Exchangeable ion determinations in $BaCl_2$

Durkovicova

Observation and experienes

- Extraction and assesment of the soil samples in the project BIOSOIL have shown interesting observations. I would like to share them with you.

- Jana Ďurkovičová, operater of ICP and head of CFL NFC Zvolen

Topic for discusion

- Recovery of Al^{3+} in the reference material FSCC Ref1
- Influence of shaking on the recovery of Al^{3+}
- The dependance Fe^{2+} and pH in $BaCl_2$
- The dependance Mn^{2+} and pH in $BaCl_2$

A few Notes acquired during the determination of exchangeble ions in $Bacl_2$

- We have processed and assessed about 2000 soil samples from 112 monitoring plots in the Biosol project
- Samples were processed and determined analytically according to the procedures from the Manual on methods and criteria for harmonized sampling, assesment, monitoring and analysis of the effects of air pollution on forests Part III a Sampling and Analysis of Soil ICP FOREST
- Determinations of exchangeable ions in the 0,1 ml BaCl2 difusion were processed according to the method SA 10 of the Manual …
- As a control material we used the LRM FSCC REF 1 for acid soil as well as our own soil reference materials LRM 3 for soil with pH = 3
  LRM 5 for soil with pH = 5
  LRM 7 for soil with pH = 7

We found out that

Our results of Al3+ in the sample FSCC REF 1 were significantly lower in comparison with another results of ICP Forest participants.

Another elements Ca2+ ,Fe 2+ ,Mg 2+ ,Mn 2+ in the sample FSCC REF 1 were determined with a large dispersion - CV when their values oscilated closely to LOD .
It was necessary to find out the cause of the low concentration of Al3+ element .

We repeated the SA 10 procedure in the LRM FSCC Ref 1 material several times **without the increasing Al3+ concentration.**

We repeated also the three steps extraction method according to the norm ISO 11260 in the LRM FSCC Ref 1 material.

Difference betwen BaCl2 and oxalat leaching procedure

- **BaCl2 – leaching procedure**

2,5 g of sample was loaded into the **50 ml centrifuge tube**, subsequently added 30 ml 0,1 N BaCl2 and shaken for 2 hours by the SA 10 procedure.

- **Oxalat – leaching procedure**

1 g of sample was loaded into the **100 ml PE bottle** added 50 ml oxalat reagent and shaken for 4 hours....

After shaking 35 ml solution was transfered to the **50 ml centrifuge tube** and separafed.

- The intensity of shaking was higher in the whole volume and recovery of Al and Fe reactive was satisfactory and approached to the 90-100 %.

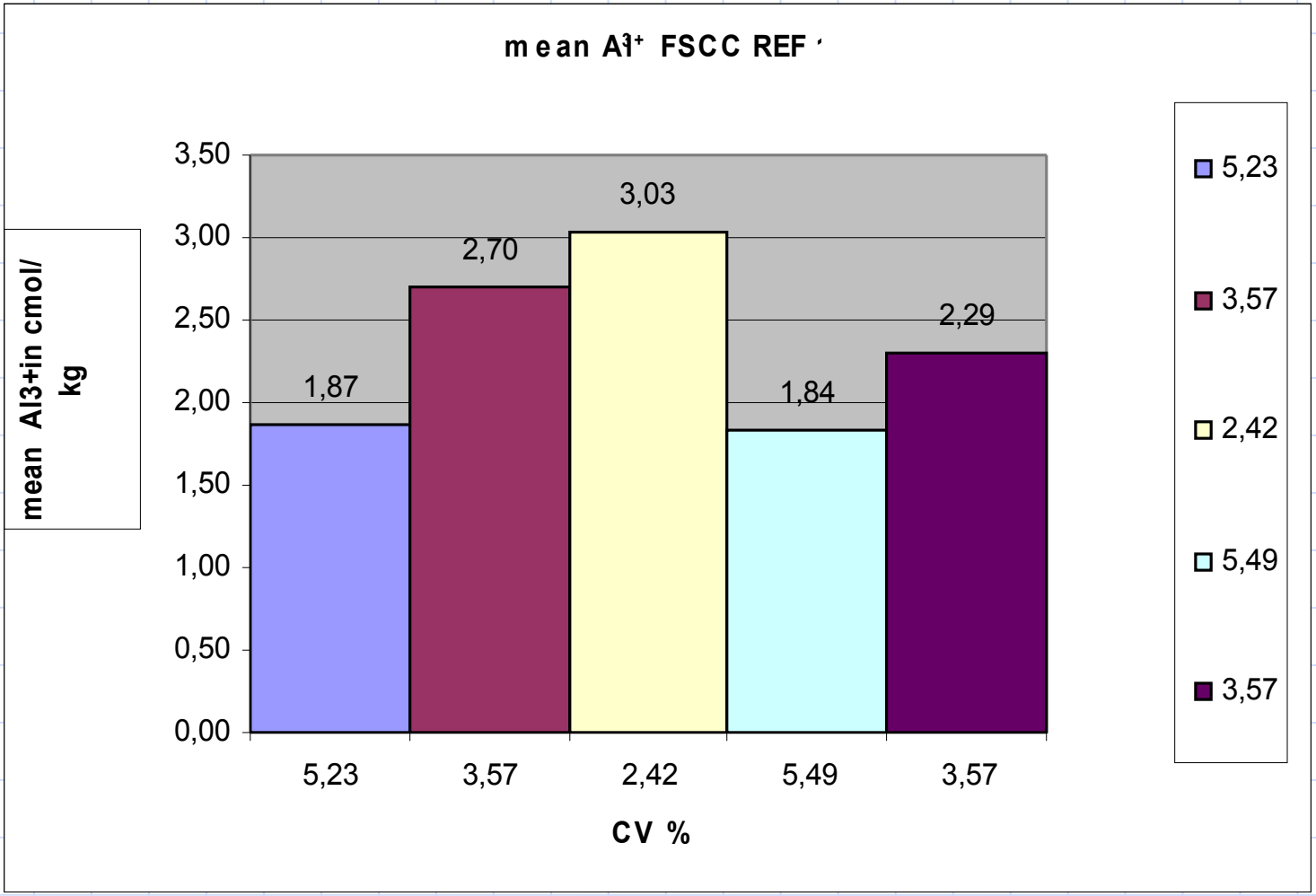
And this recognition forced us to change the leaching procedure for the determination of exchangeble ions in BaCl2

- It means that before the centrifugation in the 50 ml tube we should ensure that the sample was mixed in a whole volume in the 100 ml PE bottle **not in 50 m tube**.
- Then we observed the higher intensity of shaking in the whole volume of the sample. The concentration and the recovery of Al3+ increased significantly and the dispersion - CV of values was lower than at the first attempt.

The mean of Al^{3+} $cmolkg^{-1}$ in FSCC Ref 1 and shanking

FSCC Ref1	Number of me	8	8	8	102	52
Declared value.	2,81	Al3+	Al3+	Al3+	Al3+	Al3+
		shaking in	shaking in	3- step extrac	15,3,07-30,5,08	2,6,08-26,5,09
dlhodobý mean	1,948	50 ml centr.fl	100 ml PE bo	ISO 112 90	50 ml centr.fl	in 100 ml PE b
		cmol/kg	cmol/kg	cmol/kg	cmol/kg	cmol/kg
mean		1,87	2,70	3,03	1,84	2,29
median		1,88	2,74	3,11	1,83	2,28
stdv		0,22	0,22	0,16	0,23	0,18
CV %		5,23	3,57	2,42	5,49	3,57
recovery %		66,45	96,12	107,73	65,42	81,57
min		1,59	2,31	2,79	1,36	1,92
max		2,32	2,98	3,21	2,65	2,80

Comparison of Al $^{3+}$ average values in a relation with the shaking procedure



Cause and comparision

- Low recovery of Al3+ in the FSCC REF 1 was caused by the incompleted shaking of mixture **in the 50 ml** centrifuge tube. This tube is too narrow and high, thus its shape did not allow sufficient shaking of samples in the whole volume. Especially these ones with a higher **specific gravity mass.**

We found out that

- 1. The intensive shaking of the mixture in the 100 ml PE bottle caused that the concentration of Al 3+ in FSCC Ref 1 was significantly increased and approached declared value.
- 2. Al 3+ amount achieved of the three step extraction method by the norm ISO 11260 was much more higher than the one step extraction by the SA 10 method.
- By using the 3 – step method nearly whole amount of Al^{3+} was leached into the solution from the soil .
- Unlike the 1 - step pocedure, in which the equalization of Al^{3+} in soil and solution was not finished.
- I think If the acid soils are heavier than neutral or alkaline ones

- It turned out that not all the samples were equally intense and, above all, shaken on their whole volume. Milder samples, perhaps clay-like, had sedimented on the bottom, thus shaking was observed on the top of suspension only. Some samples that did not sediment at all, showed shaking in the whole volume, not only on the surface. This lead to a more intensive particle drenching and following outflow of the Al^{3+} ion into the solution from the whole volume of the sample

Conclusion

- For the achievement of the optimal values of exchangeable ion concentrations and their sufficient recovery it appears, that the most important factor is an intensive shaking in the whole mixture volume and ensuring the complete drenching of sample particles.

