## Application Work AW US6-0249-062017

# Analysis of Chloride, Phosphate, Malate, Sulfite, Tartrate, Sulfate, and Oxalate in Red and White Wine

**Branch**

Food, stimulants, beverages, flavors

**Keywords**

IC; 940; Conductivity; Chloride; Phosphate; Sulfate; Sulfite; Malate; Tartrate; Oxalate; Anions; 858; MagIC Net 3.2; Metrosep A Supp 10-100/4.0; Ultrafiltration; Wine

**Summary**

Product consistency and quality is of utmost importance to winemakers. It is also critical to monitor and evaluate yeast performance and efficiency throughout the fermentation process. This wine analysis can aid vintners with ensuring predictable flavor and aroma characteristics in finished wine by monitoring common indicators of acidity, mouthfeel, and balance. It also evaluates nutrients and other additives which could potentially have deleterious effects on efficiency and production during the fermentation process. This application work shows the use of Metrohm IC to analyze red and white wine for chloride, phosphate, sulfite, sulfate, malate, tartrate, and oxalate. For this work, a Metrohm Professional IC with sequential suppression and conductivity detection was used in combination with the 858 Sample Processor with Ultrafiltration. The in-line Ultrafiltration protects the column and system components from particulates and ensures trouble-free operation. The rapid analysis enables high throughput laboratories to maximize production. Dosino regeneration and STREAM rinsing are used for the MSM.

**Reagents**

- Sodium Carbonate, CAS 497-19-8: Sigma Aldrich 223484-500G, 99.95 – 100.05%
- Sodium Bicarbonate, CAS 144-55-8: Sigma Aldrich S6014-500G, 99.7 – 100.3%
- Sodium Sulfite, CAS 7757-83-7: Sigma Aldrich 71989-250G, 98%
- Tartaric Acid, CAS 87-69-4: J.T. Baker 4104-01
- Malic Acid, CAS 617-48-1: J.T. Baker P494-07
- Oxalic Acid, CAS 144-62-7: Sigma Aldrich 658537-100G, 99.999% trace metals basis
- Perchloric Acid, CAS 7801-90-3: Sigma Aldrich 311421-50mL, 99.999% trace metals basis
- Sulfuric acid, CAS 7664-93-9
- Ultrapure water, resistivity >18 MΩ·cm (25 °C)
- Metrohm Individual Anion Standards, 1000 ppm
  - o Chloride, Metrohm USA ERA-IC1002
  - o Phosphate, Metrohm USA ERA-IC
  - o Sulfate, Metrohm USA ERA-IC1007

**Instruments**

| | |
|---|---|
| 940 Professional IC Vario ONE/SeS | 2.940.1400 |
| IC conductivity detector | 2.850.9010 |
| 858 Professional Sample Processor | 2.858.0020 |
| Sample Rack 148 place + 3 Special Beakers | 6.2041.440 |
| MagIC Net 3.2 | 6.6059.322 |
| Metrosep A Supp 10 - 100/4.0 | 6.1020.410 |
| 800 Dosino | 2.800.0010 |
| Dosing Unit 2 mL | 6.3032.120 |
| Ultrafiltration Equipment | 6.5330.110 |
| 20 µL sample loop | 6.1825.210 |
| MSM Rotor A | 6.2832.000 |
| Filtration Membrane, 0.2 µm | 6.2714.020 |
| Pump tubing LFL (yellow/yellow) | 6.1826.390 |
| Pump tubing LFL (black/black) | 6.1826.340 |


**Solutions**

**Eluent:** 5.0 mmol/L sodium carbonate + 5.0 mmol/L sodium bicarbonate + 5 µmol/L perchloric acid

**Regenerant for Suppressor:** 500 mmol/L sulfuric acid

**Samples**

Red wine

White wine

**Standards**

1000 ppm stock standards were used for all analytes. Sulfite, tartrate, malate, and oxalate stocks were prepared

from salts. Chloride, phosphate, and sulfate were prepared using commercially purchased standards.

