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ION-CHROMATOGRAPHIC FINGERPRINTING OF INORGANIC IONS FROM BLEEDING SAP IN *VITIS VINIFERA*

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Introduction

Water, minerals and other organic substances in the xylem are transported from the root system initially in the xylem, moving upwards; several studies have shown that grapevine xylem sap has a complex composition (it contains trace elements, sugars, organic acids, phenols, amino acids, etc.), but comprehensive data on major inorganic ions it has not yet been reported for the bleeding period. Since the xylem sap composition reflects the ability of roots to uptake water and nutrients from the soil, such investigations are important to elucidate the contribution of soil to plant nutrition, as well as in plant physiology (Bigard et al., 2020; Glad et al., 1992).

Research objectives

The aim of this work was to determine the xylem sap composition in major inorganic ions for different vines in order to obtain more information on the solutes transported by the xylem stream. The targeted analytes were sodium, ammonium, potassium, magnesium, calcium, chloride, nitrite, nitrate, phosphate and sulfate, all of these being analyzed in one run using parallel ion chromatography.

Materials & Methods

Biological material: 27 genotypes of *Vitis vinifera* grown on the experimental vineyard of the University of Agricultural Sciences and Veterinary Medicine Cluj Napoca: Big burgundy, Busuioacă de Bohotin, Cardinal, Coarnă albă, Coarnă neagră, Furmint, Gamay Beaujolais, Gamay Freaux, Gâmza de Varna, Grasă de Cotnari, Greaca, Muscadelle, Muscat Ottonel, Muscat timpuriu de Bucuresti, Napoca, Pink Silvaner, Pink Traminer , Pinot gris, Rayon d'or, Riesling of Rhine, Rkațâteli, Saint Emilion, Sangioveze, Șarbă, Someșan, Tămâioasă românească, Timpuriu de Cluj, Traminer d'ore

Sampling and sample preparation: bleeding sap from vines was collected in early spring in 0.5 L polyethylene flasks, then filtered through 0.47 μm membrane filters.

Ion chromatographic analysis was accomplished using a dual channel Prominence system (Shimadzu Corporation, Japan) in the following configuration: a DGU 20As online degasser, a LC-20AP solvent delivery module, an automatic sample injector SIL-10AF, a CDD-10Avp conductivity detector, a CTO-20A column oven, a FCV-10AH2 valve unit, and a CBM-20A system controller. Optimized chromatographic conditions derived from a previous research (Muntean and Mihaiescu, 2016) lead to baseline separations for five cations (sodium, ammonium, potassium, magnesium and calcium) using an Allsep Universal Cation 7u column (100 x 4.6 mm) and of five anions (chloride, nitrite, nitrate, phosphate and sulfate) on an Allsep Anion 7u column (150 x 4.6 mm), with isocratic elution in both cases (1 mL/ min flow rate of 3 mM methanesulfonic acid for cations and 2.5 mM p-hydroxibenzoic acid for anions), in a total run time less than 15 minutes. Quantifications were based on the external standard method; a summary of validation parameters is presented in tables 1 and 2

Data analysis: chromatographic data analysis was accomplished using LCSolution (Shimadzu), then data were subjected to descriptive statistics in Excel (Microsoft).

Table 1. Summary of validation parameters for the ion chromatographic method - cations

	Na^+	NH_4^+	K^+	Mg^{++}	Ca^{++}
Concentration range [mg/L]	0.5- 25	0.1 - 23	4 - 53	2 - 21	11 - 50
Limit of detection [mg/L]	0.12	0.15	0.28	0.25	0.31
Limit of quantification [mg/L]	0.36	0.45	0.84	0.75	0.93
Liniarity (R^2)	0.9983	0.9951	0.9879	0.9959	0.9986
Recovery [%]	93.71	98.05	89.02	93.25	95.72

Table 2. Summary of validation parameters for the ion chromatographic method - anions

	Cl^-	NO_2^-	NO_3^-	PO_4^{---}	SO_4^{--}
Concentration range [mg/L]	1.2- 54	1.3 - 22	1.5 – 35	1.1 - 21	1.5 - 52
Limit of detection [mg/L]	0.18	0.09	0.13	0.31	0.24
Limit of quantification [mg/L]	0.54	0.27	0.39	0.93	0.72
Liniarity (R^2)	0.9982	0.9985	0.9972	0.9762	0.9823
Recovery	96.38	92.19	89.02	91.15	85.71

