

Application Work AW IC ES6-0007-082017_G

Sulfite determination in Cider by amperometric detection with Metrosep Carb 2

Branch

Food, stimulants, beverages, flavors

Keywords

IC, DC, Amperometric detection, 930 858 Drinks, Food, Alcohols, Sulfite, Sulphite, Cider, Metrosep Carb 2-150/4.0, branch 7

Summary

Sulfite IC Conductivity determination presents two difficulties: one is the chemical instability of this anion due to its nature and low peak resolution of chromatograms with sulfate analyte. Nevertheless, Sulfite anion has electrochemical activity that allows DC amperometric detection

Due to sulfite chemical low stability in aqueous solution is necessary to stabilize samples and standards with a stability solution (e.g. Formaldehyde and NaOH) which produces a Formaldehyde peak near sulfite retention time with DC amperometric detection.

This AW describes the combination an IC high capacity Column as Metrosep Carb 2 with NaOH- NaOAc (300mM-300mM) eluent to improve peak resolution between sulfite and stability solution with DC amperometric detection.

Previous studies with lower columns capacity showed less peak resolution causing a slightly matrix effect on sample results.

Samples

Cider and sulfite spiked cider samples

Instruments

930 Compact IC pro	2.930.2460
858 Professional Sample Processor	2.858.0020
IC Amperometric Detector	2.850.9110
IC equipment Wall-Jet cell: Carb (Au, Pd)	6.5337.010
Metrosep Carb 2 150/4.0	6.1090.420
Metrosep Carb 2 Guard	6.1090.500
MagIC Net™ 3.2 Professional	6.6059.322
IC equipment for ultrafiltration	6.5330.110
Adsorbing tube, large and bent	6.1609.000



Reagents

- Sodium hydroxide, puriss. 50 – 52%
CAS 1310-73-2, Fluka 72064
- Sodium Acetate anhydrous >99,0 % CAS 127-09-3;
Sigma-Aldrich S2889
- Formaldehyde solution ≥34.5 wt.% 15512 SIGMA-ALDRICH
- Sodium sulfite 71988 SIGMA BioUltra, anhydrous, ≥98% (RT)
- Soda lime p.a., with indicator, pellets; CAS 8006-28-8;
Sigma-Aldrich 72073
- Ultrapure water (UPW) resistivity >18.2 MΩ·cm (25 °C), type I grade (ASTM D1193) from Flex 5 ELGA water system

Solutions

Eluent	Sodium Hydroxide 300.0 mmol·L ⁻¹ Sodium Acetate 300.00 mmol·L ⁻¹ <i>CO₂ free ultrapure water</i>
Rinsing Solution	UPW : Methanol (1:1)
Stabilization solution (SS)	Formaldehyde 1.00 mmol·L ⁻¹ Sodium Hydroxide 0.20 mmol·L ⁻¹

Standard solutions

Sulfite anion solution from 0.5 to 50 mg·L⁻¹ with stabilization solution

Sample preparation

Samples prepared with stabilization solution

Analysis

Every solution was filtrated with 0.2 um inline ultrafiltration previously to injection

Eluent Flow	0.5 mL·min ⁻¹
Detector Mode	DC
E(V)	150 mV
Range	AUTO
DAMPING	OFF
DETECTOR TEMP	35 °C
Range	200 µA
Channel measurement	Current (nA)
Col. Oven temperature	35 °C
Sample Loop	20 uL

Calculation

Automatic integration using peak areas evaluated with MagIC Net™ 3.2

Results

See appendix with chromatograms below

Comments

Other studies showed DC amperometry as a good solution for Sulphite determination. To improve peak resolution between the stability solution and the analyte is always a key point because of the possibility of a slightly sample matrix effect.

In the present AW, the combination a very high capacity Column as Metrosep Carb 2 with the eluent NaOH-NaOAc (300mM-300mM) reveled an important improvement of peak resolution between Formaldehyde and Sulfite, reducing sample matrix effect.

