

CZE-ESI/QTOF-MS analysis of organic acids in red Vranec wines from different locations

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Introduction

Organic acids are important compounds influencing the stability, flavor, aroma and color of grapes and wine and contributing to the pH, chemical and microbiological stability of the wines. Main organic acids in wine are: tartaric, malic, lactic, succinic, citric and shikimic acids (Fig. 1). Therefore, monitoring during the whole vinification process: starting from the grapes juices, continuing to the alcoholic fermentation and wine stabilization processes, is necessary.

➤ The aim of the work was to evaluate the organic acids composition of Vranec wines produced in different wine regions in Republic of Macedonia, applying capillary electrophoresis hyphenated to mass spectrometry as well as an accurate-mass quadrupole time-of-flight mass spectrometer (QTOF-MS) [1].

Materials and methods

Wine samples: Vranec wines from different wine regions produced in experimental winery; grapes: 100 kg, traditional winemaking

Sample preparation: Wine diluted with deionized water (ratio 1:5), filtered with a 0.22 μm membrane filter (PVDF syringe filter, Nantong FilterBio Membrane Col, Ltd, China) and injected into the capillary electrophoresis system.

CZE-ESI/QTOF-MS instrumentation

➤ 7100 Capillary Electrophoresis (CE) system (Agilent Technologies, Waldbronn, Germany).

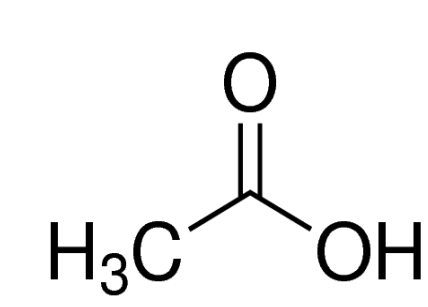
➤ Detection: 6530 Accurate-Mass Quadrupole Time-of-flight Mass Spectrometer (QTOF-MS) coupled to the CE instrument.

➤ Separation – Capillary: 80 cm x 50 μm internal diameter, fused-silica capillary (Polymicro Technologies, Phoenix, USA).

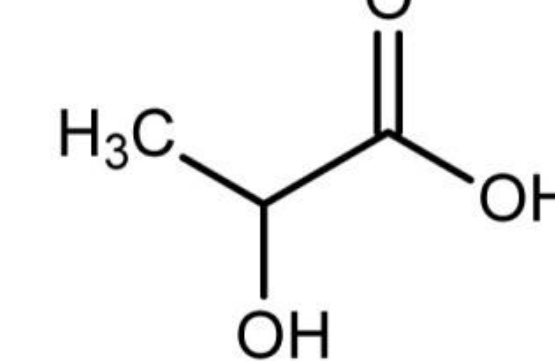
➤ 1% (v/v) solution of formic acid, sheath liquid

