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Determination of volatile phenols in wine using high-performance liquid chromatography with a coulometric array detector

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Abstract

A new high-performance liquid chromatography method using a coulometric array detector to simultaneously analyse 4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol, and 4-vinylguaiacol in wine was established. This procedure offers important advantages as it does not require sample preparation, with the exception of filtration, and performs chromatographic separation in short time, making control of wine production processes easier. The method is linear up to concentrations of 2000 $\mu g\,L^{-1}$ and precise (R.S.D. < 3%). Limits of detection are low (1–3 $\mu g\,L^{-1}$) and suitable for analytical requirements in the oenological field. When compared to gas-chromatography-flame ionisation detection, the proposed method gives similar results with a shorter execution time.
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Keywords: Wine; Vinylphenols; Ethylphenols; Electrochemical detector; Coulometric array

1. Introduction

In the wine production field, the term "volatile phenols"(VPs) usually means the group of compounds made up of 4-ethylphenol (4-EP), 4-ethylguaiacol (4-EG), 4-vinylphenol (4-VP) and 4-vinylguaiacol (4-VG). 4-EP was found in wine for the first time in 1969 by Webb [1], and its presence, together with the other phenols cited, was confirmed in 1970 by Dubois and Brulè [2]. VPs are usually present in wine in concentration varying from a few dozen to several hundreds microgram per liter [3,4], while amounts of a few milligram per liter can be observed more rarely in notably and irremediably defective wines. In fact, such compounds are liable to give sensory characteristics generally classified among the "off flavours" and described in general as phenolic, medicinal, pharmaceutical, smoky, spicy and clove-like [5,6]. 4-VP, even if under the sensory threshold, is deemed to negatively affect and mask the fruity scent of white wines [7,8] conferring odours resembling "band-aid" and gouache [9]. However, it can be considered less negatively, contributing, when combined with 4-VG, to the genista-like floral aroma of Chardonnay wines [10]. 4-VG contributes to the spicy note of Gewuertztraminer wines [11], as well as to the typical characteristics of some beers from Belgium and Bavaria, e.g. Lambic and Weizen [12,13]. 4-EF is liable to confer the odour defined as stable-, horse sweat-, leather-like [14], while 4-EG is also described as sweet [15]. Blends of ethylphenols in red wine give stable and animal-like odours [3].

Vinyl phenols are formed during alcoholic fermentation by *S. cerevisiae* strains able to decarboxylate the *trans* forms of *p*-coumaric and ferulic acids [4,16,17]. Ethyl phenols come from the enzymatic activities of decarboxylation of the cinnamic acids and subsequent reduction of vinyl phenols by the *Brettanomyces*/*Dekkera* genus' yeast [3], apart from very small quantities produced by *Lactobacillus plantarum* [18].

Technologically, the role of volatile phenols in commercial wines is remarkable, if one considers for instance that roughly one-third of the wines from a large sample in France had amounts of volatile phenols over the sensory threshold [4]. Analytically, GC equipped with flame ionization or mass spectrometric detector is the most commonly adopted approach for the quantification of volatile phenols, giving detection limits of a few microgram per liter and wide ranges of linearity of about three orders of magnitude [19,20]. Several extraction methods are used, i.e. liquide/liquide [3,11,18,19,21,22] and the most recent

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techniques solid phase extraction (SPE) [23,24], solid phase micro extraction (SPME) and head space-solid phase micro extraction (HS-SPME) [20,25–28], and stir bar sorptive extraction (SBSE) [29].

High-performance liquid chromatography (HPLC) with fluorimetric detection [30–33] has also been used to quantify volatile phenols after suitable sample extraction, although less extensively than gas chromatography (GC). The use of the coulometric electrode array (Coularray) system is reported in literature for HPLC analysis of simple phenolic constituents in natural beverages [34], but the analytes studied did not include "volatile phenols". As a result of its high sensitivity and selectivity this detector is applied more successfully in the biomedical field [35,36].

In this paper, we present a new HPLC-Coularray method for measuring 4-ethylphenol, 4-ethylguaiacol, 4-vinylphenol, and 4-vinylguaiacol in wine without any preparation of samples.