Proposal

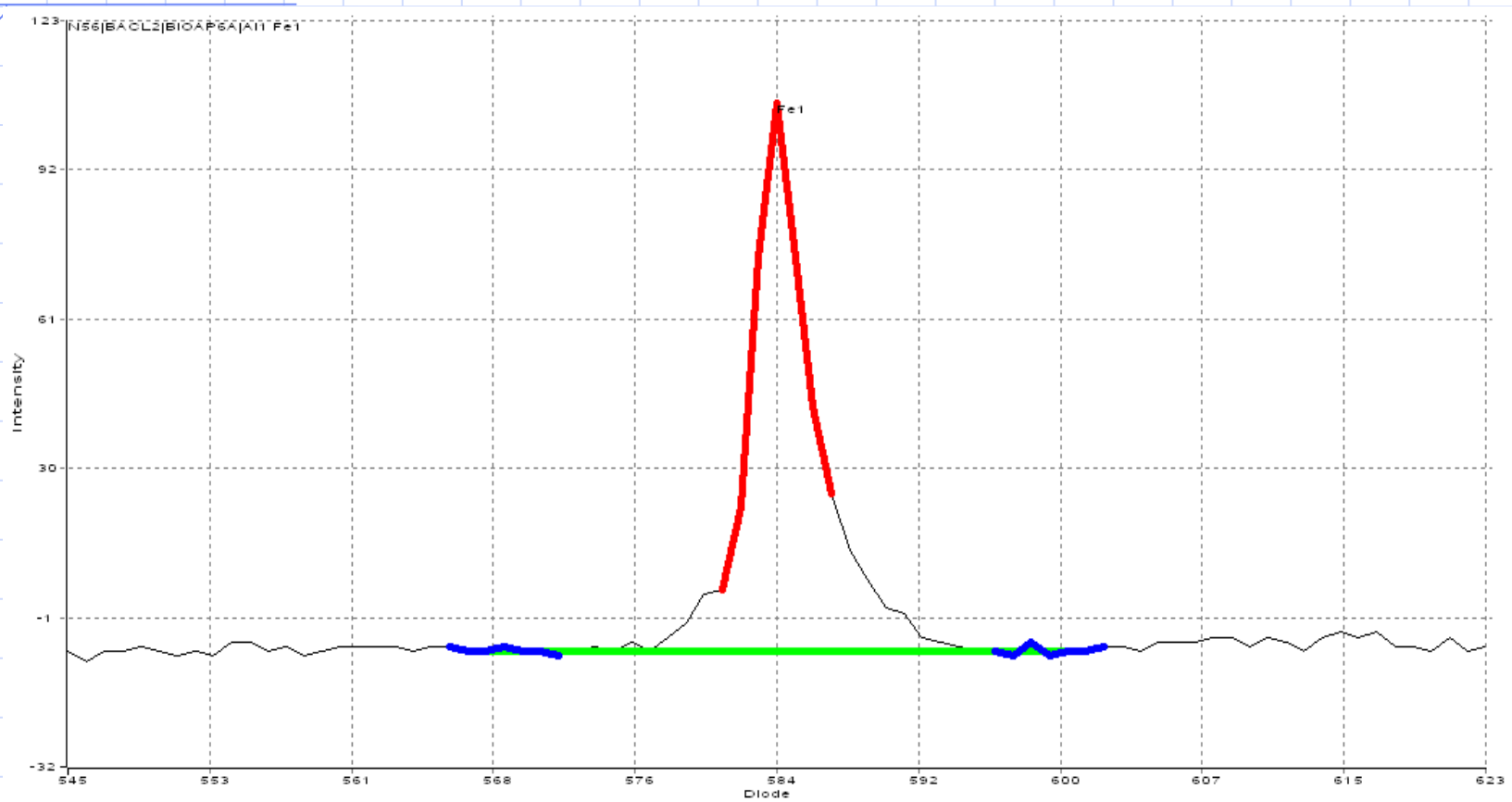
- I propose to make a change in the sample treatment supernatant procedure SA 10 as follows: 2,5 g of the sample to place into the 100 ml PE bottle, add 30 ml of $BaCl_2$ solution, intensively shake for 2 hours in the whole volume of the soil mixture.
- After shaking the mixture to transfer quantitatively to the 50 ml centrifuge tube, then continue with the SA 10 procedure
- If 50 ml centrifuge tubes are lower and wider and able to ensure an intensive shanking in the whole volume, then this change is not necessary.
- This change was significant for us because our 50 ml centrifuge tubes are high and very narrow

Our observation of the dependance Fe^{2+} and pH in $BaCl_2$

- PH < 5,0 Fe signal is observed at its typical pixel 585. Its peak is decreased with the higher pH but it remains exactly at the pixel585
- The certain pH point and the specific kind of soil, shifts its peak to the pixel 589. This is no characteristic for Fe^2. The concentration of Fe^2 is false high.
- This signal can be caused by some background interferences.
- We did not have enough time to investigate this phenomenon. Since it is known that the exchangeable form of Fe is not found in soil at pH>6, these results can lead to incorrect conclusions.

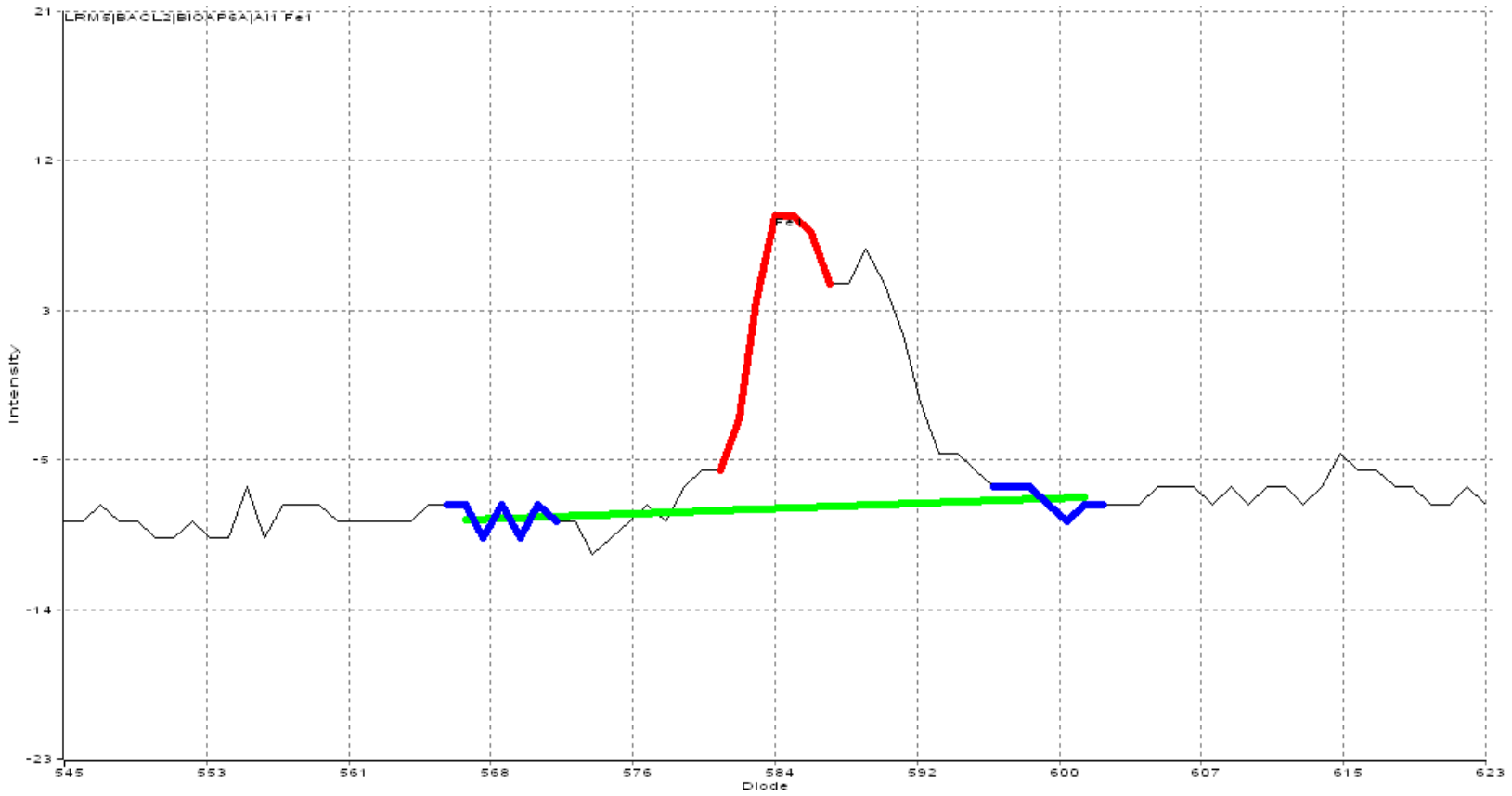
Sample	pH	Fe^{2+} mgl^{-1}	Pixel	Al^{3+} mgl^{-1}
FSCC Ref1	4,3	0,465	585	
LRM 5-06	5,2	0,092	585	
3460	5,39	0,069	585	1,35
3465	5,17	0,094	585	2,74
3466	5,82	0,103	585	0,44
3467	5,8	0,091	585	0,48
3281	5,05	0,118	**582**	1,16
5944	**6,12**	**2,25**	**589**	noise
5955	**7,23**	**1,82**	**589**	noise

pH = 4,3 FSCC Ref 1 Fe = 0,465 mgl^{-1} 584 pixel
238,204 nm Al = 4,17 mgl^{-1} 396,152 nm