Sulfite was calibrated separately due to sulfate contamination in the sodium sulfite salt. Sulfite stock standard was fixed with 10% isopropanol and working standards were fixed with 2% isopropanol in order to prevent oxidation of sulfite to sulfate.

In ultrapure water (ppm)

| | S1 | S2 | S3 | S4 | S5 | S6 |
|---|---|---|---|---|---|---|
| Chloride | 1 | 5 | 10 | 25 | 50 | 100 |
| Phosphate | 1 | 5 | 10 | 25 | 50 | 100 |
| Malate | 1 | 5 | 10 | 25 | 50 | 100 |
| Sulfite | 1 | 5 | 10 | 25 | 50 | 100 |
| Tartrate | 1 | 5 | 10 | 25 | 50 | 100 |
| Sulfate | 1 | 5 | 10 | 25 | 50 | 100 |
| Oxalate | 1 | 5 | 10 | 25 | 50 | 100 |

## Sample Preparation

Wine samples were gravimetrically diluted 1:10 and 1:50 in ultrapure water. Vial caps were used to minimize oxidation. Samples were then directly injected by the 858 with ultrafiltration.

## IC Parameters

| | |
|---|---|
| Anion eluent flow | 1.0 mL/min |
| Column temperature | 35°C |
| Injection volume | 20 µL |
| Anion $P_{max}$ | 20 MPa |
| MSM Rinsing | STREAM |
| MCS | On |
| Degasser | On |
| Recording Time | 20 minutes |

## Calculation

Automatic integration with MagIC Net 3.2 software using peak area for all analytes.

## Results

All results summarized in the appendix.

## Comments

This application may be deployed utilizing a 930 Compact IC Flex, and is also suitable for use with Metrohm's In-Vial Dilution Technique (MiVDT).

Acetate was not quantified and is shown in the sample chromatograms for identification purposes. If oxalate is not present, the run time may be slightly reduced.

## References

**AW US6-210-122014:** Metrohm In-Vial Dilution Technique (MiVDT) for Anions with Intelligent Dilution, Ultrafiltration, Analyte Delimiter Logic, and Eluent Production Module