Chemical structure of organic acids in wine

a) Monoprotic acids

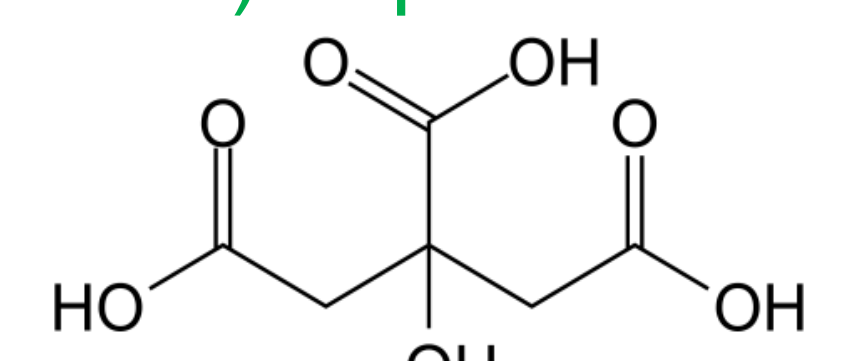


Acetic acid



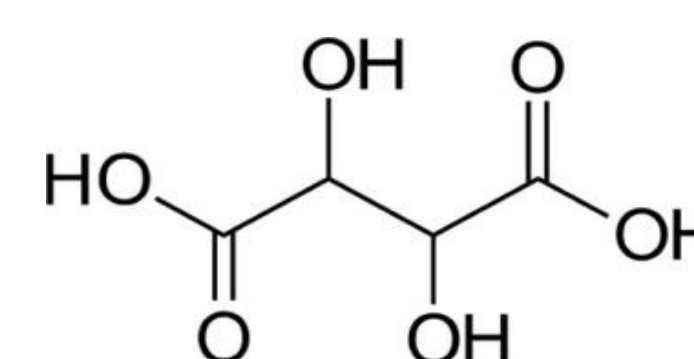
Lactic acid

c) Triprotic acids

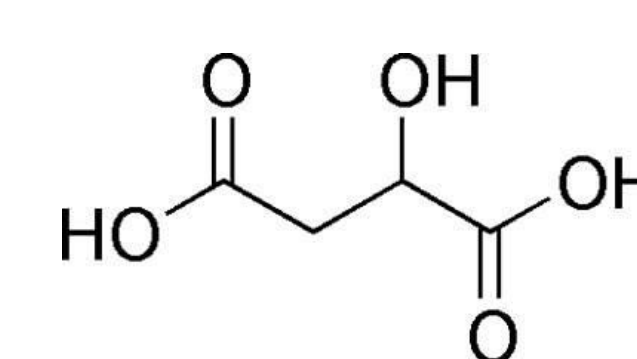


Citric acid

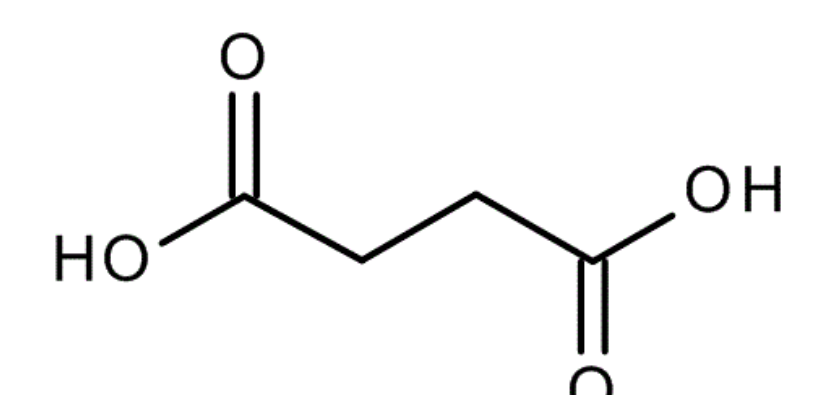
b) Diprotic acids



Tartaric acid



Malic acid



Succinic acid

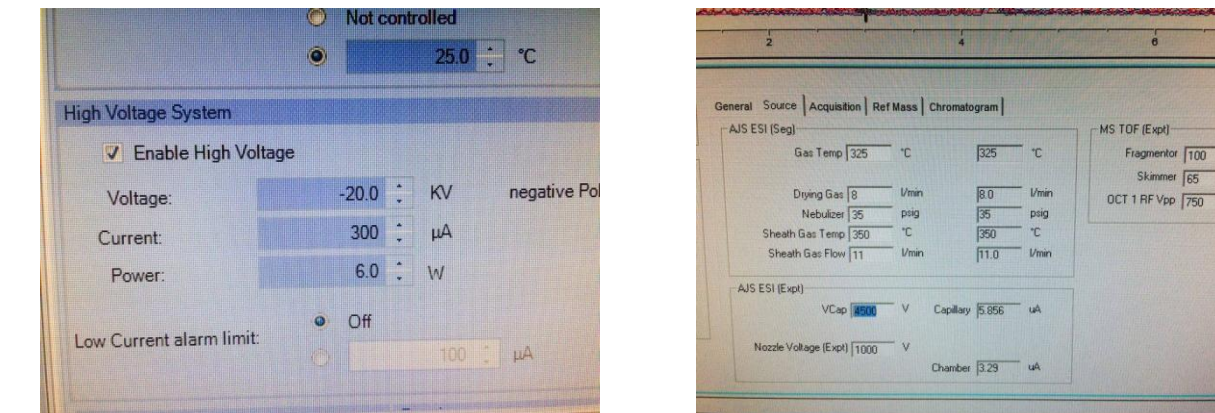
Vranec grapes



CZE-ESI/QTOF-MS



Working conditions

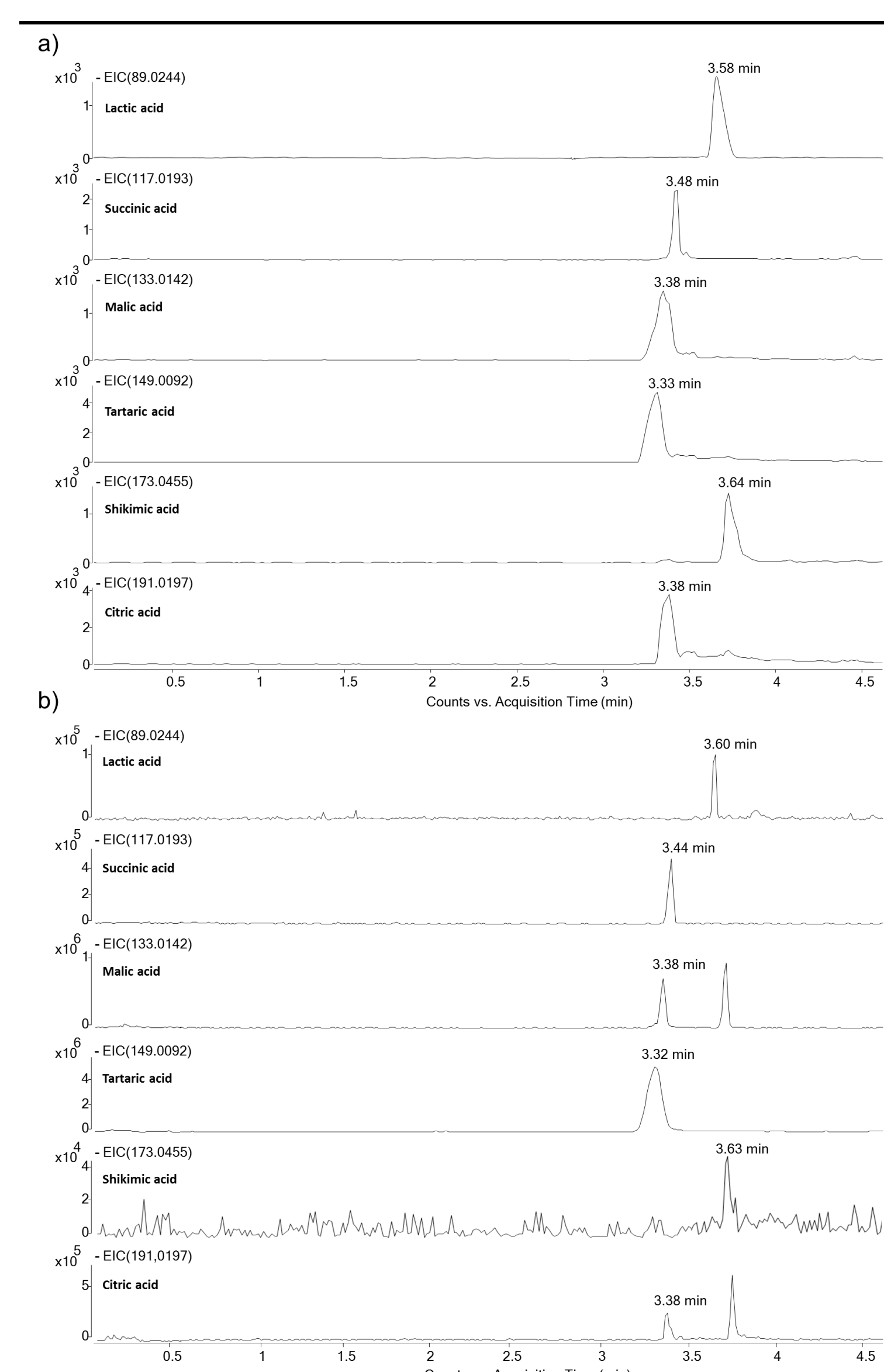


Vranec wines	Locality	Wine region
V1	Bistreni	Tikveš
V2	Barovo	Tikveš
V3	Demir Kapija	Tikveš
V4	Disan	Tikveš
V5	Drenovo	Tikveš
V6	Gradsko	Tikveš
V7	Krivolak	Tikveš
V8	Kurija	Tikveš
V9	Lepovo	Tikveš
V10	Manastirec	Tikveš
V11	Veles	Tikveš
V12	Vilarov	Tikveš
V13	Ridiste	Tikveš
V14	Štip	Tikveš
V15	Bitola	Bitola
V16	Gevgelija	Gevgelija-Valandovo
