.1   Interferences originating from the base material (iron)

Because of the high proportion of sample in solution
necessary for the precise recording of the boron contents of
interest to us, the direct sample solutions present a high saline /89
concentration which originates on the one hand, significant
nebulization and transportation interferences, and on the other, a
considerable increase of the spectral baselines, carrying with it
a diminution in the peak/baseline ratio, and consequently less

favorable values for the determinable minimum contents.

Because of these difficulties the process evolved included massive elimination of iron using ethyl ether. Following this process, described in Section 3, "Preparation of the Test Solution", it was verified that, for weighings of 2.5 g of sample, with a final measurement at 50 ml, the concentration of iron remaining unseparated was in all cases less than 50 ppm. Next, a study was made to verify the spectral interferences produced by this residual quantity of iron in the boron analytical lines. Lines 2088.93 Å and 2089.59 Å in their next measurement showed no significant emission from iron. Line 2496.78 Å, although very close to the iron line 2496.53 Å, was not interfered with appreciably by the residual iron, thus verifying that the emission corresponding to 0.1 ppm of boron is not affected by the presence of up to 100 ppm of iron. Finally, line 2497.73 Å proved to be affected by iron line 2497.82 Å, even at the residual levels of unseparated iron in the solution.

Table II shows the values corresponding to the emission of 0.1 ppm of boron in the presence of different quantities of iron, in lines 2496.78 Å and 2497.73 Å, since these are the lines located close to each of the iron lines.

Table II. Spectral interference produced by iron.

Å			⊥ Valores de emisión		
	H₂O	0,1 ppm B	0,1 ppm B +50 ppm Fe	0,1 ppm B +100 ppm Fe	0,1 ppm B +250 ppm Fe
2496,78	500	1180	1190	1182	1250
2497,73	800	2125	2250	2520	4800

⊥- Emission values

As can be observed in table II, boron line 2496.78 Å is not spectrally influenced by the iron remaining after the extraction process.

2.1.2.2 Interferences caused by any other elements present

The elements usually present in steels as alloy or residual materials, cause the spectral interferences shown in Table III.

Tungsten causes spectral interferences in the four lines considered, making necessary its elimination during the preparation of the test solution, by means of ammoniacal washing of the residue in acids.

Though lines 1825.9 Å and 1826.4 Å were not studied, the literature indicates a clear interference coming from the 1826.3 Å sulphur line. On the other hand, it has been observed that cobalt presents an emission in the testing of the boron 2496.78 Å line, an emission which does not cause appreciable interferences within the concentration levels tested.

Table III.   Lines of the elements interfering in the determination of boron

B λ, Å	$\perp$ Elementos interferentes λ, Å
2088,93	Ni — 2088,98 W — 2089,14
2089,52	Mo — 2089,52 W — 2089,14
2496,78	W — 2496,63
2497,73	W — 2497,50

1- Interfering elements.

Finally, and in consideration of the sensitivity and interference studies carried out, the boron 2496.73 Å line was selected for determination of this element in steels.

3. PREPARATION OF THE TEST SOLUTION

2.5 mg of sample is weighed and attacked in a teflon vessel with 30 ml of 5N sulphuric acid. When the reaction subsides, the solution is oxidized with 10 ml of concentrated nitric acid. The resulting solution is diluted with approximately 25 ml of [omitted] and is filtered while hot through medium porosity paper, washing it with with 1 to 9 diluted hot hydrochloric acid. Soluble boron is determined in the filtrate liquids, and insoluble boron, in the filtered residue.

3.1 Soluble boron

After attack of the sample with acid (Section 3) the resulting solution is concentrated to approximately 15 ml; 30 ml of concentrated hydrochloric acid is added and it is transferred to a decanting funnel or plastic flask, using as a washing liquid, 20 ml of 1 + 1 diluted hydrochloric acid (the chlor-hydric molarity of the resulting solution falls between 6 and 8M).

Then the iron is extracted with 60 ml of ethyl ether. With agitation for 1 minute the aqueous phase is separated, and another treatment of 60 ml of ethyl ether. The aqueous phase is concentrated to approximately 10 ml and diluted to 50 ml with water. This solution contains soluble boron and is equivalent to 5 g of sample per 100 ml.

3.2 Insoluble boron

After attack of the sample with acid (Section 3) the resulting solid residue is washed with ammonia, roasted in a platinum crucible and fused with 1g anhydrous Na_2CO_3. The fused mass is extracted with 15 ml water and 5 ml concentrated hydrochloric acid, and diluted to 50 ml with water. This solution contains insoluble boron and is equivalent to 5 g of sample per 100 ml.

4. CONTROL TEST

The analysis was paralleled by a control test using the same proportions of reagents and following the entire operating procedure for both soluble and insoluble boron.

5. TERMS OF REFERENCE

The terms of reference for both soluble and insoluble boron are prepared by adding ppm of boron from a master solution of this element to controls containing the same reagents in the same proportions as in the problem sample. Given the linearity of the technique employed and on the basis of the small contents sought to determine, these terms can be the control test and one which contains 0.5 ppm of boron in an identical medium.

6. RESULTS AND CONTRASTING SAMPLES

Using the test solutions prepared according to subsections 3.1. and 3.2. against the respective control tests (Section 4), and calibrating the results as indicated in Section 5, the soluble and insoluble boron content in the sample (as a function of the minimum determinable ppm indicated in Table I) can be determined

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with precision and accuracy down to 1 ppm.

The method developed has been contrasted with master samples from the firms BCS (Nos. 326 to 330 and 458 to 460) and NBS (Nos. 361 to 365), the total boron content of which varies between 5 and 100 ppm. The results are given in Table IV. These same samples have been analyzed for both soluble and insoluble boron by spectrophotocolorimetry, and the results are in agreement with those yielded by the method developed.

Table IV. Results

1 Muestras	2 ppm boro soluble ICP	3 ppm boro insoluble ICP	4 ppm boro total (certificado)
BCS 326	8,2	4,0	10
BCS 327	27,8	1,1	30
BCS 328	39,0	2,8	40
BCS 329	74,1	10,0	80
BCS 330	72,7	<0,5	70
BCS 458	38,8	8,7	45
BCS 459	91,6	8,2	100
BCS 460	11,9	15,0	25
			5 ppm boro total aproximado (no certificado)
NBS 361	6,1	1,0	5
NBS 362	30,0	<0,5	25
NBS 363	14,2	0,8	10
NBS 364	120,3	<0,5	140
NBS 365	0,5	<0,5	—

1- Samples; 2- ppm soluble boron ICP; 3- ppm insoluble boron ICP; 4- ppm total boron (certified); 5- approximate ppm total boron (uncertified).

7. CONCLUSIONS

- A plasma (ICP) methodology has been perfected for determination of boron in steels at levels in the order of ppm.

- The soluble boron and insoluble boron present in these materials have been separated by a wet method procedure.

- The iron matrix has been for the most part eliminated by extraction with ethyl ether in a hydrochloric medium $\approx$ 8M.

- The validity of the method has been verified by comparison of its results with those obtained by spectrophotocolorimetry in various standard samples.

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