

# Analytical methods update

## New method for detection of meta-tartaric acid

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# company profile

- GfL established 1984 / 25 people +1
- located in Berlin, Germany
- worldwide operating service laboratory for the entire fruit juice industry, raw material suppliers, traders, bottlers, retail, affiliated industry (enzymes, fining, flavour)



## company profile

- interpretation of regulations and approval of declarations
- evaluation and judgement according to guidelines, standards, literature and own findings
- authenticity analysis (foreign fruit, adulterations, illegal treatments,..)
- quality parameters and specifications
- contaminants (heavy metals, pesticides,..)
- approx. 10.000 samples per year / 100.000 parameters
- consultancy service through comprehensive know-how and according memberships

- SGF service laboratory, advisory board member
- IFU Analytical Commission
- TCJJP – Technical Committee of juice and juice products
- AOAC – Association of Official Analytical Chemists
- VdF (RSK group, legal committee, working group bases)
- GDCh – German Chemical Society (WG fruit juice)
- BLL – Bund für Lebensmittelrecht und Lebensmittelkunde
- DIN – German Institute for Standardization
- BfR – Federal Institute for Risk Assessment (Committee for Wine and Fruit Juice Analysis)
- AIJN Aroma expert group
- GDL – Association of German Food Technologists
- BOGK – German Association of the Fruit, Vegetable and Potato Processing Ind.
- Stiftung Warentest consulting committee and several others

# meta-tartaric acid



what is it and why analyse it?

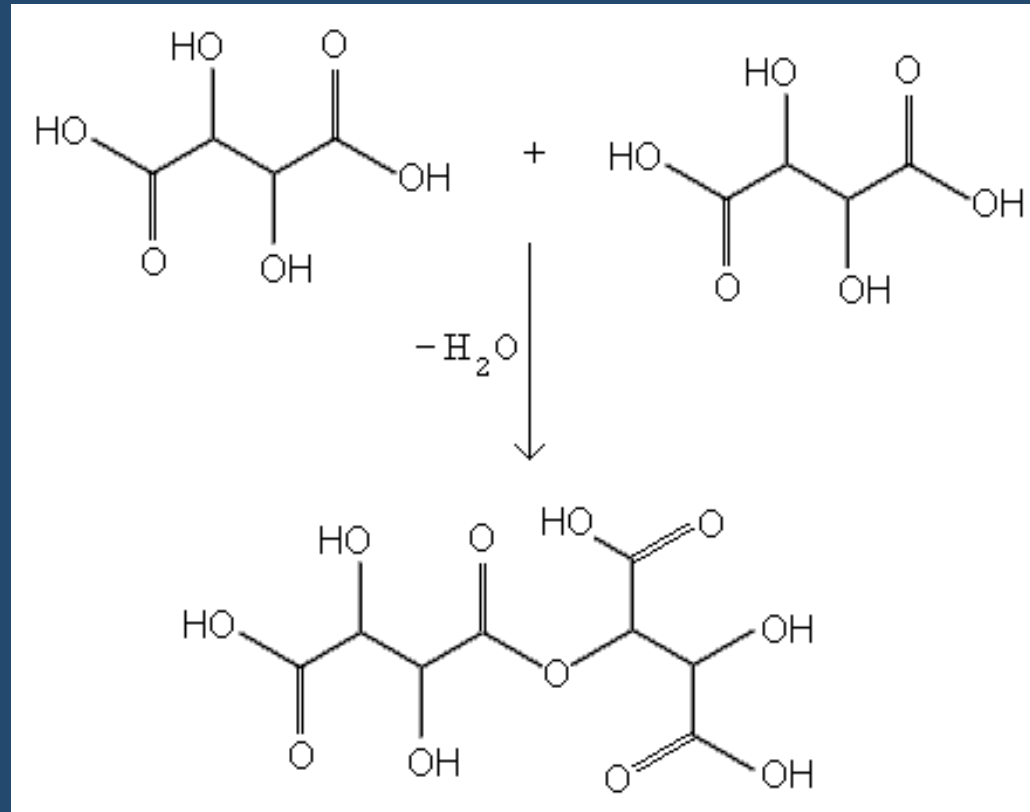
white crystalline, hygroscopic powder which can  
prevent tartar precipitation