V17	Radoviš	Strumica-Radoviš

Results and discussion

Content of organic acids (mM) in Vranec wines

Wines	Tartaric (mM)	Malic (mM)	Lactic (mM)	Citric (mM)	Succinic (mM)	Shikimic (mM)	Total acids (mM)
V1	37.4±6.18	2.48±0.43	5.64±1.05	1.88±0.13	4.80±1.16	0.16±0.01	52.37±8.96
V2	28.2±4.94	0.51±0.03	10.9±1.73	4.77±0.23	6.36±2.43	0.12±0.01	50.94±9.36
V3	47.8±10.8	12.9±1.97	4.51±1.20	1.95±0.02	3.87±0.64	0.02±0.00	71.21±16.6
V4	33.1±6.74	9.49±1.71	3.01±0.75	5.44±0.34	3.58±0.29	0.08±0.00	54.74±9.83
V5	36.8±4.94	15.5±0.60	2.56±0.60	2.68±0.02	3.64±0.23	0.04±0.00	61.25±6.40
V6	31.5±3.03	17.5±3.16	1.80±0.60	4.30±0.34	4.51±0.29	0.31±0.04	59.90±7.47
V7	23.5±5.06	5.21±0.60	0.83±0.30	3.42±0.27	1.21±0.23	0.03±0.00	34.19±6.46
V8	44.0±6.52	14.2±0.60	2.63±0.83	1.74±0.07	4.10±0.40	0.08±0.01	66.80±8.42
V9	41.1±4.61	12.3±0.68	3.23±0.90	3.49±0.13	3.58±0.29	0.03±4.45	63.77±11.1