## Date

June 14, 2017

## Author

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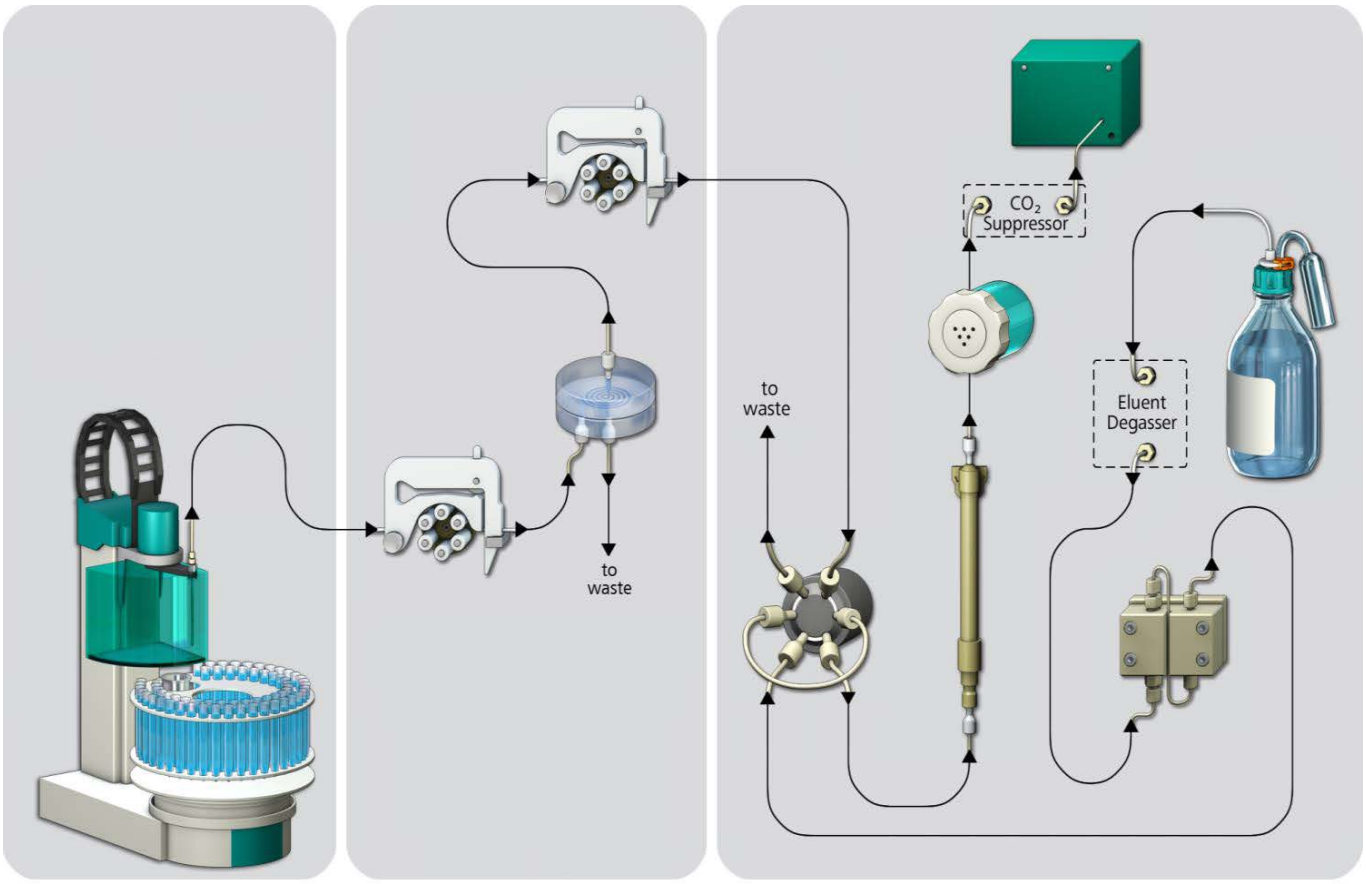
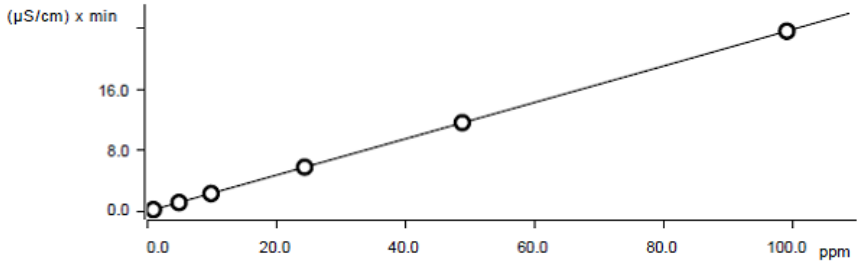
Metrohm USA Inc.