## production

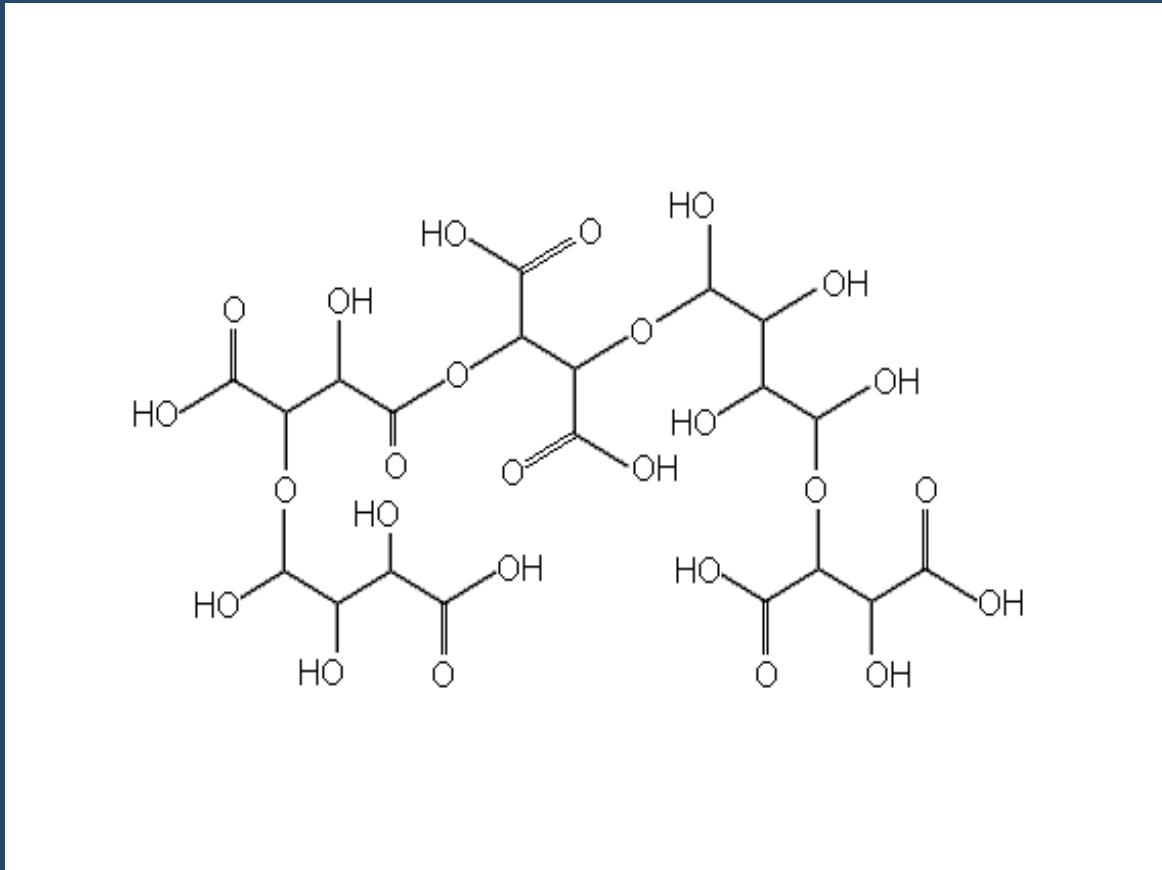
- heat tartaric acid to 170°C in dryness for several minutes / vacuum
- esterefication → polymerisation
- variation of the process will leed to different degrees of esterification
- technical product with no defined chemical structure

## Esterification of tartaric acid



the mass of a oligomer follows the function  $M = n \cdot 150 - (n-1) \cdot 18$   
for a possible ring formation another water has to be subtracted

## Theoretical structure of a tartaric acid pentamer



actual oligomer distribution and polymer sizes are not known

- stabilization is based on polymeres wich function as protective colloides and prevent clustering of tartar and formation of crystals
- recommanded dosage is approx. 100 mg/l
- classical stabilisation by cooling is in comparasion much more time consuming /expensive

## authorisation

- meta-tartaric acid is a legal additive (E353) acc. directive 95/2/EC which may be added to made wine and
- to wine acc. regulation EC 1622/2000
- in each case the maximum level is 100 mg/l
- but not permitted for grape juice