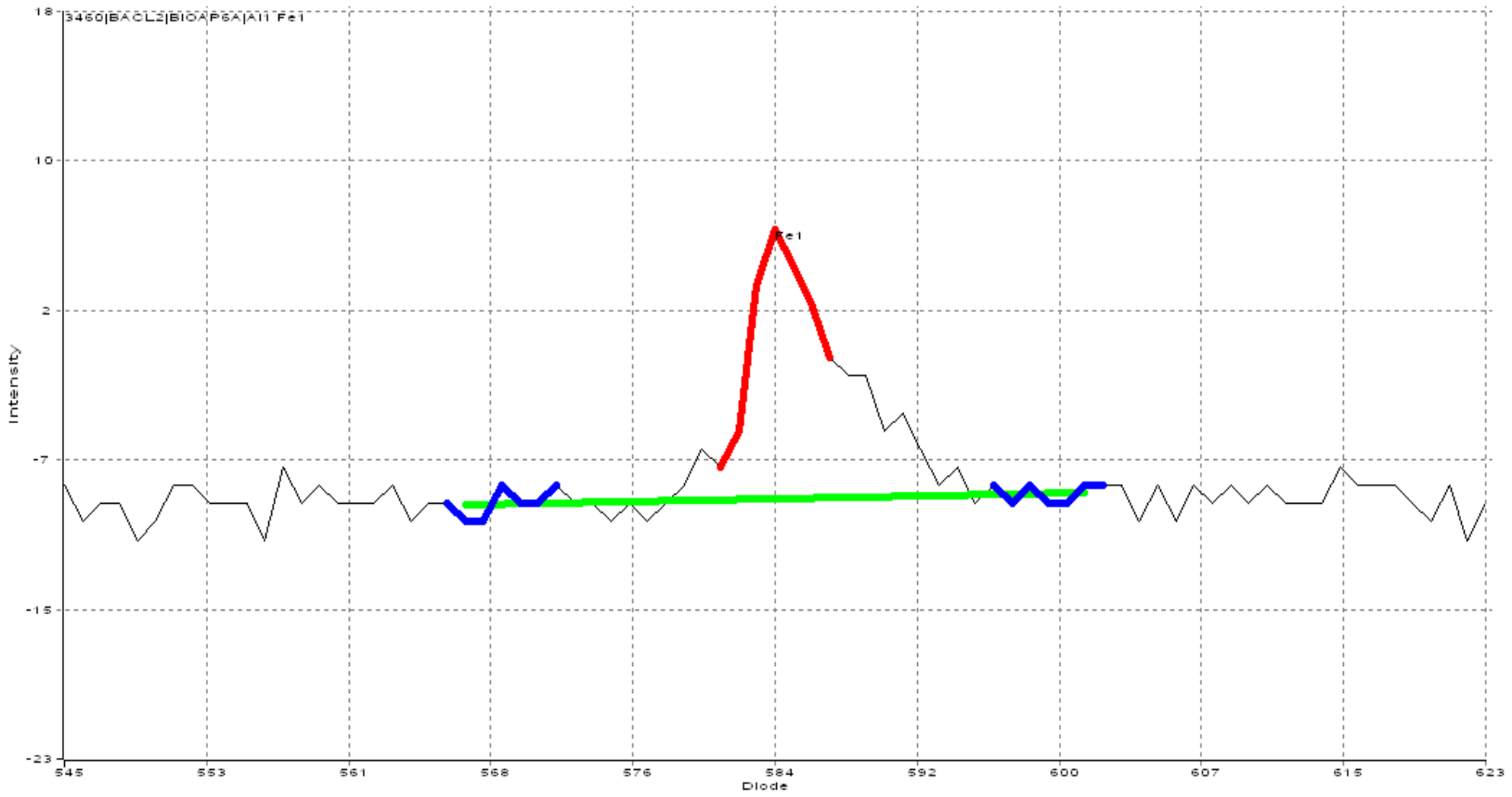
pH = 5,2 LRM 5-06 Fe = 0,092,mgl^{-1} 584 pixel

Al = 0,54 mgl^{-1}



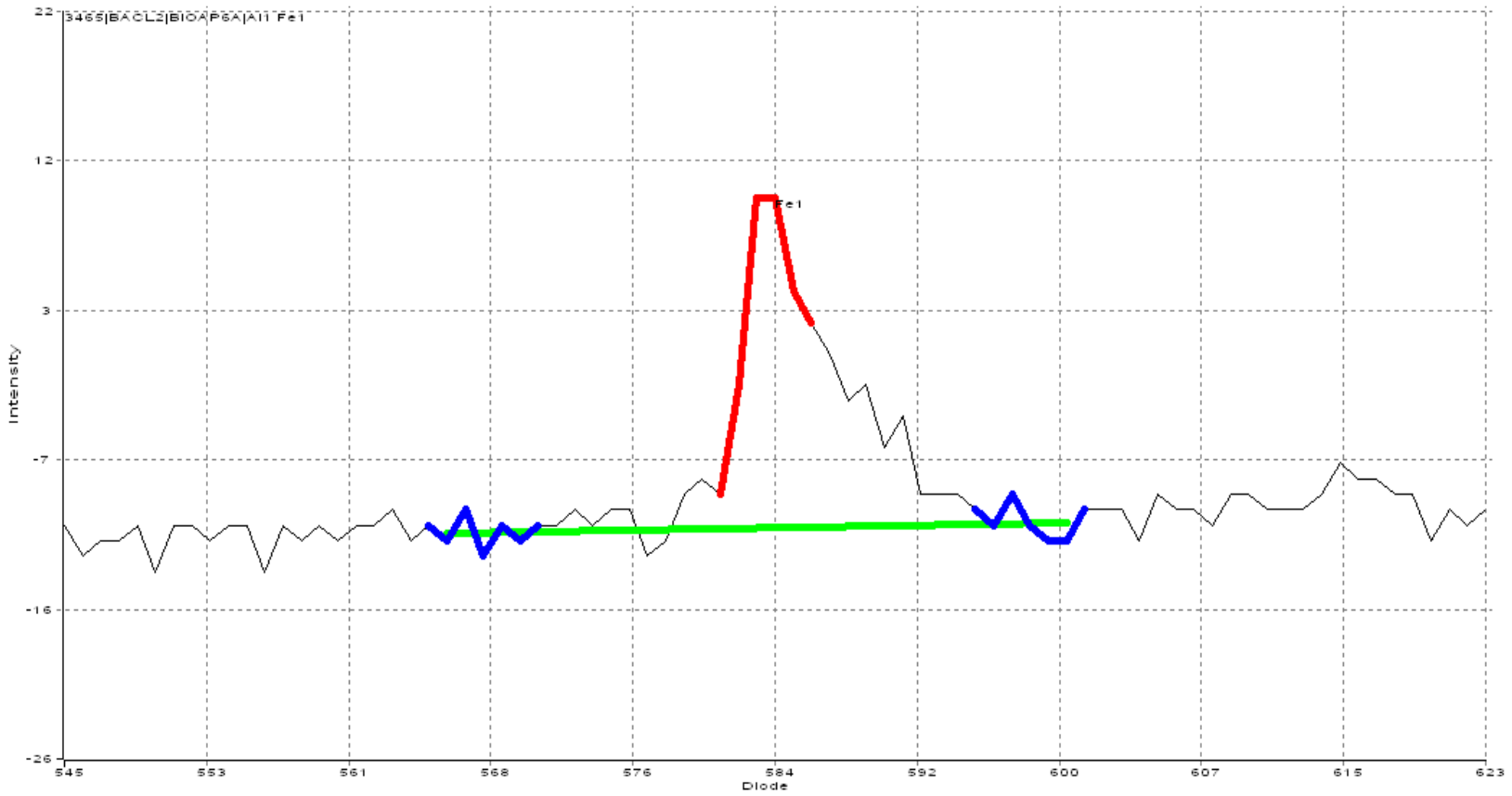
pH = 5,39 3460 Fe = 0,069 mgl^{-1} 584 pixel