Is important to note, as existing AWs about amperometric detection revealed, the combination of high concentration NaOH (300 mM) eluent with the Metrosep Carb 2 column showed high stability of retention times of analytes almost for 4-5 days working with the same eluent bottle. Using of degassed water and plastic bottle (HDPE) for eluent are necessary to achieve optimum eluent stability results

References

- [1] AW IC CH6-1089-032012 - Determination of sulfite using the Amperometric Detector with the DC Mode and two different stabilization solutions
- [2] AN-S-225 Sulfite in the presence of standard anions in beer on the column Metrosep A Supp 10 - 100/4.0
- [3] Determination of Lactose in Lactose-free Yogurt, with Pulsed Amperometric Detection Ion Chromatography (PAD-IC). AW IC ES6-0003-092013_G Gomensoro IC team SPAIN

Date

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Appendix

Example Calibration Chromatograms for 20 μL injection volume

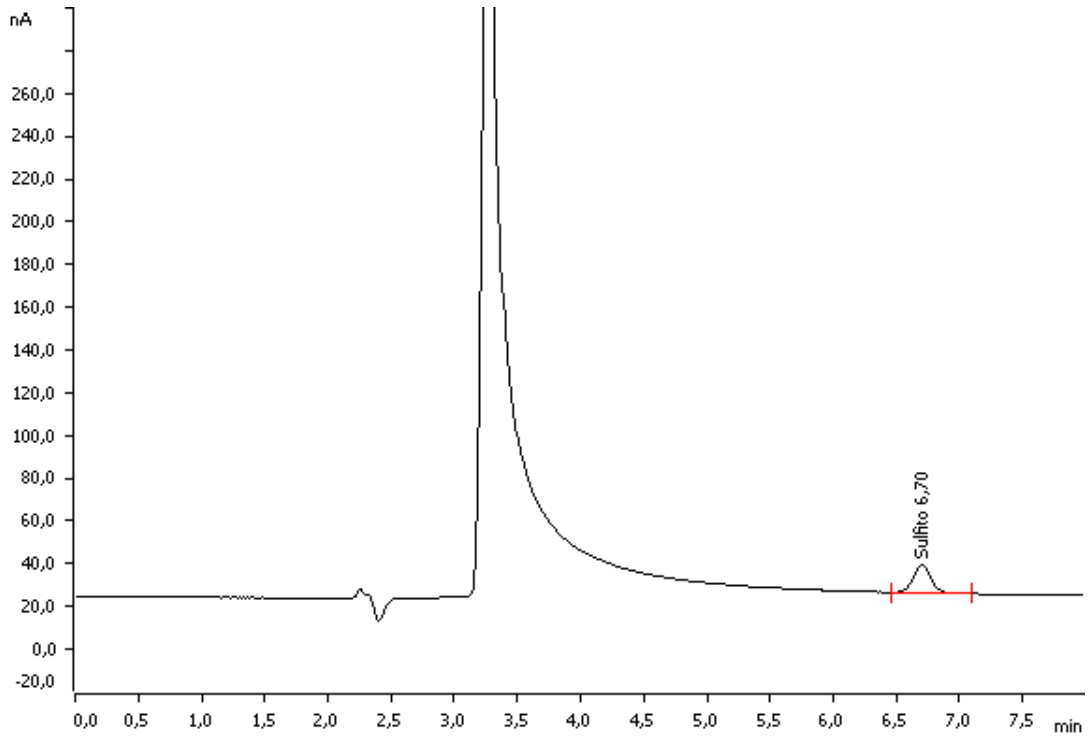