2. Experimental

2.1. Chemicals and reagents

Acetonitrile (ACN) (HPLC grade; VWR-International, Darmstadt, Germany), sodium monobasic phosphate (NaH_2PO_4) (98–102%; Carlo Erba Reagents, Rodano, Milan, Italy), phosphoric acid (H_3PO_4) (85%; VWR-International), methanol (MeOH) (HPLC grade; VWR-International) and HPLC grade water (Milli-Q system; Millipore, Bedford, MA) were used for the preparation of HPLC mobile phases. *n*-Pentane (HPLC grade; Carlo Erba Reagents) and methylene dichloride (HPLC grade; VWR-International) were used for the SPE procedure in GC analysis. 4-Vinylphenol (4-VP) (Aldrich Chemical Co., Milwaukee, MI), 4-vinylguaiacol (4-VG), 4-ethylphenol (4-EP) and 4-ethylguaiacol (4-EG) (Lancaster, Eastgate, White Lund, Morecambe, UK) were used as standards.

Salicylic acid, *p*-hydroxybenzoic acid, sinapaldehyde (Carlo Erba Reagents), caffeic acid, vanillic acid, ferulic acid (Roth, Germany), *p*-coumaric acid, protocatechic acid, tryptophol, tyrosol, eugenol (Fluka Chemical, Buchs, Swiss), sinapic acid, gentisic acid, 4-methyl guaicol, syringaldehyde, syringol, stearic acid, vanillin, umbellipheron, epicatechin (Sigma–Aldrich, Steinheim, Germany), gallic acid (VWR-International), siringic acid (Soc. D.ri Mascia-Brunelli Reagents, Milan), guaiacol (Lamberto Gallo Reagents, Milan, Italy) malvidin-3-monoglucoside (in home purification) [37] were used to evaluate method selectivity.

2.2. High-performance liquid chromatographic method

Two milliliters of wine were filtered with a 25 mm × 0.45 μm polytetrafluoroethylene syringe filter (Alltech, Deerfield, IL) and transferred without any additional preparation into a 2 mL glass screw-top vial. A HPLC 2695 Alliance system, controlled by an Empower Pro 2002 data station (Waters Corporation, Milford, MA) was used, equipped with an eight-electrode coulometric array electrochemical detector 5600 A and CoulArray for Windows 2.00 data processing module (ESA, Bedford,

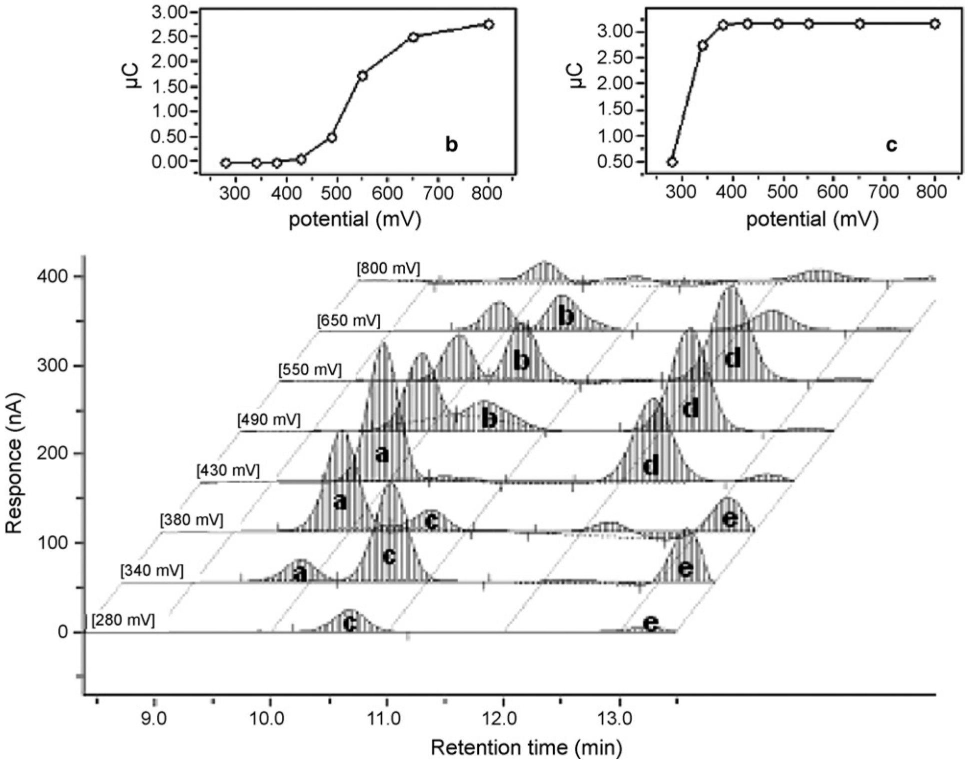

Fig. 1. Chromatographic separation of 4-vinylphenol (a), unknown compound (b), 4-vinylguaiacol (c), 4-ethylphenol (d) and 4-ethylguaiacol (e) in wine using eight electrodes. The hydrodynamic voltammograms of 4-vinylguaiacol and the unknown compound are also shown.

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