Al = 1,35 mgl^{-1}



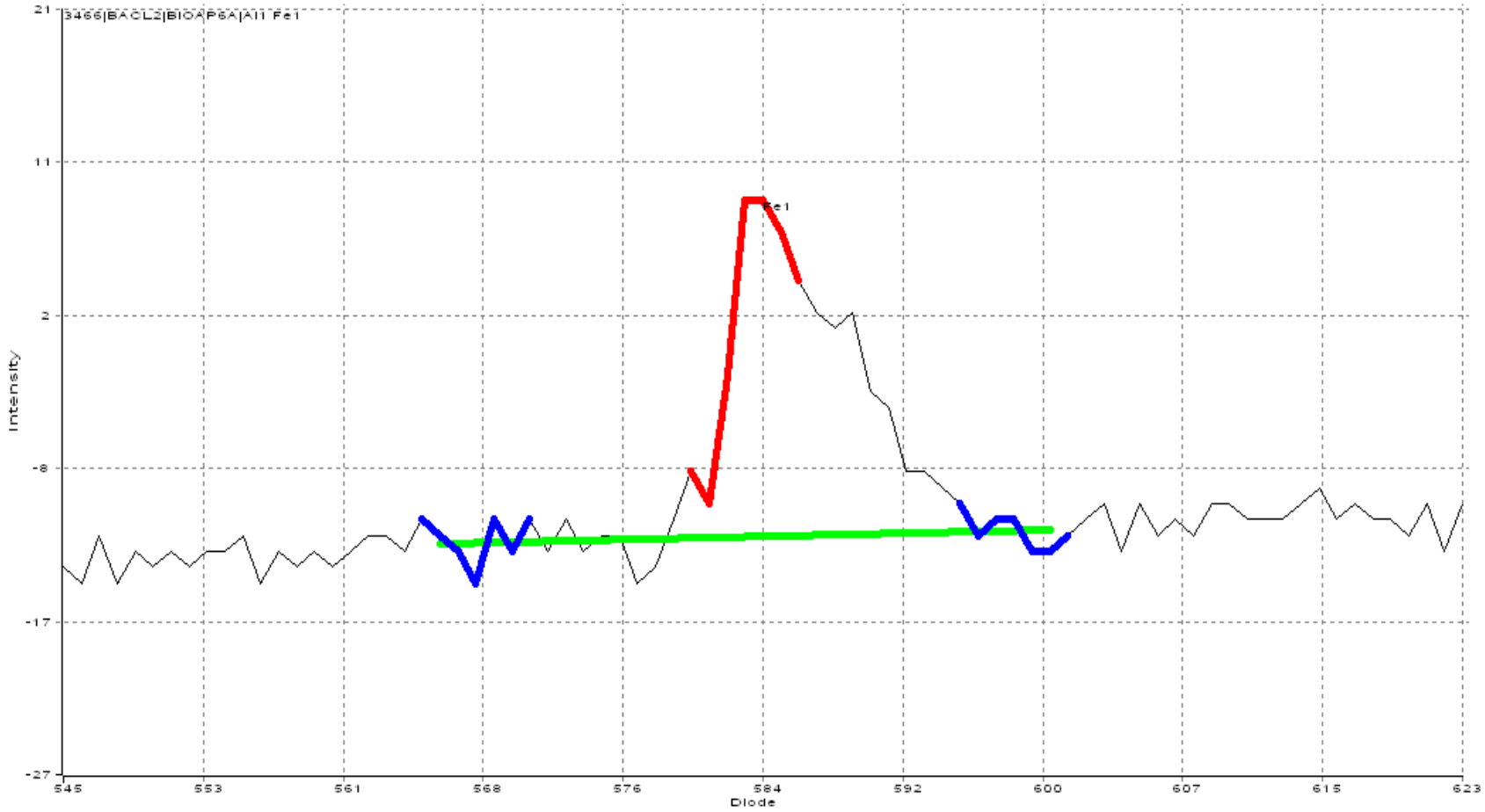
pH = 5,17 3465 Fe = 0,094 mgl^{-1} 584 pixel

Al= 2,74 mgl^{-1}



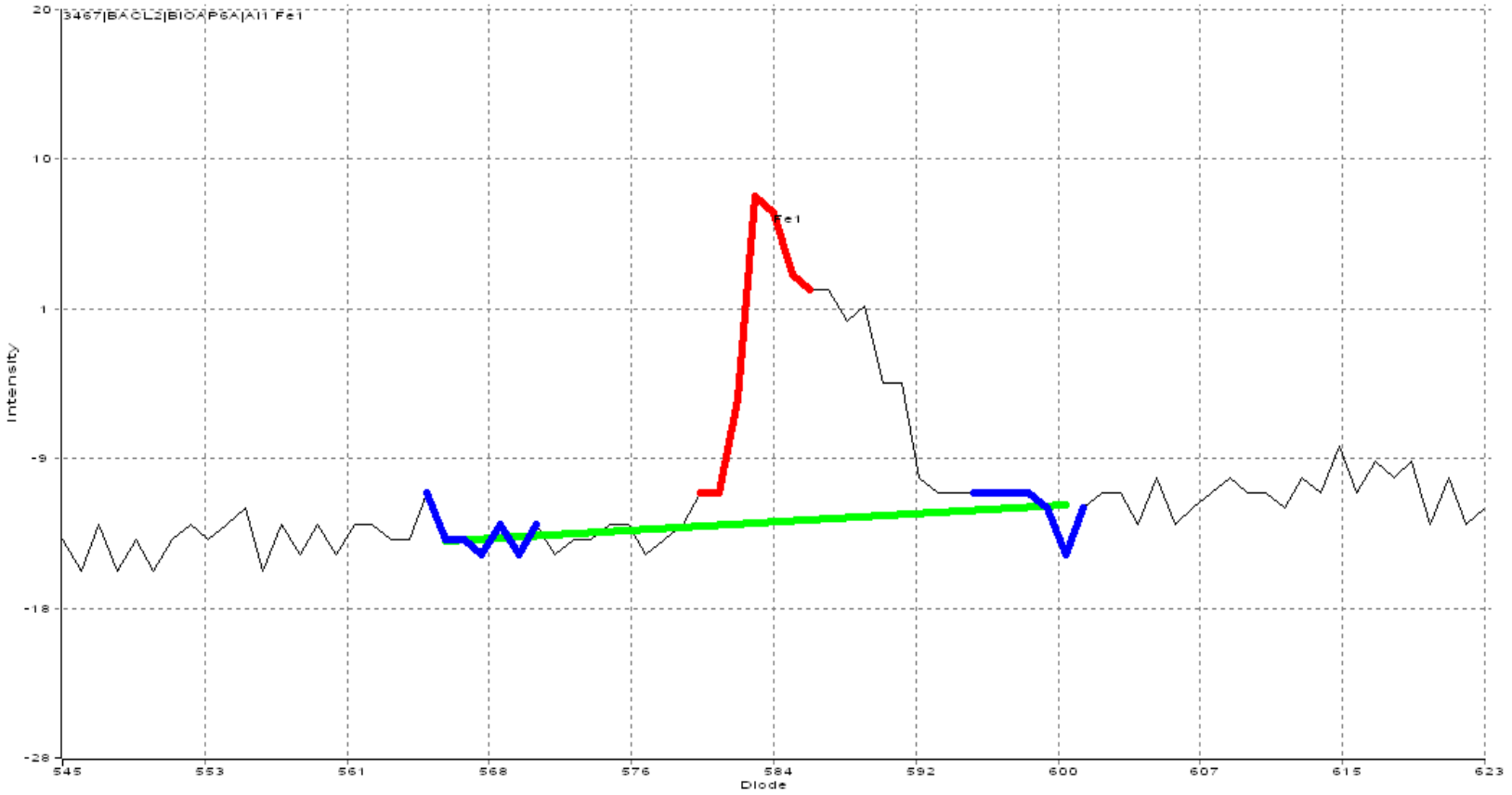
pH = 5,82 3466 Fe = 0,103 mgl^{-1} 583 pixel

Al = 0,44 mgl^{-1}



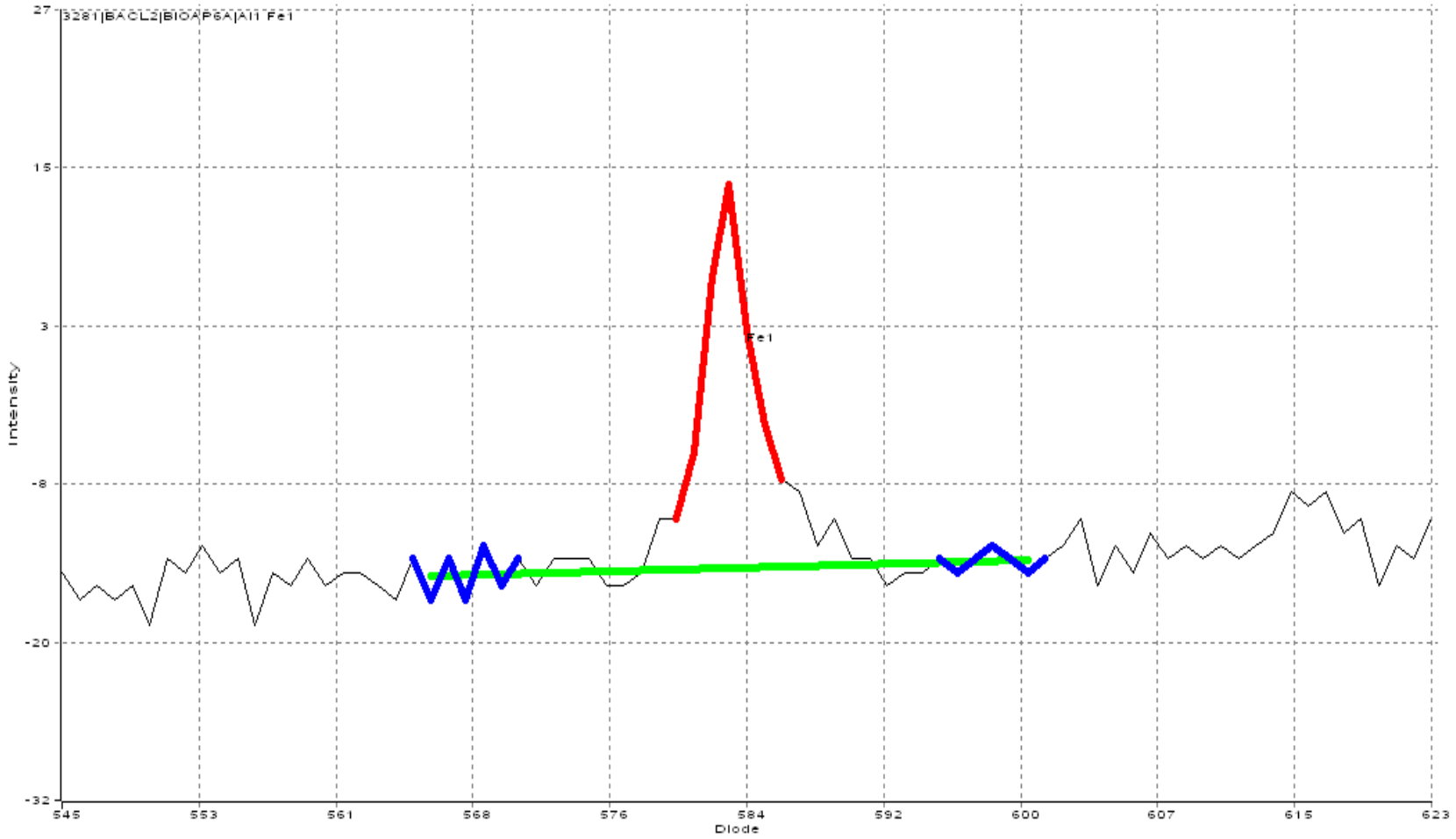
pH = 5,80 3467 Fe = 0,091 mgl^{-1} 583 pixel