## analysis methods

### OIV-method MA-F-AS313-21-METTAR

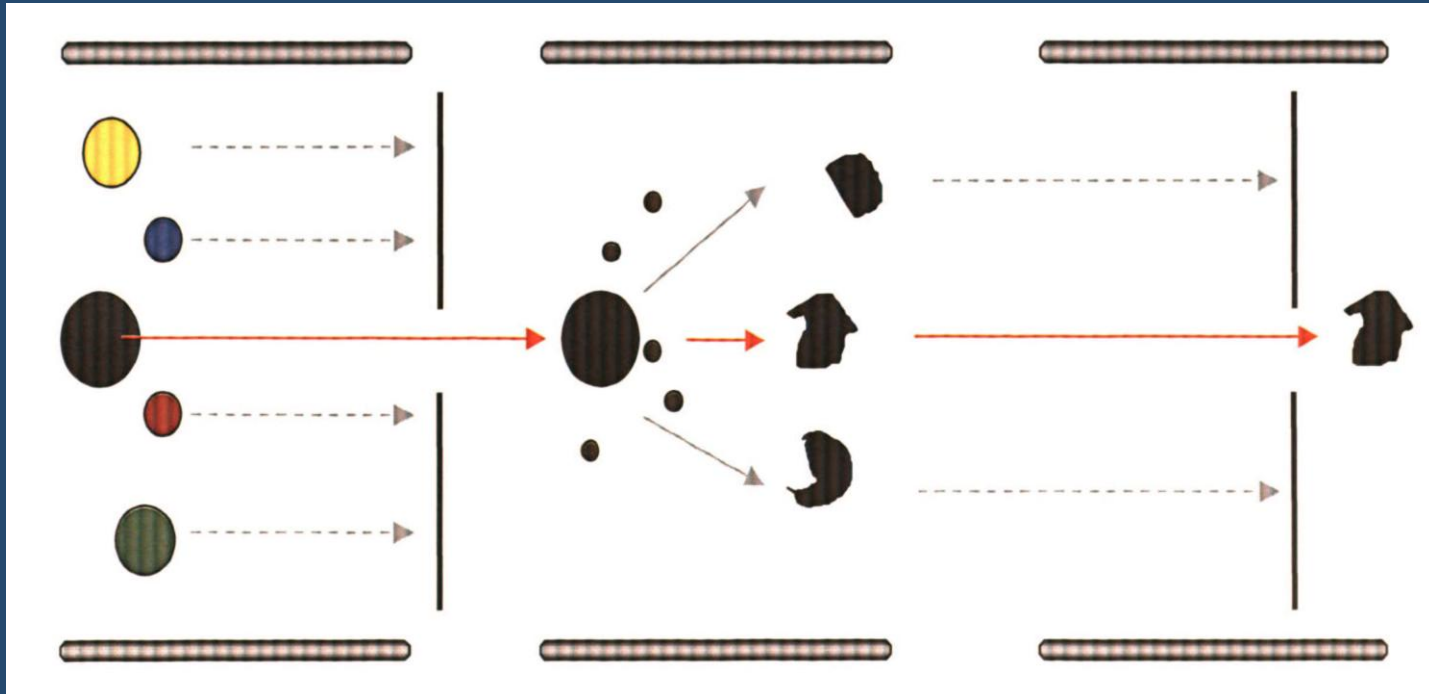
- precipitation of m-TA with Cd-acetate
- the precipitate is washed and dissolved by heat and NaOH
- by addition of ammonium vanadate an orange complex is formed (spectrophotometer absorbance at 530 nm)
- problems: false positive possible since tartaric acid can also precipitate, environmental aspects, safety at work

# meta-tartaric acid

TID-method, Cayotte et. Al, fl.Obst 9/2003, p.531ff /  
conductivity method / INRA method

- Tartaric instability degree with and without hydrolysis of meta-TA
- conductivity is measured while sample is cooled
- a tartar precipitation is enforced by potassium tartrate addition
- problems: not specific / indirect proof by stability
- natural stabilizing collides may lead to false positive results

## the theory of MRM



→ only the chosen mother/daughter combination gives a signal

## advantages over other methods

- can be used universally, no specific characteristics necessary (UV/fluorescence activity, ect.)
- most selective method / “no“ risk of false positive results
- in general very low LOD / favorable signal to noise ratio
- but molecules of interest must be known / no screening of unknown targets

