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Analytical Methods

Determination of free fatty acids in beer

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A B S T R A C T

Free fatty acids (FFA) content of beer affects the ability to form a stable head of foam and plays an important role in beer staling. Moreover, the presence of saturated FAs is related sometimes to gushing problems in beer. The aim of this research was to validate an analytical method for the determination of FFAs in beer. The extraction of FFAs in beer was achieved via Liquid–Liquid Cartridge Extraction (LLCE), the FFAs extract was purified by Solid Phase Extraction (SPE), methylated by boron trifluoride in methanol, and injected into GC-FID system. The performance criteria demonstrate that this method is suitable for the analysis of medium and long chain FFAs in beer. The proposed method was tested on four experimental beers.

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1. Introduction

Although free fatty acids (FFA) are quantitatively only minor constituents of beer their presence has long been considered to have adverse effects on beer quality. A stable foam is an important aspect of beer quality as perceived by the consumer (Segawa, Yamashita, Mitani, & Masachika, 2002). Beer contains foam-positive compounds (proteins and iso-α-acids) and foam-negative compounds (alcohols and FFAs). FFAs weaken the foam film by absorbing on the gas bubble surface or by interaction with foam-generating proteins. Moreover, the detrimental effect caused by the different FFAs is related to their surface absorption properties. Considering that the molecular hydrophobicity of the saturated FAs increased as chain-length increased and that the unsaturated FAs are more hydrophilic compared with the saturated with the same carbon-chain length (double bonds are more hydrophilic than single bonds). Therefore, an unsaturated FAs absorbs more weakly at the surface of gas-bubbles than a saturated FAs of the same chain length (Dickie, Cann, Norman, Bamforth, & Muller, 2001; Segawa et al., 2002).

Beer consists of many compounds (volatile and non-volatile) that affect beer flavor, many of these aroma compounds are synthesized by yeasts during fermentation, others derive directly from the raw materials. FFAs represent one group of these compounds that affect beer taste, and also the foam stability of beer (Bamforth, 1985; Clapperton, 1978; Horak et al., 2009; Meilgaard, Dalgliesh, & Clapperton, 1979). Medium-chain fatty acids such as hexanoic, octanoic, and decanoic acids, responsible for rancid or goaty flavor characteristics, are formed by yeasts during fermentation, and their formation is influenced by yeast strain, original gravity, wort composition, and degree of aeration (Horak et al., 2009). Off-flavors

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due to these acids normally arise from excess formation during fermentation and not for other causes such as infection or raw materials. Since the aroma contributions for medium-chain FFAs are additive, the rancid and goaty off-flavors can occur in beer even though none of the individual FAs are present above threshold concentrations (Horak et al., 2009). Long-chain unsaturated FAs, such as linoleic and linolenic acids, directly deriving from raw materials or from the yeast metabolism, are of great importance because their oxidative degradation may lead to the formation of a characteristic aging flavor (Bravi, Perretti, Buzzini, Della Sera, & Fantozzi, 2009; Horak et al., 2009; Kaneda, Kano, Kamimura, Osawa, & Kawakishi, 1990; Vanderhaegen, Nevin, Verachtert, & Derdelinckx, 2006) and, although their level is normally very low in beer, an unexpected increase, coupled with wrong storage conditions, can result in undesirable stale flavor (Vanderhaegen et al., 2006). Finally, saturated FAs, derived from both raw materials and yeast, seem to be related to the spontaneous over foaming (gushing) in beer (Carrington, Collett, Dunkin, & Halek, 1972; Christian, Titze, & Ilberg, 2011; Muller, Schmid, Becker, & Gastl, 2010).

Due to their involvement in different aspects of beer quality, simple and reliable methods for analyzing FFAs content and profile in beer are desirable. Both HPLC and GC method has been used for the determination of FAs in beer (Bravi, Perretti, Montanari, Favati, & Fantozzi, 2007; Irwin & Thompson, 1987; Kaneda et al., 1990; Kobayashi, Kaneda, Kano, & Koshino, 1993; Ng, 2002; Van der Meersche, Devreux, & Masschelein, 1979). Chromatographic methods for analyzing fatty acids required a sample preparation step. The extraction is a very critical step which often needs complex procedures resulting in low recoveries. In the past, the approaches to the problem of extraction and concentration of the FFAs in beer have been based on steam distillation (Irwin & Thompson, 1987; Van der Meersche et al., 1979) and liquid-liquid solvent extraction techniques (Chen, Jamieson, & Van Gheluwe, 1980; DeVries, 1990; Kaneda et al., 1990; Kobayashi et al., 1993; MacPherson & Buckee, 1974; Ng, 2002; Taylor & Kirsop, 1977). The steam distillation techniques are time-consuming and labor intensive. Liquid-liquid extraction procedures suffer from problems of emulsion formation, responsible for analyte loss; moreover, they are complex, time-consuming and labor-intensive and require large volumes of organic solvents. On the other hand, the extraction of samples with small volumes of solvent results in poor reproducibility and extractability of some FAs because of their low solubility in the solvent (Bravi, Benedetti, Marconi, & Perretti, 2014; Hawthorne, Jones, Barrett, Kavanagh, & Clarke, 1986; Horak et al., 2009).