Al = 0,48 mgl^{-1}



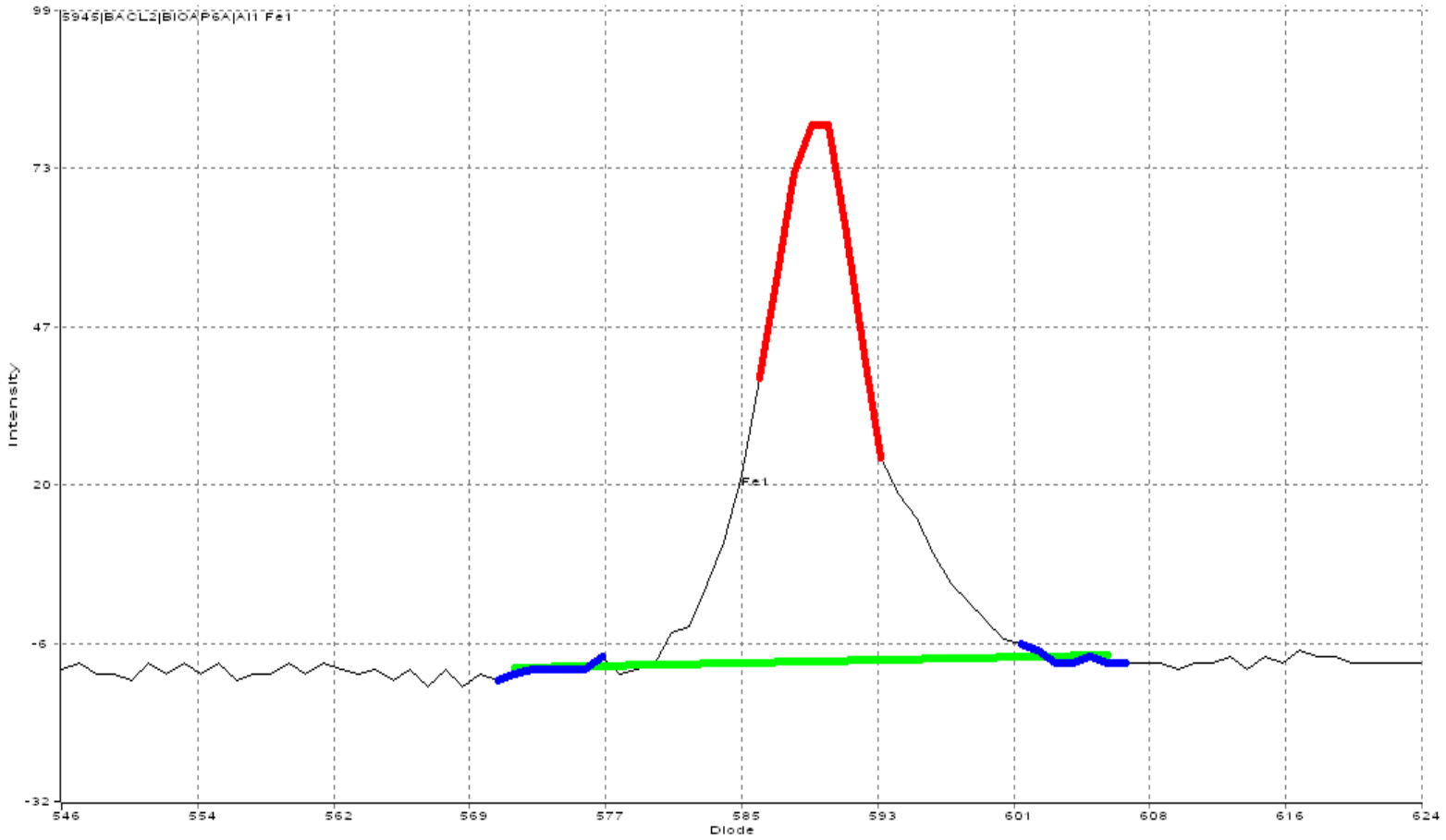
pH = 5,05, 3281 Fe = 0,118 mg-l 583 pixel

Al = 1,16 mgl^{-1}



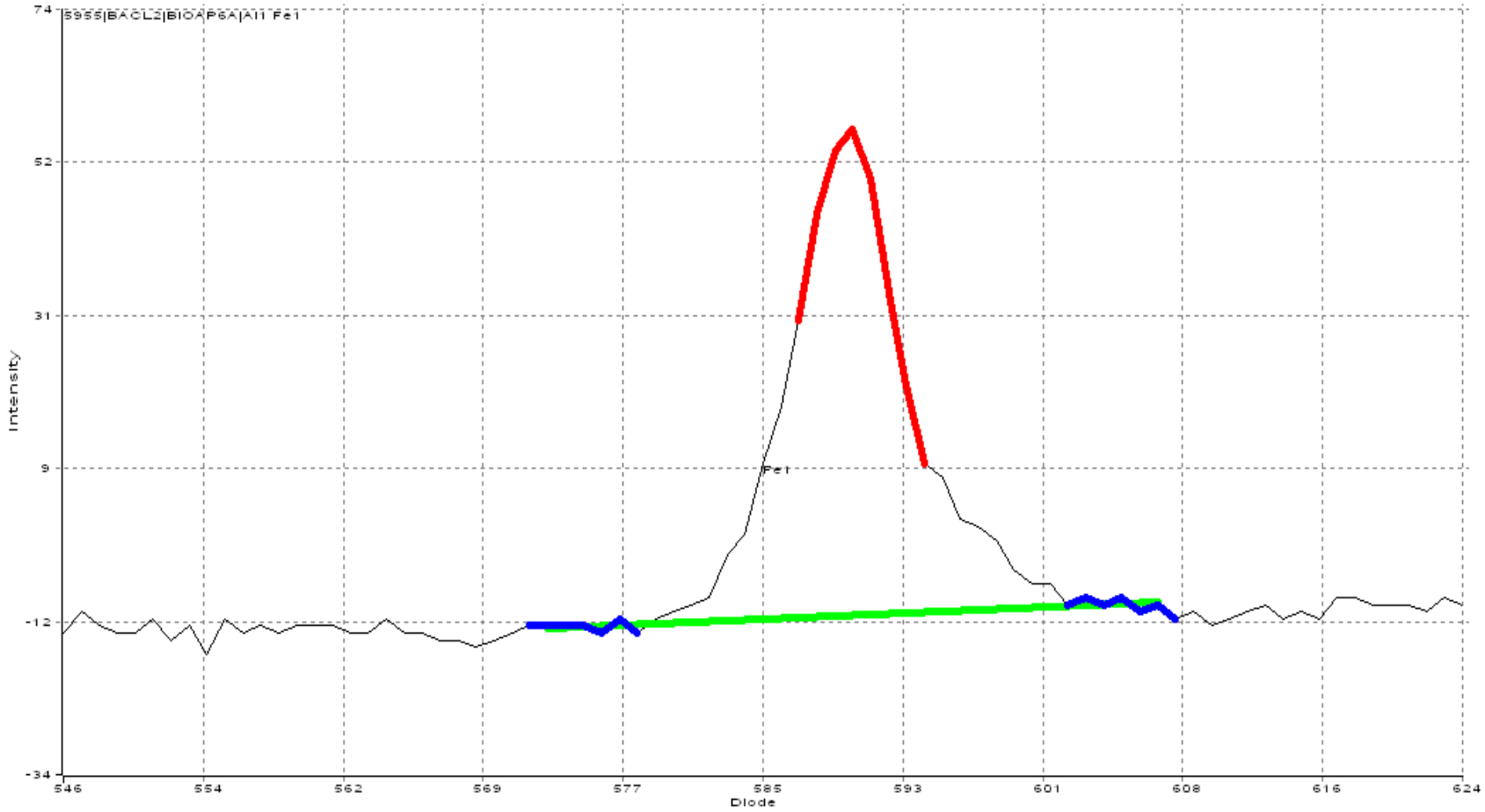
pH = 6,12 5945 Fe = 2,25 mgl^{-1} 589 pixel