Fig 1. 20 μL injection of sulfite standard 500 $\mu\text{g}\cdot\text{L}^{-1}$

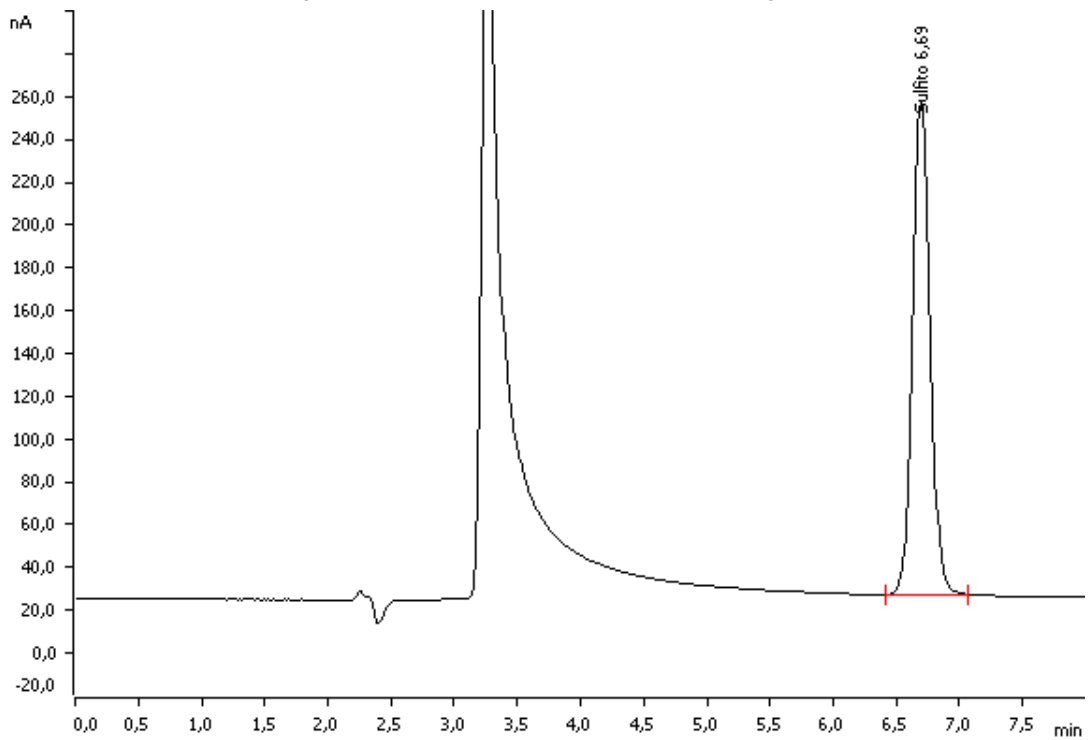


Fig 2. 20 μL injection of sulfite standard 10 $\text{mg}\cdot\text{L}^{-1}$

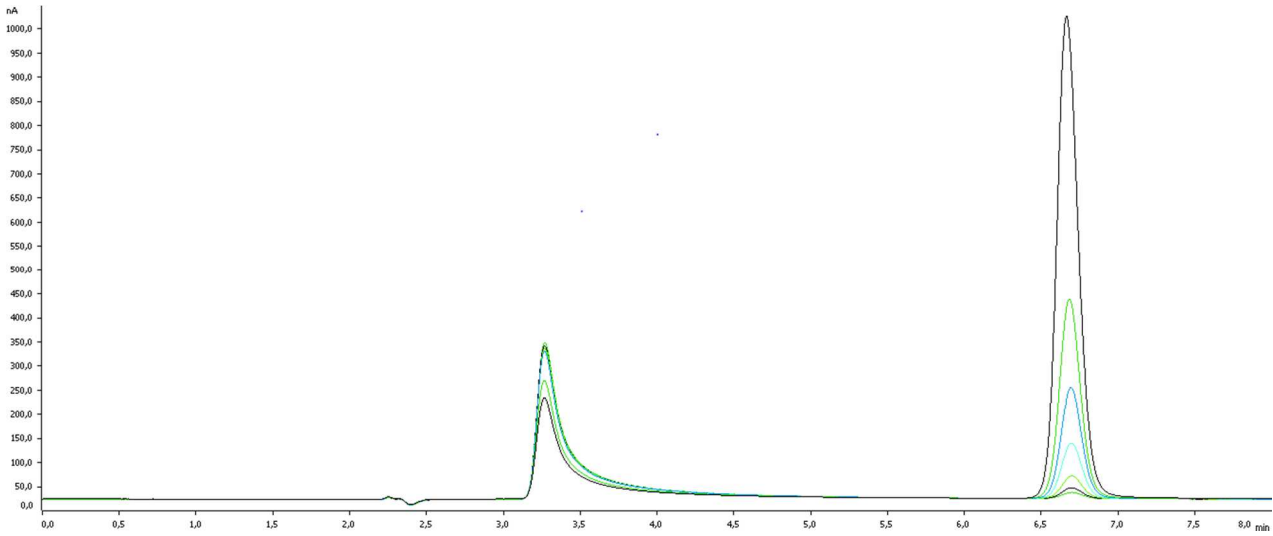
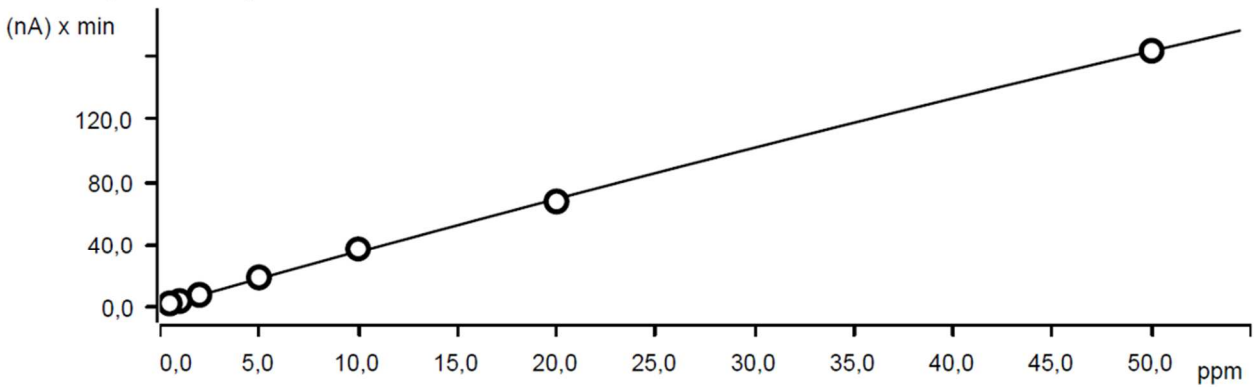


Fig 3. Overlay of Chromatograms of Sulfite standards

Sulfite (SULFITOS)



Function: $A = 0,179340 \times Q - 1,59677E-5 \times Q^2$

Relative standard deviation 2,745135 %

Correlation coefficient 0,999829

Fig 4. Calibration curve for sulfite standards (0.5 – 50 mg.L⁻¹)