Some authors developed more modern procedures, based on the use of solid-phase extraction (SPE). These procedures are quite easy and fast, if compared with the previously mentioned methodologies, reproducible and allow to minimizing solvent consuming. Battistutta, Buiatti, Zenarola, and Zironi (1994) reported on the developed of a method for the determination of medium chain FAs in beer by SPE, thus excluding the long chain FAs which are also potentially dangerous for beer flavor. Schutz and Back (2005) developed a method for the analysis of long chain FAs by SPE, thus excluding the medium chain FAs (potentially dangerous for beer flavor and foam). Other authors (Horak, Culik, Jurkova, Cejka, & Kellner, 2008) reported on the Stir Bar Sorptive Extraction (SBSE) of medium chain FAs in beer, thus excluding the long chain ones. Moreover, low recoveries of short chain FAs and an interference by ethanol concentration of beer, that could reduce the versatility of the method, were observed. Horak et al. (2009) discussed the advantages and the limitations of three different extraction methods (SPE, used as reference, SPME, and SBSE) for the determination of FFAs in beer. For all the three methods, the medium chain were determined as free fatty acids while the long chain as methyl esters, so two run into GC-FID system were needed. The SPME is limited because allows only the determination of medium chain FAs, the SBSE is a time-consuming procedure, the SPE technique is quite fast and lead good recoveries and reproducibility. Nevertheless, no validation procedure was carried out and the suitability of the method for the quality control for the brewing process and the assessment of the final product quality not guaranteed.

In order to determine low amounts (ppm) of FFAs in a aqueous matrix, such as beer samples, the development of a simple, accurate and efficient extraction method which avoids emulsion formation and which allows the simultaneous extraction of a wide range of fatty acids (with different chain length) is required. The same authors reported on the development of a method for the determination of medium and long chain FFAs in beer wort using a sorbent assisted liquid–liquid extraction (by the use of the inert support of ChemElut cartridges) that, avoiding emulsion formation, facilitate efficient extraction of small amount of FFAs. In order to evaluate the quality and to predict the stability of beer, by modifying the method developed for the beer wort, the authors developed and validate a reliable method for the quantification of FFAs in beer. The proposed method was tested on four experimental beers.

2. Experimental methods

2.1. Materials

The unmalted and the flocked *T. monococcum* (emmer), variety Monlis, both dehulled, samples were supplied by Prometeo srl (Urbino, Italy).

Twenty commercial beer samples of the same brand and batch were purchased from local market and were used for the development and validation of the method. Beer experimental samples were supplied by CERB (Italian Brewing Research Centre, University of Perugia) and were used to test the developed method. Amber beer sample (AB) was obtained using a mixture of different malts, 80% of Pilsner, 15% of Carared®, and 5% of Caramunich® (Weyermann, Germany); blond beer sample (BB) was obtained using 80% of Pilsner, 10% of Carapils®, 5% of Carahell® (Weyermann, Germany), and 5% of crude wheat (Prometeo srl, Italy); an emmer beer sample (EB) was obtained using 75% of Pilsner, 15% of Carapils® (Weyermann, Germany), and 10% of crude emmer (Prometeo srl, Italy); finally, an emmer malt beer (EMB) was obtained using a mixture of two malts obtained by experimentally malted emmer, 95% of Pils emmer and 5% of Caramel emmer. Emmer was malted in an automatic micromalting system from Custom Laboratory Products (Scotland) following the procedure described by Mayer, Marconi, Perretti, Sensidoni, and Fantozzi (2011).

Two liters of each experimental beer sample were use for the application of the developed method, all the experimental beer samples were unfiltered.

The experimental beer samples were prepared as follows: mashing was performed in a 110 L pilot plant and was carried out on by infusion for all the considered beer samples.

For AB the temperature profile of mashing was as follows: (i) first steady-state at 52 °C for 5 min, (ii) first rise of temperature from 52 to 65 °C in 12 min, (iii) second steady-state at 65 °C for 46 min, second rise of temperature from 65 to 72 °C in 8 min, (iv) third steady-state at 72 °C for 20 min, (v) final rise from 72 to 76 °C in 5 min, and final steady state at 76 °C for 5 min.

For BB the temperature profile of mashing was: (i) first steady-state at 52 °C for 10 min, (ii) first rise of temperature from 52 to 65 °C in 13 min, (iii) second steady-state at 65 °C for 44 min, second rise of temperature from 65 to 72 °C in 7 min, (iv) third steady-state at 72 °C for 20 min, (v) final rise from 72 to 78 °C in 10 min, and final steady state at 78 °C for 3 min.

For EMB the temperature profile of mashing was as follows: (i) first steady-state at 52 °C for 30 min, (ii) first rise of temperature

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