

A simple analytical method for determination of ions in virgin olive oils by capillary electrophoresis with contactless conductivity detection

¹Maria A.T. Lemos (PG), ¹Ricardo J. Cassella (PQ), ²Dosil P. Jesus (PQ)

¹ Universidade Federal Fluminense; ² University of Campinas

¹ Instituto de Química, Universidade Federal Fluminense, Niterói, R.J., Brazil

² Institute of Chemistry, University of Campinas, Brazil, UNICAMP, P.O. Box 6154, 13083-970

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Introduction

The consumption of virgin olive oil (VOO) has been increasing worldwide, including Brazil, because of the health benefits due to this foodstuff. Thus, the monitoring of quality and integrity of VOO are of interest of its consumers. Presence of inorganic anionic species, such as chloride, nitrate, sulfate, and fluoride, might be beneficial or not, depending on their concentrations. Formate can be founded in VOO, owing to lipid oxidation, due to the deterioration of the oil¹. The mentioned anions are important in terms of nutritional, toxicological, and technological issues. The goal of this study was to separate and quantify the anions Cl⁻, NO₃⁻, SO₄²⁻, F⁻, and HCOO⁻ (formate) in VOO samples employing capillary electrophoresis with capacitively coupled contactless conductivity detection (CE-C⁴D).

Results and Discussions

The separation was performed using a silica capillary column with 60 cm in length (52.0 cm effective) and 75 μm i.d. The background electrolyte (BGE) was composed of 15 mmol L⁻¹ histidine, adjusted to pH 4.0 with lactic acid. Cetyltrimethylammonium hydroxide (CTAOH) was added (0.6 mmol L⁻¹) to the BGE as an electroosmotic flow modifier. The samples were hydrodynamically injected into the capillary by pressure (10 kPa) during 5 s. The separation potential was -20 kV and the C⁴D was operated at 610 kHz (sinusoidal) and 2.0 V (peak to peak amplitude). The extraction was conducted as described by Lemos et al.² with a few modifications. A mass of 10.0 g of VOO samples was used for the analysis of Cl⁻, NO₃⁻, SO₄²⁻, and F⁻, whereas for the determination of HCOO⁻, 1.0 g of sample was used. A 10 times diluted BGE solution (1 mL) was added to the samples, which were manually stirred (2 min) and then sonicated (15 min). In the sonication step, the samples were manually homogenized (3 times per minute). Finally, the aqueous extraction solutions were centrifuged (10 min at 4000 rpm), filtered, added internal standard (tartrate at 30.00 mg L⁻¹), and injected into a home-made CE-C⁴D equipment.

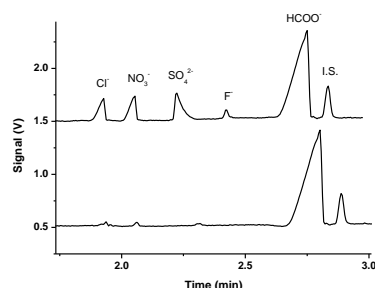


Figure 1. Electropherograms of the aqueous extraction solutions from (A) a non-spiked VOO sample and from (B) the VOO sample spiked with Cl⁻, NO₃⁻, SO₄²⁻, F⁻, and HCOO⁻ at concentrations of 3.55, 6.20, 9.61, 1.90, and 4.50 mg kg⁻¹, respectively. Tartrate was added (30.00 mg L⁻¹) to the extractions solutions as internal standard (I.S.).

The migration times (min) were: 1.93 ± 0.071 (Cl⁻), 2.06 ± 0.04 (NO₃⁻), 2.23 ± 0.04 (SO₄²⁻), 2.69 ± 0.05 (F⁻), and 2.69 ± 0.07 (HCOO⁻). The determination coefficients for the calibration curves varied from 0.9984 to 0.999. The detection and quantification limits ranged from 0.02 to 0.04 mg kg⁻¹ and from 0.01 to 0.7 mg kg⁻¹, respectively. The recovery tests were conducted in three different levels, and the results ranged from 70.2 to 118% with RSD varying from 0.7 to 19.4%. We found that formate was present in all analyzed VOO samples at concentrations higher than 1 mg kg⁻¹. This anion may be a chemical marker of the deterioration of the oil by oxidative processes.

Conclusions

The CE-C⁴D method demonstrated to be simple, rapid, and sufficiently accurate for the determination of the interested ions in VOO. As formate can be a chemical marker for oxidative processes in VOO, the proposed method can also be useful for studies of VOO deterioration.

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