Sample Chromatograms for 20 μ L injection volume

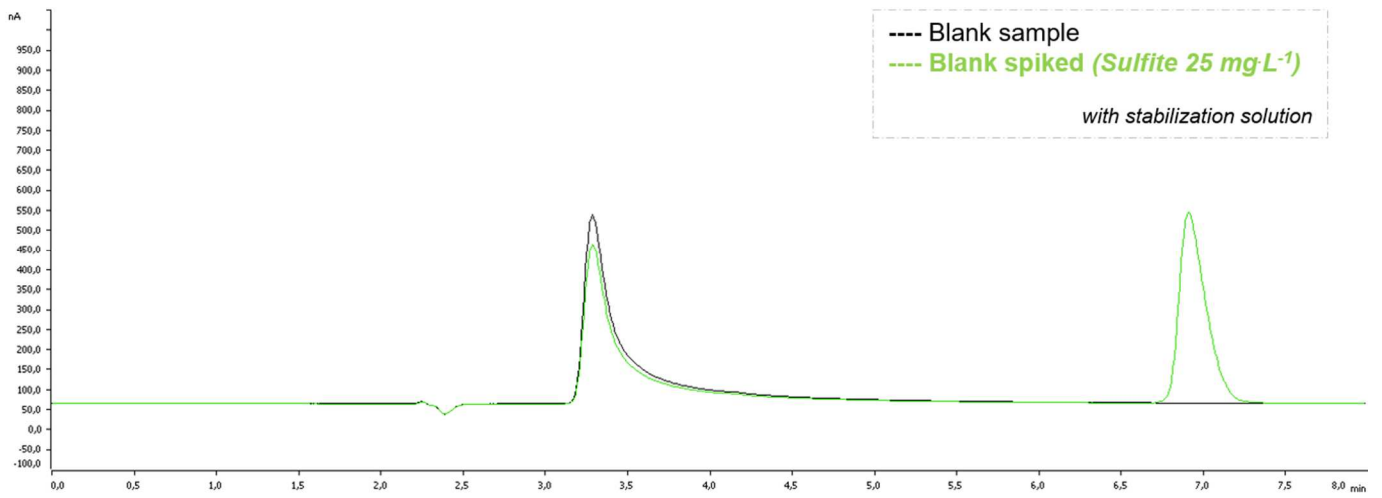


Fig 5 Overlay of Blank sample and Blank sample spiked with sulfite (stabilization solution)