Al = noise



pH=7,23 5955 Fe = 1,82 mgl^{-1} 590 pixel

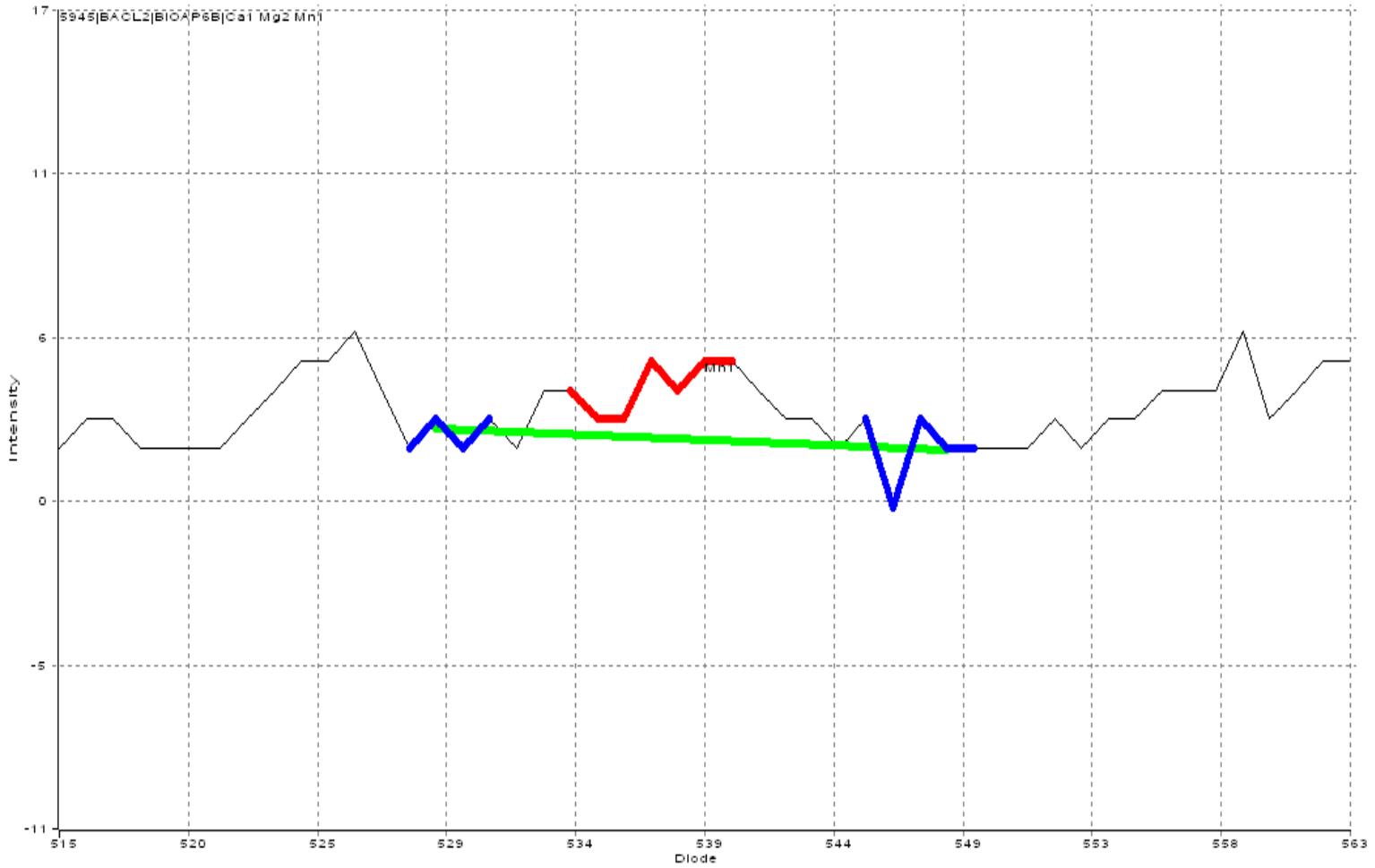
Al = noise



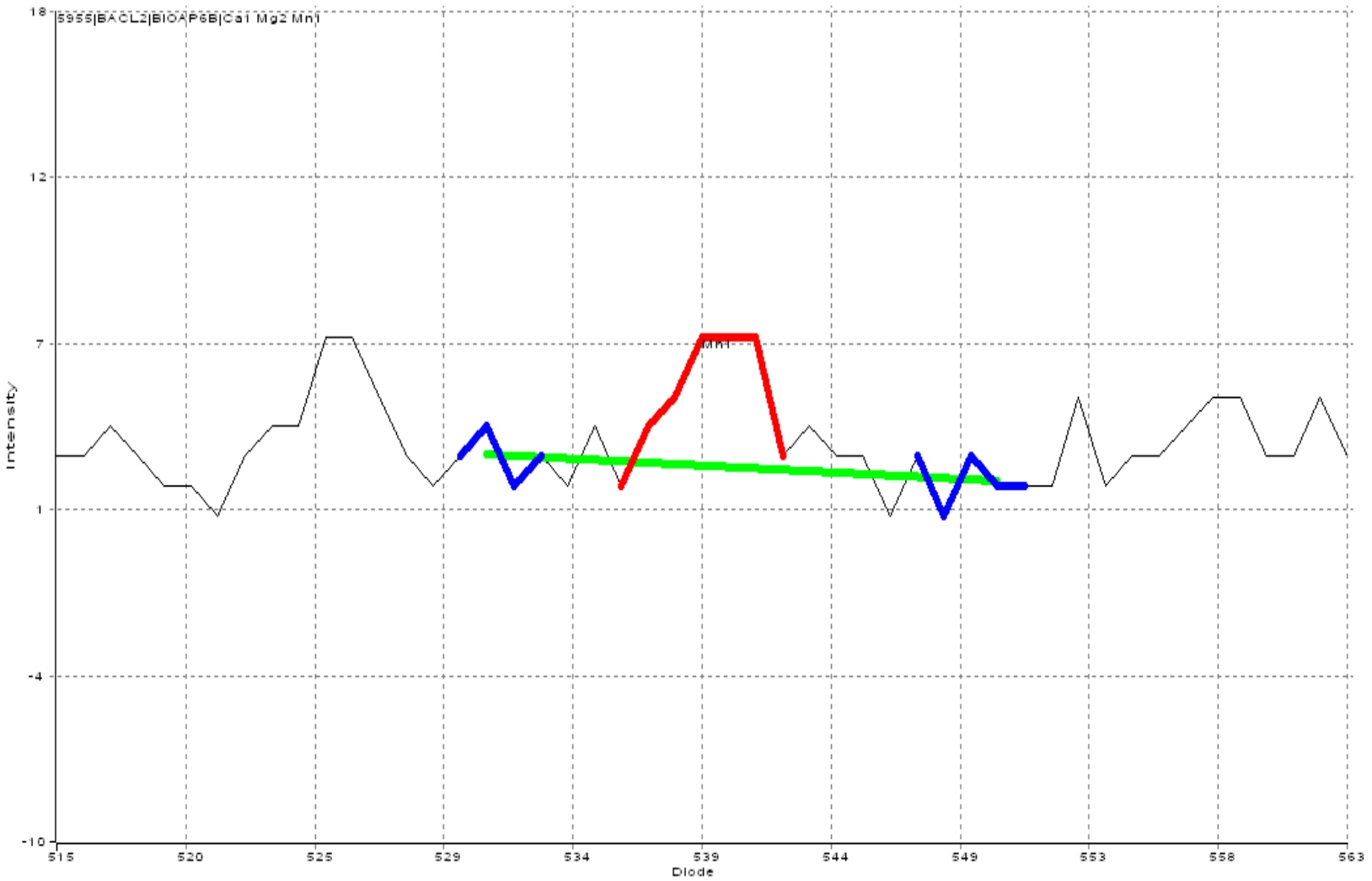
Our observation of the dependance Mn^{2+} and pH in $BaCl_2$

- pH < 5,0 signal of Mn^{2+} is observed at its typical pixel 538 and the intensity of its peak decreases with the higher pH but it stays exactly at the 538 diode
- pH = <5.0, 6.0 > the amount of Mn^{2+} is different and depends on the kind of soil
- pH > 6.0 the amount of Mn^{2+} is approaching to the LOD