**Instrumentation Set-Up**



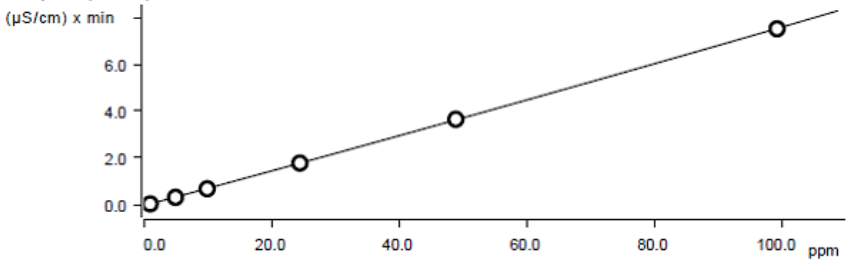
## Calibration Curves

**Chloride (Anions)**



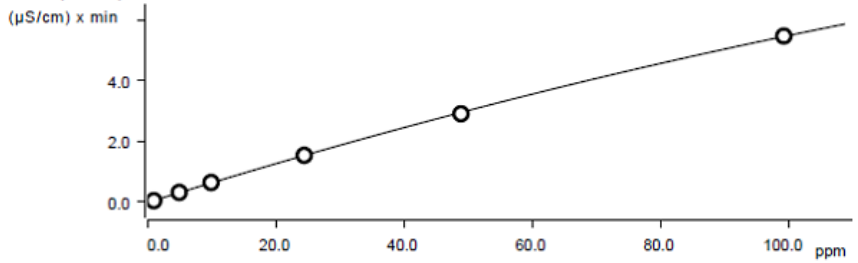

Function: . . . . . $A = -0.0264217 + 0.0118155 \times Q + 3.20010E\text{-}8 \times Q^2$
Relative standard deviation . . . . . *0.261555 %*
Correlation coefficient . . . . . *0.999999*

**Phosphate (Anions)**



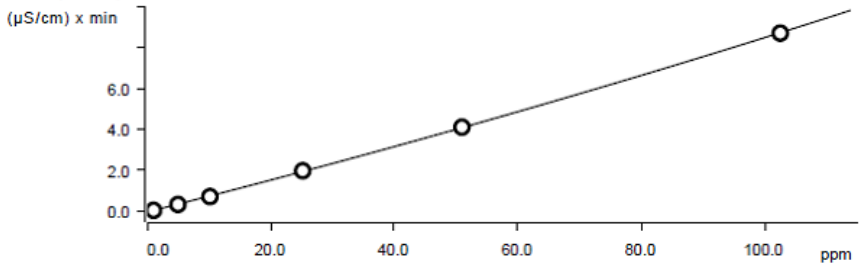

Function: . . . . . $A = -8.89112E\text{-}3 + 3.66144E\text{-}3 \times Q + 6.57402E\text{-}8 \times Q^2$
Relative standard deviation . . . . . *0.843057 %*
Correlation coefficient . . . . . *0.999985*

**Malate (Anions)**



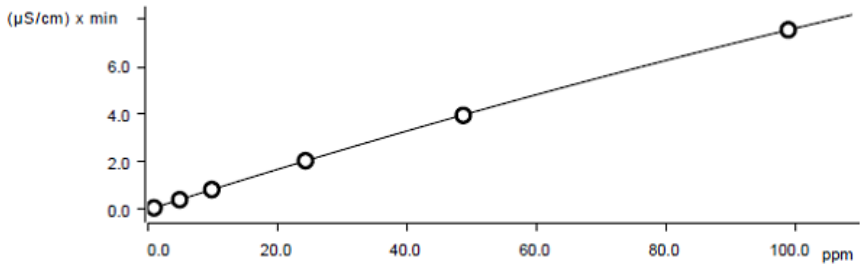

Function: . . . . . $A = -7.98903E\text{-}4 + 3.30240E\text{-}3 \times Q - 2.78528E\text{-}7 \times Q^2$
Relative standard deviation . . . . . *1.603212 %*
Correlation coefficient . . . . . *0.999939*

**Sulfite (Anions)**



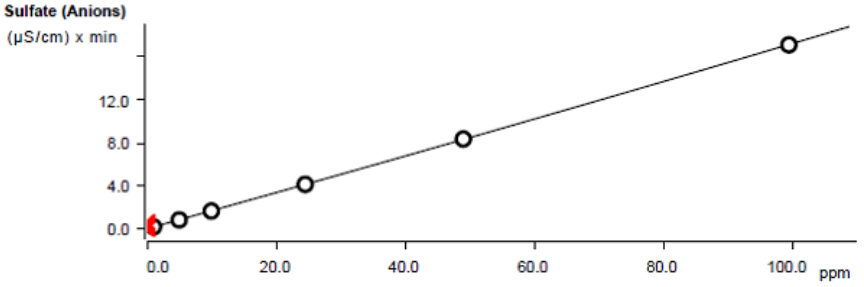

Function: . . . . . $A = -0.0340779 + 3.81770E\text{-}3 \times Q + 2.23093E\text{-}7 \times Q^2$
Relative standard deviation . . . . . *1.366768 %*
Correlation coefficient . . . . . *0.999964*