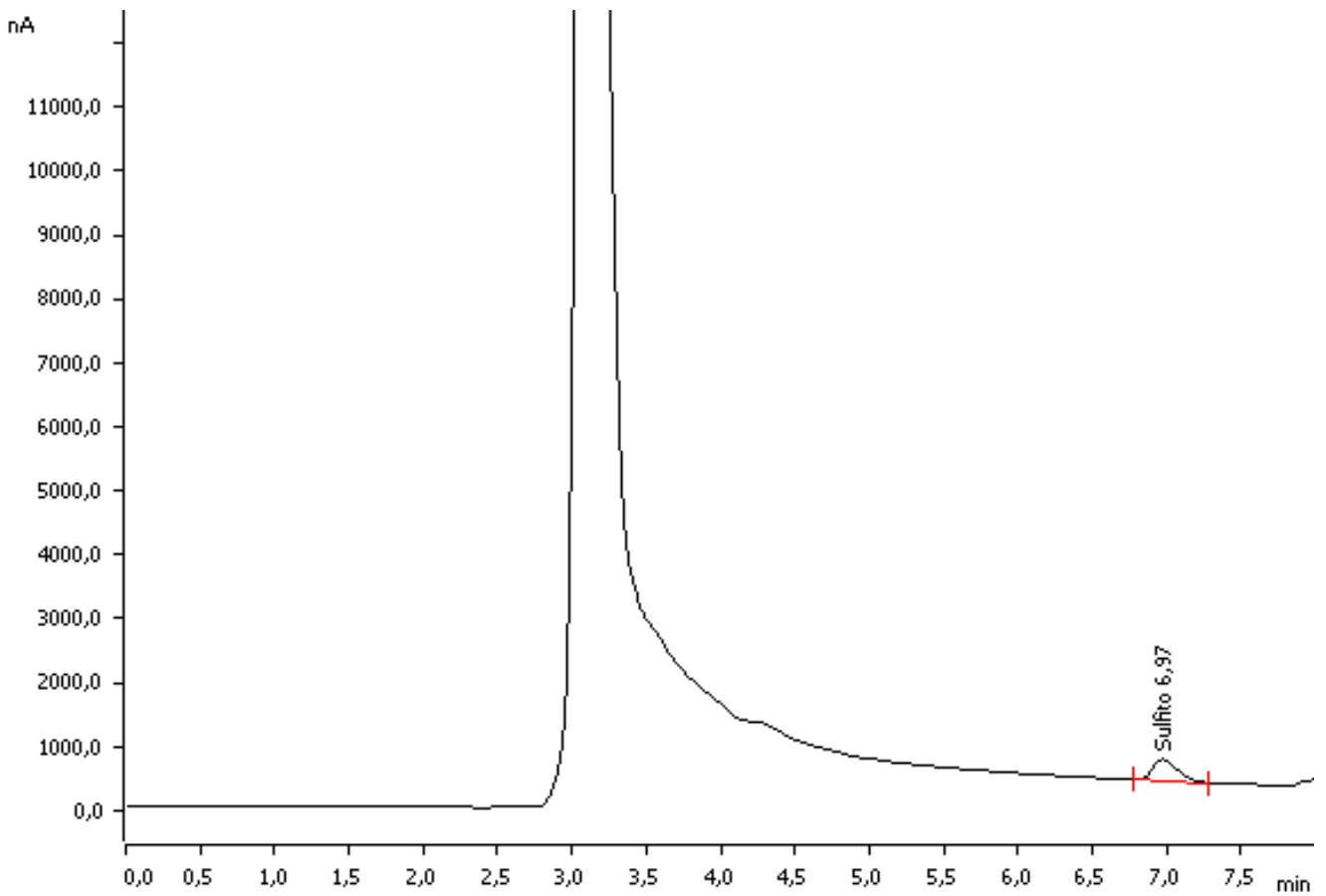


Fig 6. Cider Sample with Formaldehyde – Sodium Hydroxide stabilization solution

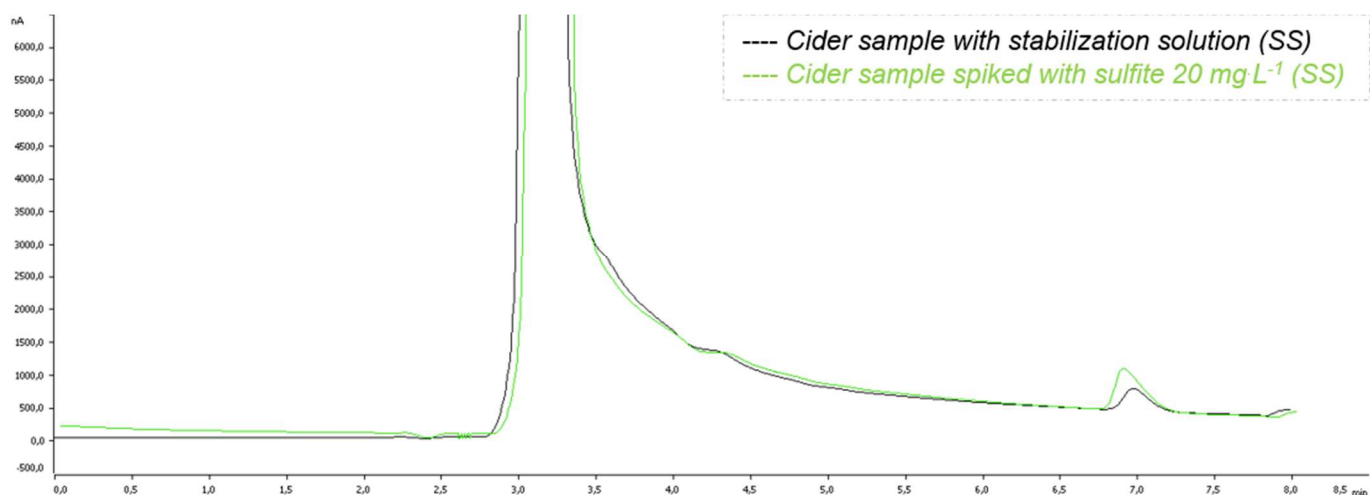


Fig 7. Overlay of Cider sample and Cider sample sulfite spiked with 20 mg.L⁻¹ with stabilization solution