## principle of the new method

- theoretical masses of tartaric acid oligomeres have been calculated
- sample clean up by weak anion exchange to separate sugars
- HPLC-MS/MS, ESI negative measurement

## clean up

- Bakerbond spe<sup>TM</sup> quarternary Amine column is conditioned with sodiumhydroxide and washed with water
- 10 ml of grape juice is put on the column
- meta-tartaric acid is eluted with formic acid
- eluate can be directly used for analysis

## HPLC conditions

- Agilent 1100 series
- column: Varian Hi-Plex H, strong cation exchange resin, oven temperatur 50°C
- mobile solvent: H<sub>2</sub>O + 0,5 ml CHOOH
- flow: 400 µl/min, injection volume 10 µl

## MS conditions

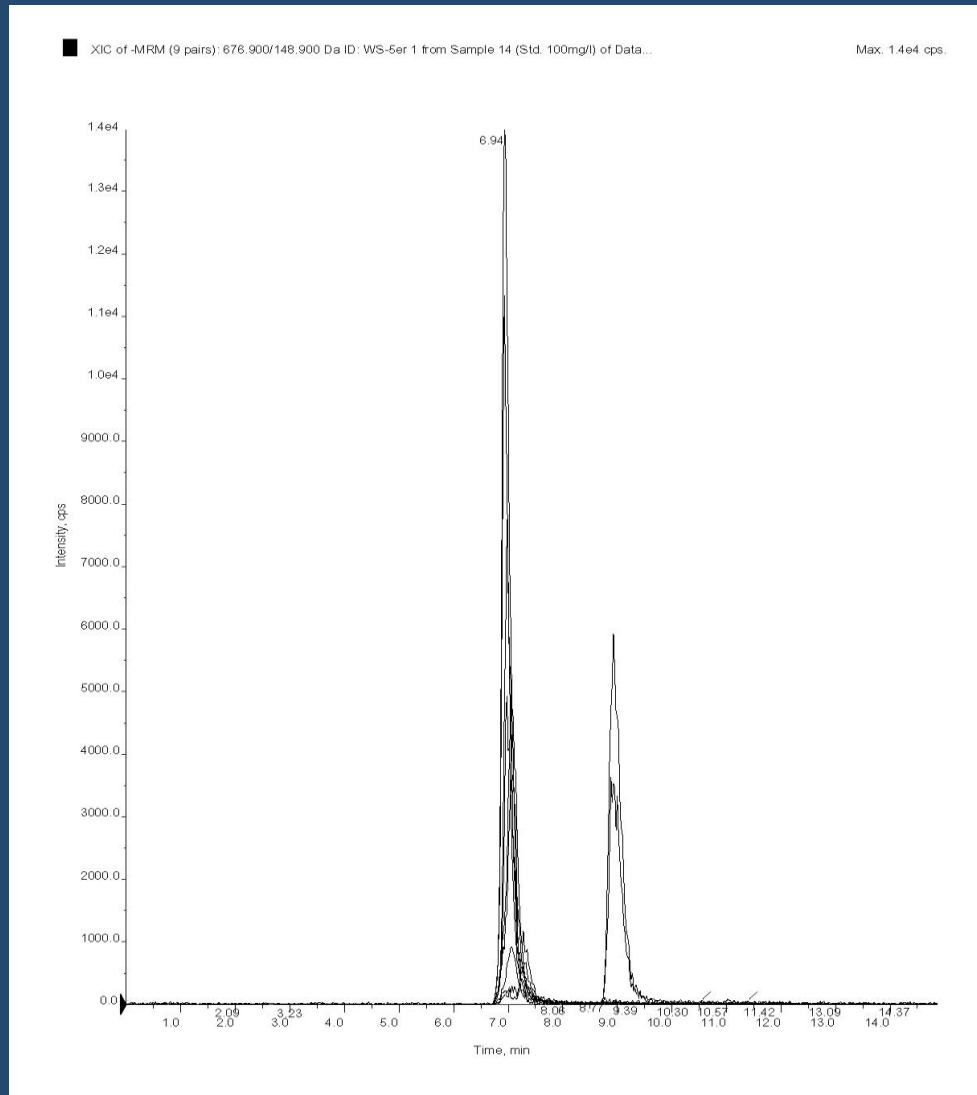
- API 3000
- source: ESI neg, -4200 Volt, turbogas 400°C
- multiple reaction monitoring (MRM) with following transitions

target	m/z Q1	m/z Q3
TA-n3	413,1	148,8
TA-n3	413,1	262,8
TA-n4	545,0	148,8
TA-n4	545,0	262,9
TA-n5	676,9	148,9
TA-n5	676,9	262,8