**Tartrate (Anions)**



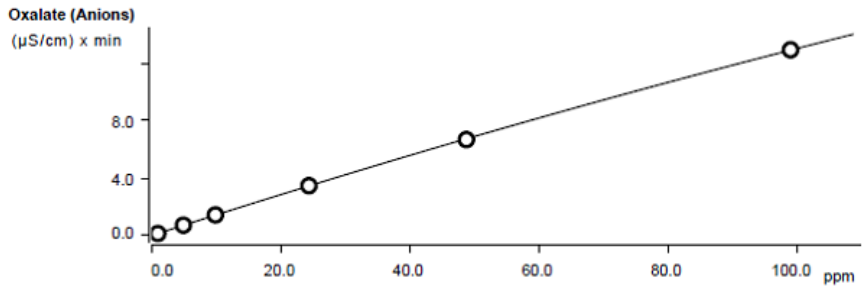

Function: . . . . . $A = -1.87955E\text{-}3 + 4.33315E\text{-}3 \times Q - 2.67851E\text{-}7 \times Q^2$
Relative standard deviation . . . . . 0.476093 %
Correlation coefficient . . . . . 0.999995

**Sulfate (Anions)**




Function: . . . . . $A = -0.0155494 + 8.35366E\text{-}3 \times Q + 1.34964E\text{-}7 \times Q^2$
Relative standard deviation . . . . . 0.621130 %
Correlation coefficient . . . . . 0.999992

**Oxalate (Anions)**




Function: . . . . . $A = -3.78364E\text{-}3 + 7.29359E\text{-}3 \times Q - 3.80156E\text{-}7 \times Q^2$
Relative standard deviation . . . . . 0.884738 %
Correlation coefficient . . . . . 0.999982