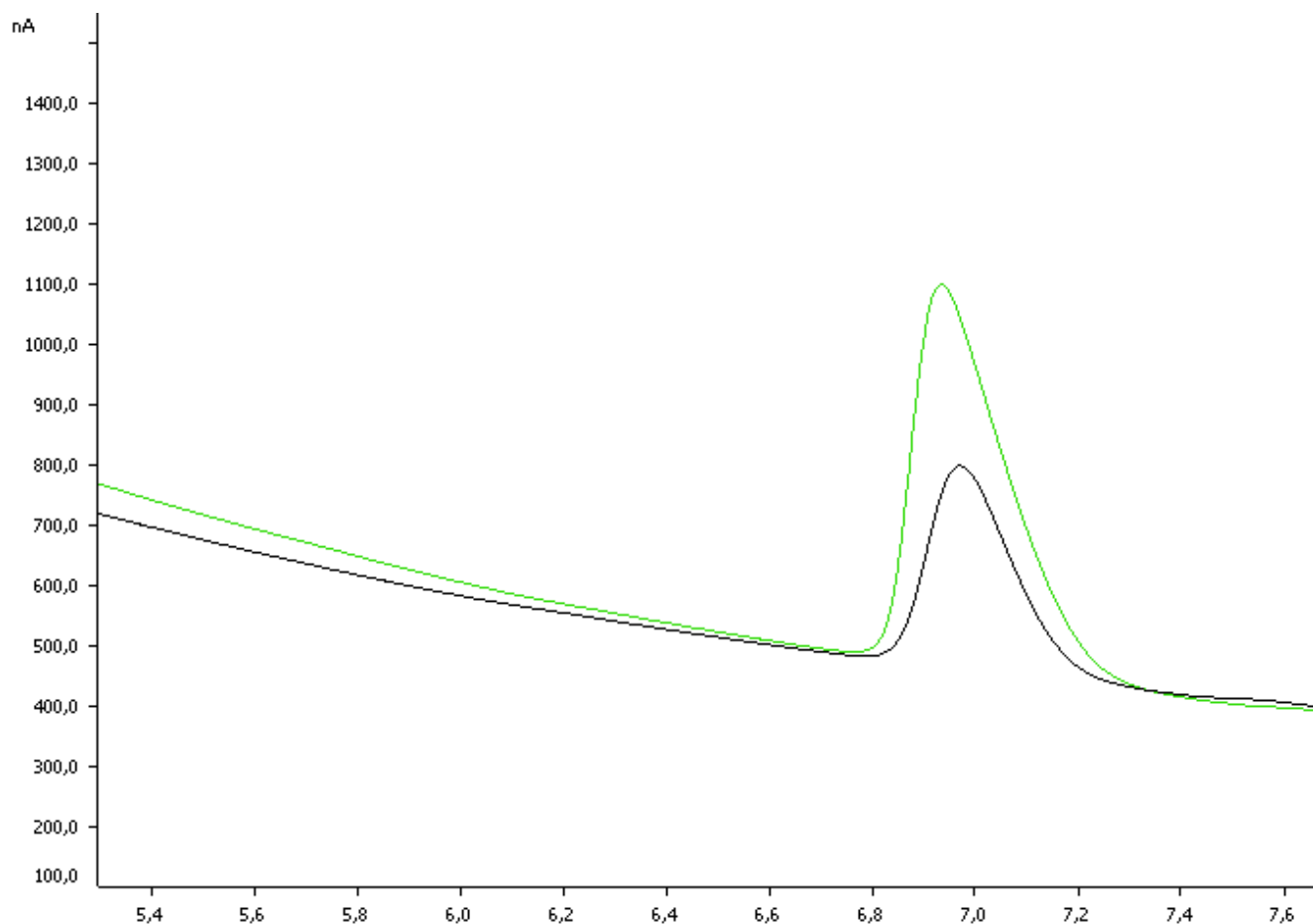


Fig 8. Magnified Overlay of Cider sample and Cider sample sulfite spiked with 20 mg.L⁻¹ with stabilization solution

Sample Results for 20 μ L of injection

Sample	Retention time min	Area (nA) x min	Concentration ppm Sulfite
Cider Sample	6,965	63,6201	18,336
Cider + 20 mg·L ⁻¹	6,865	131,5956	39,462
Cider + 40 mg·L ⁻¹	6,800	184,5955	57,315

Fig 9. *Table with results of Cider Sample and Cider sulfite spiked Sample*