# DETERMINATION OF BORON IN METAL CORROSION INHIBITORS

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Summary: A method has been developed to determine boron in inhibitors of ferrous and non-ferrous metals, i.e., complex compounds of boron with polyoxycompounds. The method allows one to determine boron by a simple alkalimetric titration by sodium hydroxide, using D-sorbitol in cases when the complex decomposition (dissociation) degree is not less than 95%.

In order to protect reservoirs, pipelines and other constructions from corrosion when these being employed both in closed and flow path cooling systems, corrosion inhibitors of ferrous and non-ferrous metals, mainly, inorganic compounds such as polyphosphates, chromates, nitrates, amines are used. The high toxicity of these compounds necessitates to pay attention to organic inhibitors, which are non-toxic and do not contaminate the environment by toxic wastes. Among such compounds are complex compounds of borate-ions and polyols, developed by the Institute of Inorganic Chemistry (RTU), which are effective corrosion inhibitors for ferrous and non-ferrous metals. Stability constants of these complexes have been determined. Anion complexes with the boron/polyol ratio 1:1 $[BPolyol]^-$, which are less stable, exhibit better inhibiting properties. With an excess of polyol, a much more stable anion $[B(Polyol)_2]^-$ is formed:

$[BPolyol]^- + Polyol \rightarrow [B(Polyol)_2]^-$,

$[B]^- + 2Polyol \rightarrow [B(Polyol)_2]^-$.
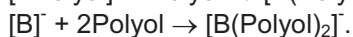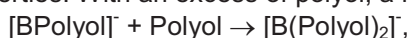
It is known that D-mannitol and D-sorbitol together with boric acid and borate-ions form complex acids, which determine the use of D-mannitol and D-sorbitol for alkalimetric determination of boron. This makes difficult to determine boron in polyborate complexes.

The most widely used method for boron determination in its complexes with polyoxycompounds is decomposition of hydrochloric and sulphuric acid complexes with the following extraction of boric acid by a 3-methylbutanediol-1,3 chloroform solution.

We tried to estimate a possibility of the boron determination in polyolborate complexes Na[BPolyol] by the classic alkalimetric method. For that, we determined the decomposition degree of the complexes in an aqueous solution versus the solution concentration from the formula:

$(Na[BPolyol] - [x]) / [x]^2 = K_{stab.}$,

where Na[BPolyol] is an initial concentration of a complex (C), [x] is the concentration of the formed borate-ion and polyol (at [B] = [Polyol]), $K_{stab.}$ – stability constant. The concentration of the formed at dissociation borate-ion complex was found by solving the equation:

$K_{stab.}[x]^2 + [x] - [BPolyol]^- = 0$.

The data in Table 1 evidence that, with the initial concentrations of corrosion inhibitors being for Na sorbitolborate 0.001-0.004 mol/l, for Na mannitolborate 0.001-0.002 mol/l, for Na dulcitolborate 0.0004 mol/l and smaller, for Na xylitolborate 0.0005-0.0023 mol/l and for Na glycerolborate 0.0005-0.0017 mol/l, the main part of the complex decomposes and the non-decomposed part does not exceed 5% that is comparable to the error at determination boron alkalimetrically. This makes possible to use D-sorbitol (excess) at the alkalimetric boron determination in the sorbitolborate complex Na[BSorb] and in mixtures containing borate-ion $[B[OH]_4]^-$ and polyol at molar ratio 1:1. In conclusion, we present a simplified determination method.

A complex additive of 0.01-0.1 (see Table 1), or a corresponding concentrate, containing 0.01-0.1 g of this complex, is placed in a 200-ml chemical glass, 100 ml of distilled water are added and the complex is dissolved by stirring by a magnetic mixer. Then, electrodes are placed into the solution, and pH7 of the solution is achieved by adding 0.05 N HCl or NaOH solution. 4 g of D-sorbitol are added to the obtained neutral solution; the solution is stirred until sorbitol completely dissolves and then titrated by 0.05N NaOH solution until pH7. Table 2 displays some analysis results.

So, the proposed method for boron determination in polyolborate complexes using D-sorbitol is applicable when the decomposition degree of the complex is not less than 95%. The relative error of boron determination is $\pm3\%$.

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Table 1.Dissociation of sodium polyolborates versus the solution concentration

Na polyolborate additive in 100ml H$_2$O, g	K$_{stab.}$	C, mol/l	[x], mol/l	[BPolyol]$^-$, mol/l	Dissociation degree, %
Na sorbitolborate	15.0				
0.1		4.036·10^{-3}	3.817·10^{-3}	0.219·10^{-3}	95.0
0.05		2.018·10^{-3}	1.960·10^{-3}	0.058·10^{-3}	97.1
0.033		1.345·10^{-3}	1.319·10^{-3}	0.026·10^{-3}	98.1
Na mannitolborate	27.0				
0.1		4.036·10^{-3}	3.672·10^{-3}	0.364·10^{-3}	91.0
0.05		2.018·10^{-3}	1.919·10^{-3}	0.1·10^{-3}	95.0
0.033		1.345·10^{-3}	1.3·10^{-3}	0.045·10^{-3}	98.6
Na dulcitolborate	130.0				
0.1		4.036·10^{-3}	2.9·10^{-3}	1.136·10^{-3}	71.9
0.033		1.345·10^{-3}	1.168·10^{-3}	0.177·10^{-3}	86.8
0.01		1.404·10^{-3}	0.384·10^{-3}	0.020·10^{-3}	95.2
Na xylitolborate	25.5				
0.1		4.588·10^{-3}	4.149·10^{-3}	0.439·10^{-3}	90.4
0.05		2.294·10^{-3}	2.175·10^{-3}	0.119·10^{-3}	95.0
0.01		0.459·10^{-3}	0.454·10^{-3}	0.005·10^{-3}	98.8
Na glycerolborate	39.3				
0.1		5.157·10^{-3}	4.396·10^{-3}	0.761·10^{-3}	85.2
0.05		2.579·10^{-3}	2.366·10^{-3}	0.213·10^{-3}	91.7
0.033		1.702·10^{-3}	1.612·10^{-3}	0.090·10^{-3}	95.0
0.01		0.516·10^{-3}	0.506·10^{-3}	0.010·10^{-3}	98.0

Table 2. Determination of boron

Test No.	Boron concentration, %		Relative error, %
	found	calculated	
1	5.71	5.58	-2.3
2	2.42	2.46	+1.6
3	5.53	5.60	+1.3
4	2.85	1.80	-2.8