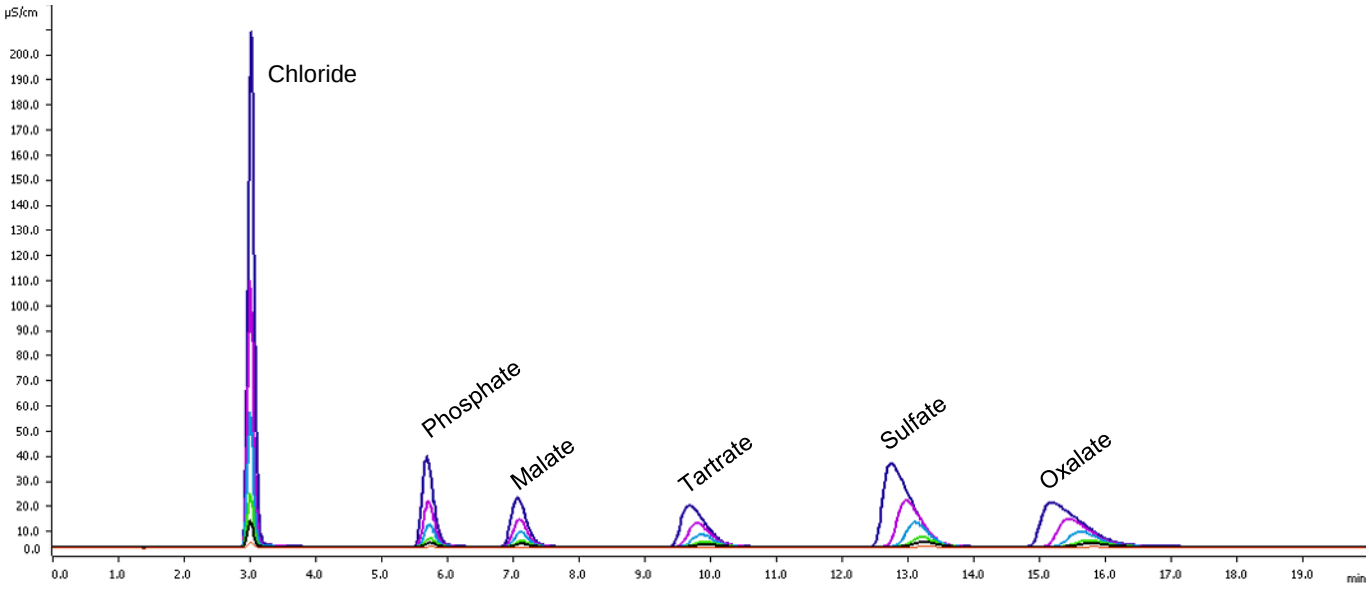
**Results**

| Red Table Wine (ppm) | Chloride | Phosphate | Malate | Sulfite | Tartrate | Sulfate | Oxalate | Dilution |
|---|---|---|---|---|---|---|---|---|
| Replicate 1 | 60.0 | 771.9 | 92.2 | 26.1 | 1754.5 | 553.0 | <10 | 10 (50 for tartrate) |
| Replicate 2 | 60.0 | 769.7 | 92.1 | 26.9 | 1754.9 | 553.0 | <10 | 10 (50 for tartrate) |
| Replicate 3 | 60.0 | 773.3 | 92.1 | 27.0 | 1757.5 | 553.0 | <10 | 10 (50 for tartrate) |
| Average | 60.0 | 771.6 | 92.1 | 26.7 | 1755.6 | 553.0 | <10 | |
| RSD (%) | 0.027 | 0.23 | 0.064 | 1.9 | 0.092 | 0.007 | | |

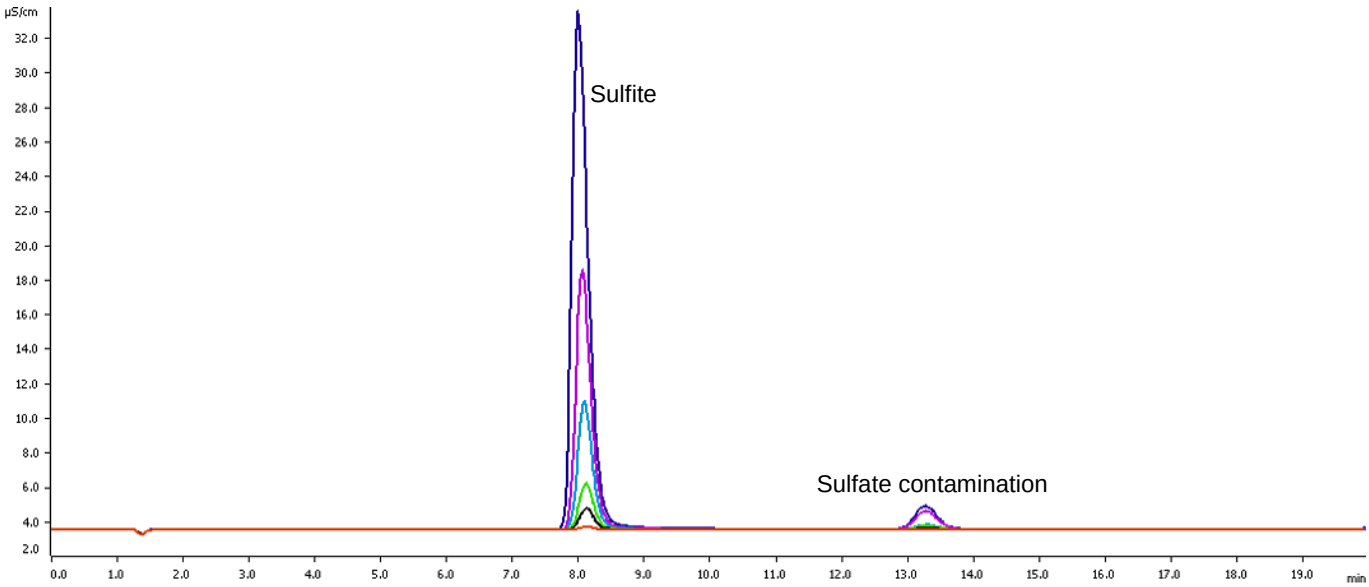
| White Table Wine (ppm) | Chloride | Phosphate | Malate | Sulfite | Tartrate | Sulfate | Oxalate | Dilution |
|---|---|---|---|---|---|---|---|---|
| Replicate 1 | 21.6 | 817.8 | 105.2 | 28.9 | 1529.8 | 366.7 | <10 | 10 (50 for tartrate) |
| Replicate 2 | 21.5 | 817.3 | 105.6 | 28.7 | 1544.0 | 366.7 | <10 | 10 (50 for tartrate) |
| Replicate 3 | 21.5 | 818.9 | 105.3 | 28.7 | 1528.8 | 366.7 | <10 | 10 (50 for tartrate) |
| Average | 21.5 | 818.0 | 105.3 | 28.8 | 1534.2 | 366.7 | <10 | |
| RSD (%) | 0.040 | 0.098 | 0.19 | 0.44 | 0.56 | 0.009 | | |