V10	55.7±9.21	7.26±0.43	2.71±0.38	2.82±0.13	4.22±0.40	<LOQ	72.74±10.6
V11	25.7±1.24	7.09±0.94	1.58±0.38	2.95±0.20	0.98±0.03	<LOQ	38.34±2.79
V12	41.8±4.04	22.9±1.20	1.50±0.60	2.42±0.07	3.24±0.40	0.11±0.02	72.06±6.33
V13	54.7±8.43	8.89±1.20	2.56±0.15	2.15±0.07	2.89±0.40	0.29±0.02	71.49±10.3
V14	29.3±2.47	34.4±5.30	2.78±0.68	5.10±0.27	4.22±0.46	0.02±0.00	75.89±9.18
V15	35.3±5.84	20.9±4.70	1.43±0.60	1.95±0.07	5.78±0.35	0.22±0.02	65.59±11.6
V16	32.7±6.40	11.9±1.37	1.65±0.45	5.97±0.40	2.49±0.46	<LOQ	54.78±9.09
V17	44.4±7.30	20.3±5.64	2.93±0.83	3.69±0.27	6.88±1.39	0.07±0.01	78.21±15.4



Conclusion

- ❖ wide variation of organic acids content
- ❖ relatively high concentration of tartaric acid, typical for this variety.



Extracted ion electropherograms of organic acids (a) standards (100 mgL⁻¹), and (b) the in Vranec wine V1