# meta-tartaric acid detection method



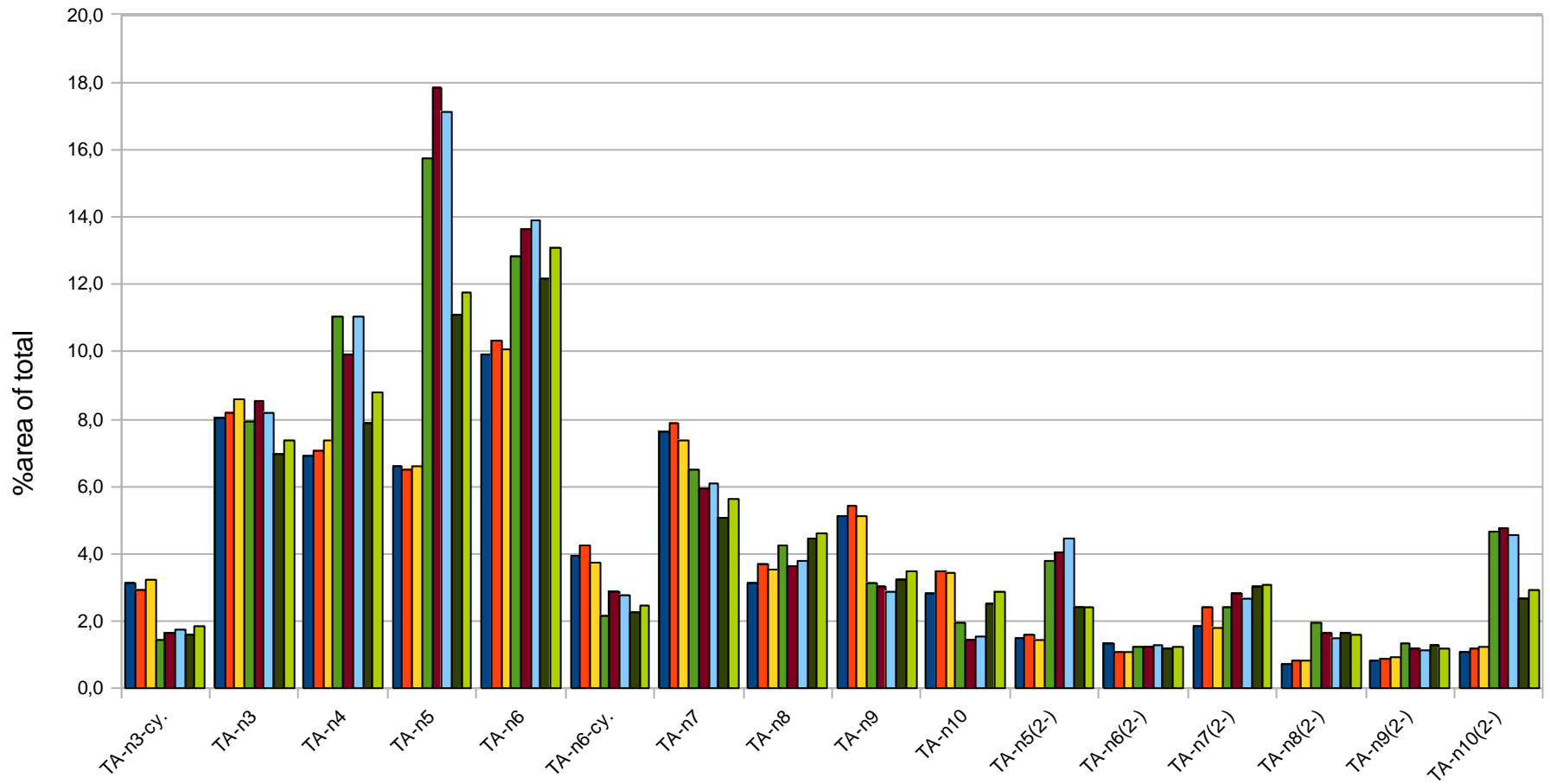
## Chromatogramm std.-solution 100 mg/l



# meta-tartaric acid detection method



different commercially available products (n=8)