**Chromatography**

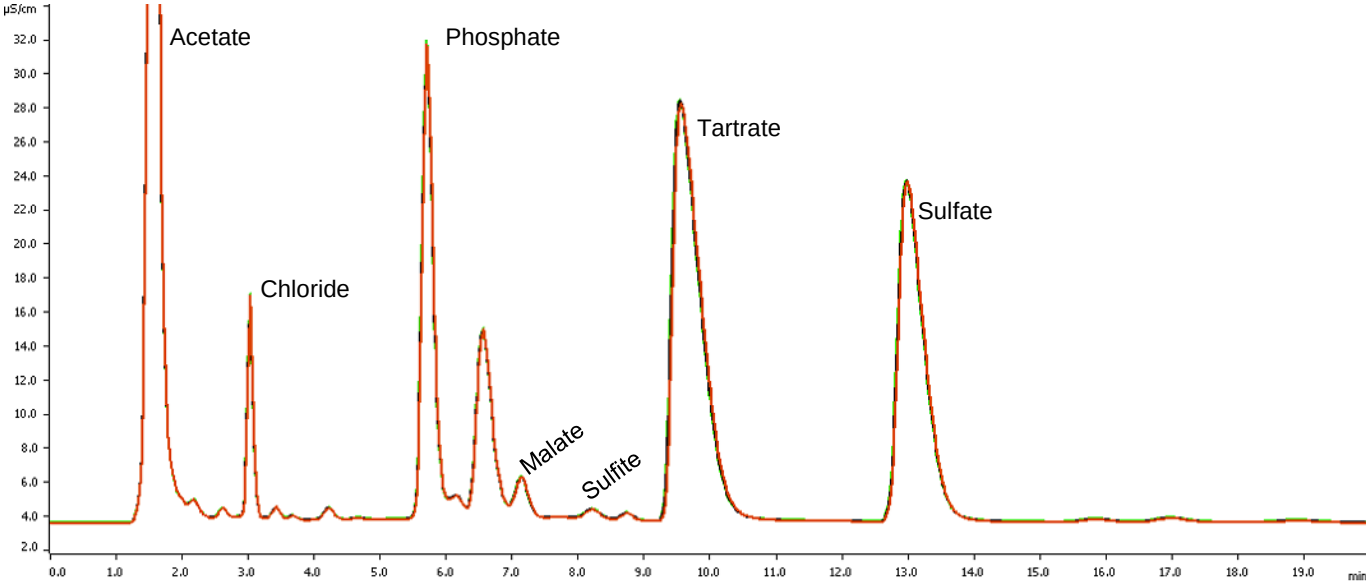
Calibration Standards, all analytes calibrated 1 – 100 ppm