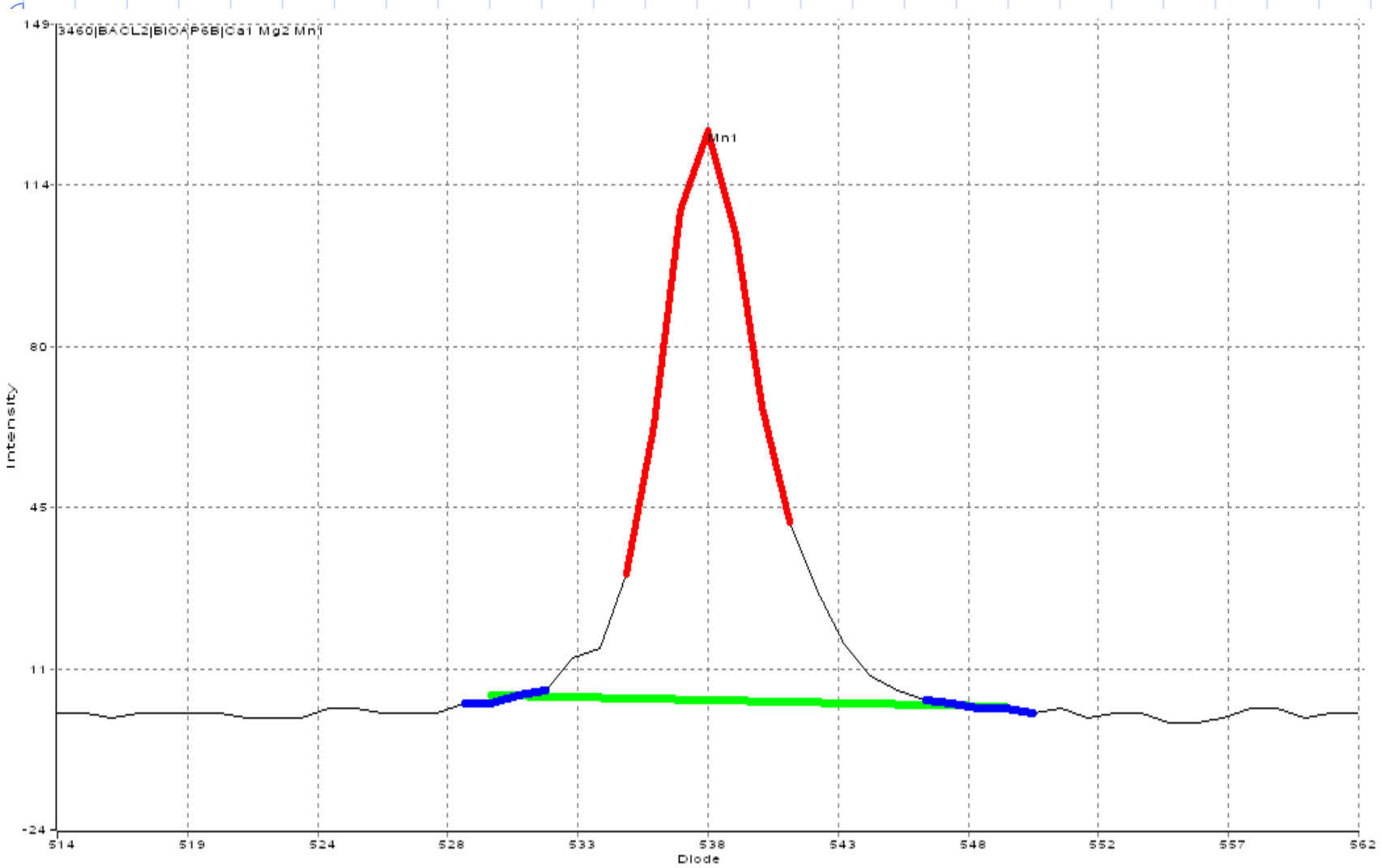
pH=6,12 5945 Mn=0,048 mgl^{-1} 539 pixel
292,30 nm



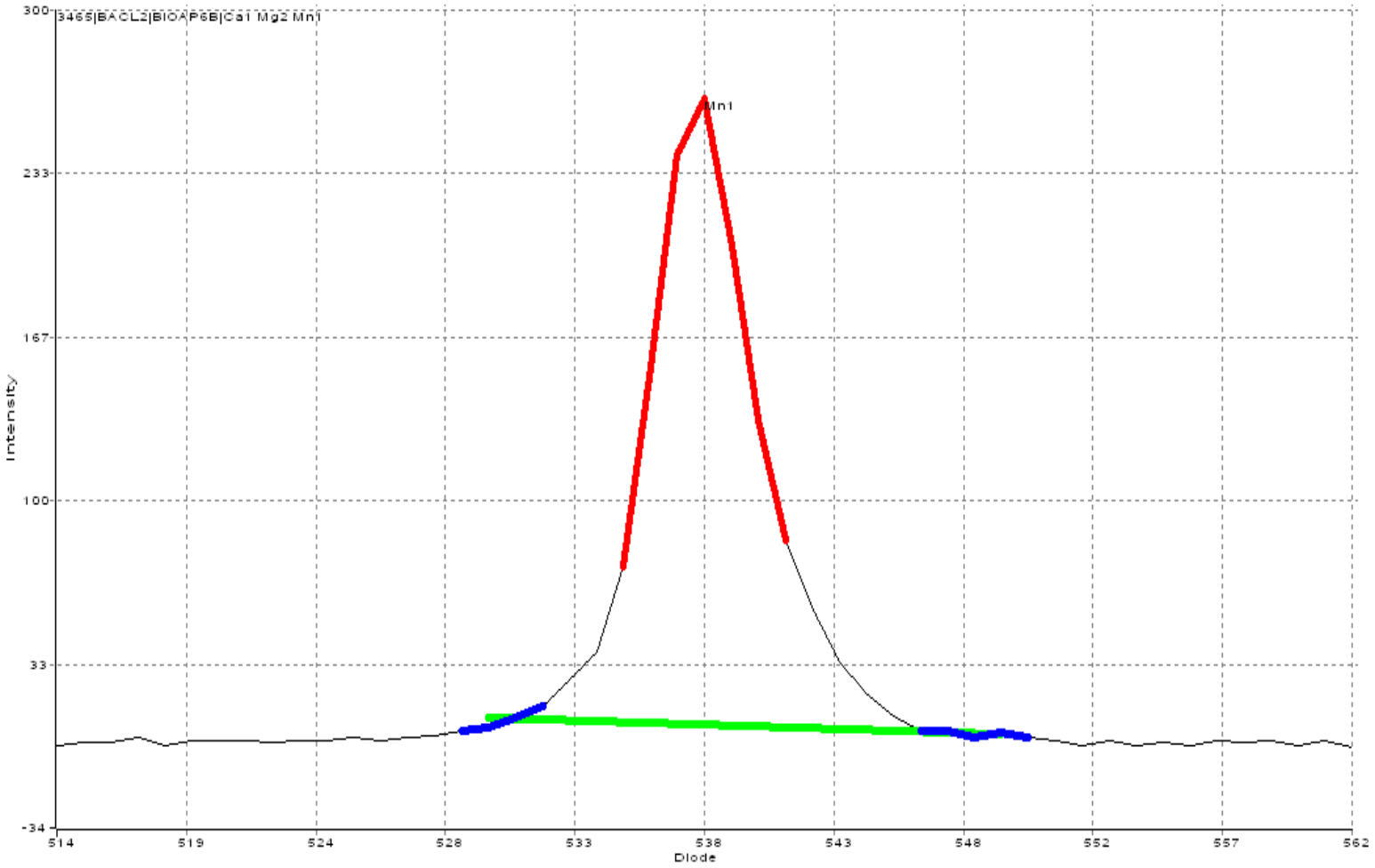
pH=7,23 5955 Mn = 0,043 mgl^{-1} 539 pixel



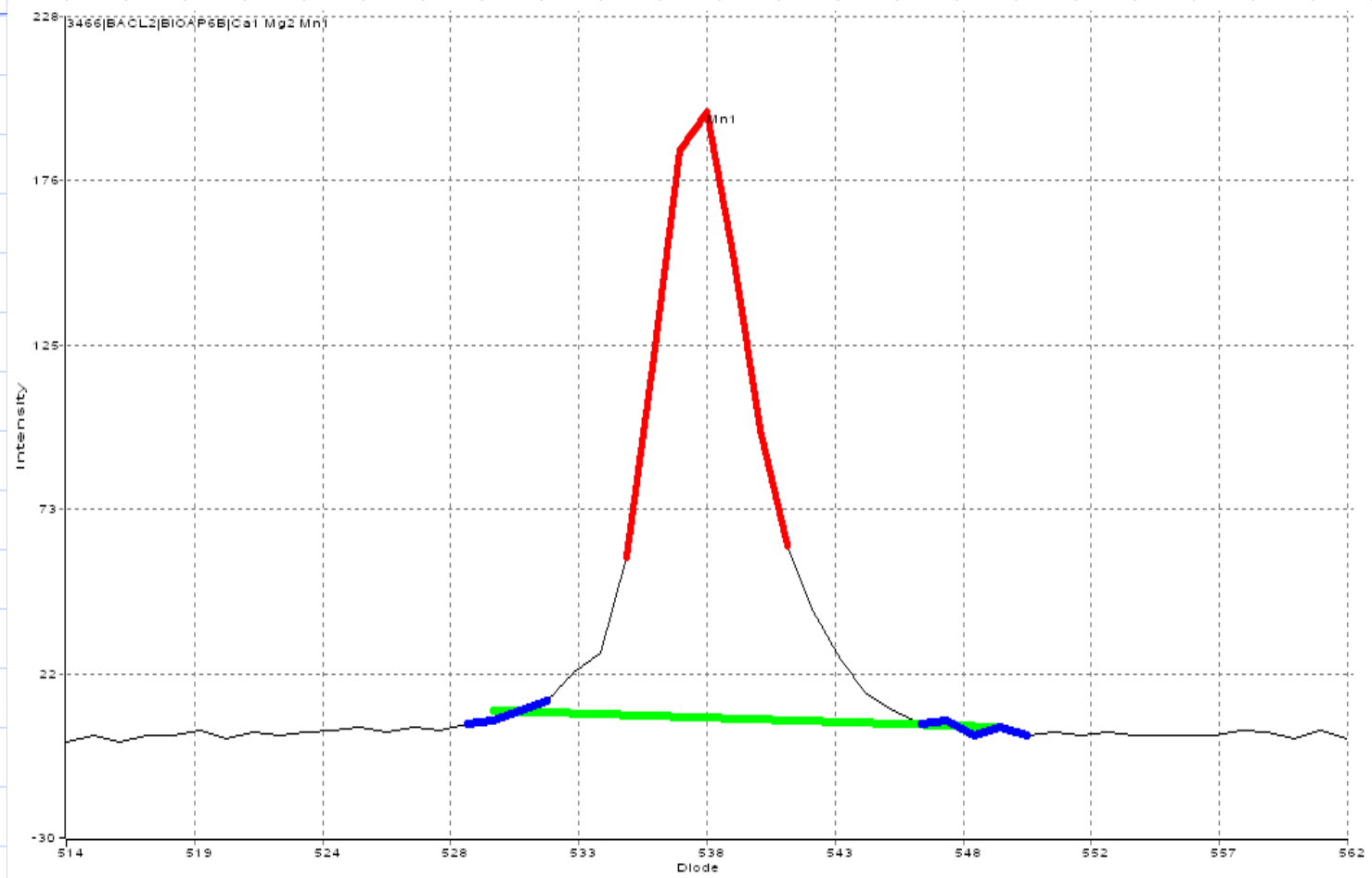
pH=5,39 3460 Mn=0,424 mgl^{-1} 538 pixel