Results

Chromatographic analysis revealed different fingerprints for the studied genotypes, depending on genetic factors; figure 1 depicts two representative cases with obvious differences in the cations''profile, but similar situations were encountered also in the case of ion chromatograms for anions (not presented here, due to the limited space)

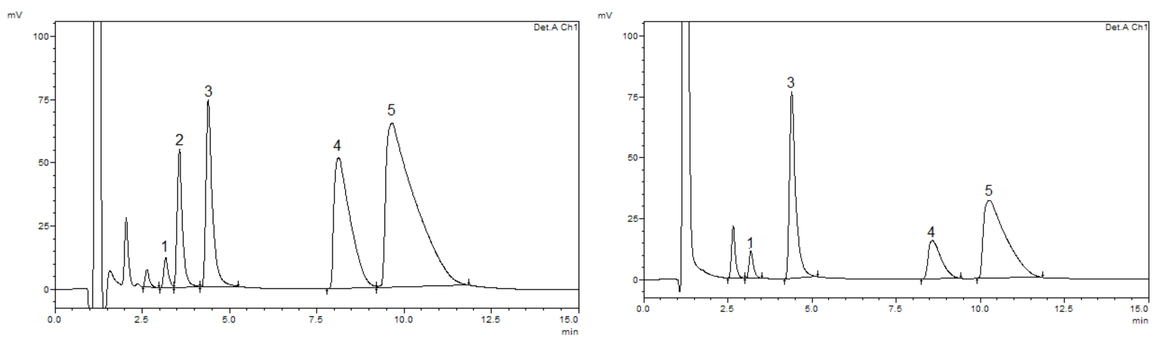

Figure 1. Ion chromatograms of major cations from two representative bleeding sap samples. Peak ID's: 1-sodium, 2-ammonium, 3-potassium, 4-magnesium, 5-calcium

The concentrations of the target inorganic ions recorded relative important variations (tables 3 and 4): the major cations were calcium (up to 254 mg/L) and potassium (up to 219 mg/L), while the anions were sulfate (up to 108 mg/L) and chloride (up to 41 mg/L).

Table 3. Descriptive statistics for major cations from *Vitis vinifera* [mg/ L]

	Na^+	NH_4^+	K^+	Mg^{++}	Ca^{++}
Min	0,51	0,47	7,53	8,44	30,49
Max	5,42	17,31	219,02	15,27	253,74
Average	2,83	3,87	58.21	7,95	82,36

Table 4. Descriptive statistics for major anions from *Vitis vinifera* [mg/ L]

	Cl^-	NO_2^-	NO_3^-	PO_4^{---}	SO_4^{--}
Min	2,11	3,09	4,50	9,26	8,37
Max	41,05	17,02	60,31	18,64	108,14
Average	10,07	5,29	29,12	12,36	27,59

Conclusions

- A simple, reliable, fast and sensitive method has been optimized for the simultaneous analysis of major inorganic ions from *Vitis vinifera* sap using ion chromatography, accomplished with a Shimadzu dual channel system with conductivity detection, enabling the separation of targeted analytes in less than 15 minutes.
- The analytical technique provides a basis for future physiology studies on inorganic ions' uptake.

References

1. *Bigard, A., Romieu, C., Sire, Y., & Torregrosa, L. (2020). Vitis vinifera L. diversity for cations and acidity is suitable for breeding fruits coping with climate warming. Frontiers in Plant Science, 1175.*
2. *Glad, C., Regnard, J. L., Querou, Y., Brun, O., & Morot-Gaudry, J. F. (1992). Flux and chemical composition of xylem exudates from Chardonnay grapevines: temporal evolution and effect of recut. American Journal of Enology and Viticulture, 43(3), 275-282.*
3. *Muntean, E., & Mihăiescu, T. (2016). Groundwater quality studies in two Transylvanian rural communities using parallel ion chromatography. Environmental Engineering & Management Journal (EEMJ), 15(12), 2, 2703-2708.*