Sulfite working standards prepared in 2% isopropanol

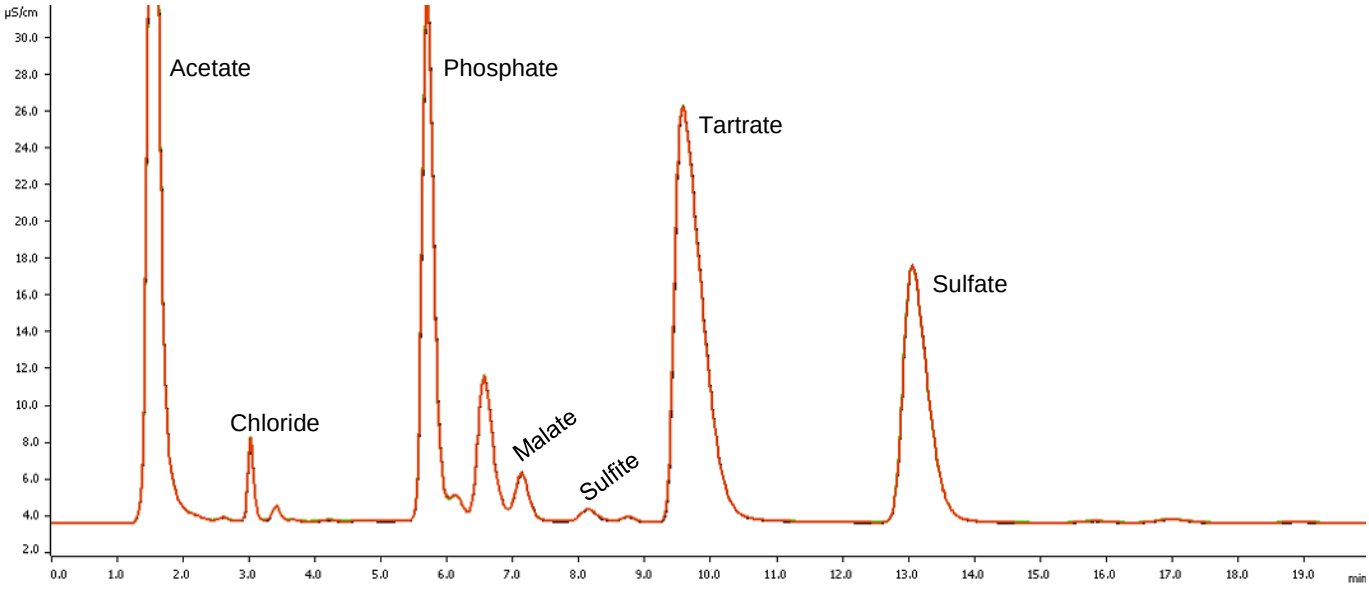


Red wine, 1:10 dilution, overlay of three injections




| Red Wine (ppm) | Chloride | Phosphate | Malate | Sulfite | Tartrate | Sulfate | Oxalate |
|---|---|---|---|---|---|---|---|
| Average | 60.0 | 771.6 | 92.1 | 26.7 | 1755.6 | 553.0 | <10 |
| RSD (%) | 0.027 | 0.23 | 0.064 | 1.9 | 0.092 | 0.007 | |
| Acetate not quantified. | | | | | | | |

White wine, 1:10 dilution, overlay of three injections




| White Wine (ppm) | Chloride | Phosphate | Malate | Sulfite | Tartrate | Sulfate | Oxalate |
|---|---|---|---|---|---|---|---|
| Average | 21.5 | 818.0 | 105.3 | 28.8 | 1534.2 | 366.7 | <10 |
| RSD (%) | 0.040 | 0.098 | 0.19 | 0.44 | 0.56 | 0.009 | |
| Acetate not quantified. | | | | | | | |