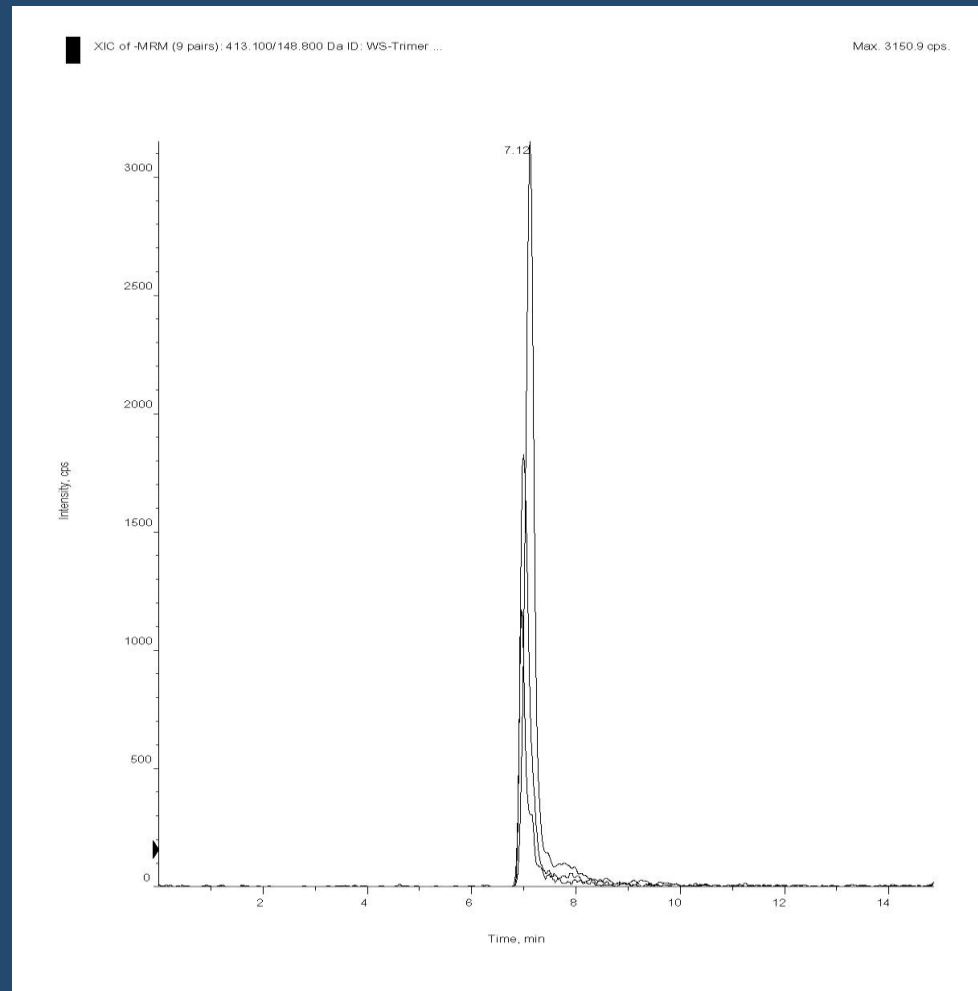
## validation

- 20 samples of red/white grape juice and concentrate analysed (origin Italy, France, Spain, Argentina, Greece) with no signal
- 4 samples of red/white wine
- lowest std-solution 5 mg/l, signal/noise ratio  $>100$  for all transitions
- stability tests are ongoing / commercial product clearly positive 6 weeks after bottling

# meta-tartaric acid detection method



- spiked red grape juice with 20 mg/l → LOD can be estimated with 10 mg/l



## summary

- a reliable analysis method has been developed for the definite detection of meta-tartaric acid
- LOD is suitable for the routine
- false positive results can be excluded
- stability in juice will need further investigation

Thanks to my colleague Dr. Fischbach, our Diplomastudent Mr. Lehner, Prof. Kroh from the Institute for Food-Chemistry at the Technical University of Berlin, the suppliers of meta-TA and

thank you for your attention

[www.gfl-berlin.com](http://www.gfl-berlin.com)