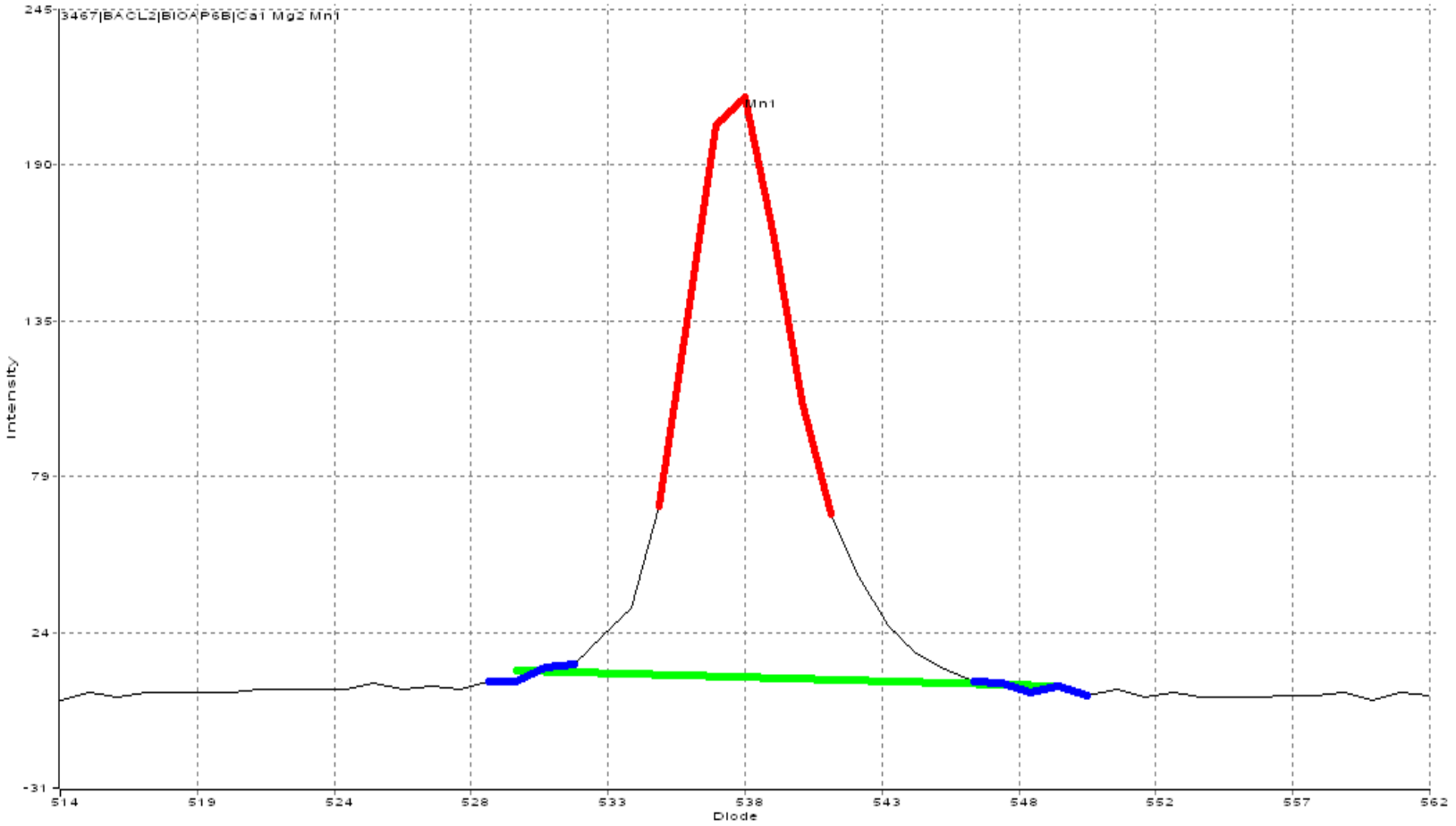
pH = 5,17 3465 Mn = 0,28 mgl^{-1} 538 pixel



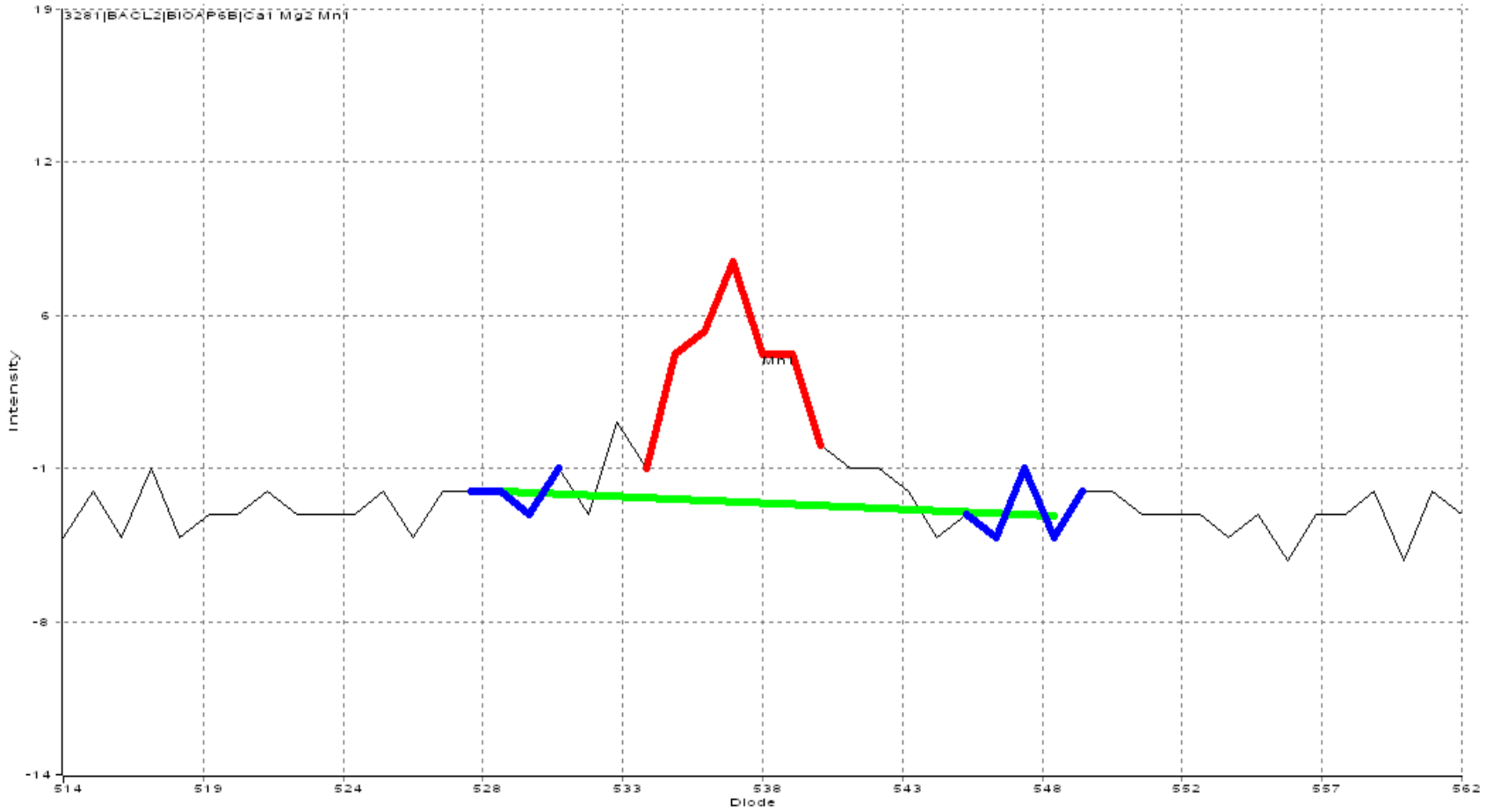
pH = 5,82 3466 Mn = 0,69 mgl^{-1} 538 pixel



pH = 5,80 3467 Mn= 0,73 mgl^{-} 538 pixel



pH = 5,05, 3281 Mn =0,034 mg-l 537 diode



- Thank for your attention
- Please, send me your questions on the e-mail durkovicova@nlcsk.org and I will answer you in written form .