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Original Research Article

A new HPLC method for simultaneously measuring chloride, sugars, organic acids and alcohols in food samples

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ABSTRACT

This paper introduces an original, rapid, efficient and reliable HPLC method for the accurate and simultaneous quantification (g/L) of chloride in samples containing sugars, organic acids and alcohols. Separation was achieved using a HI-Plex H column at 35 °C, with H_2SO_4 (0.005 N) as the mobile phase at a flow rate of 0.4 mL/min. The column effluent was monitored by a Refractive Index (RI) detector. A linear response was achieved over NaCl concentrations of 0.25–2.5 g/L and 5–40 g/L. The analytical method inter- and intra-run accuracy and precision were better than ±10.0%. Investigating the mechanism of detection using different chloride and sodium s reviled that this method can be used for determining the total concentration of chloride salts when in suspension. This method was successfully applied to 15 samples of commercial food products and the salt content obtained from this method was compared with 3 other methods for salt determination. The (HI-Plex H) column was designed for determining the concentrations of sugars, organic acids and alcohols when in solution. Hence, application of our new methodology would allow the determination of sugars, alcohols and organic acids in samples derived from seawater-based fermentation media as well as samples from salty food and dairy products.

1. Introduction

Sodium chloride (NaCl) is a common flavour and preservative component present in many food products such as cheeses, butter and pickles. Also media used in fermentations could contain high salt concentrations as seawater has been suggested as an alternative to the use of freshwater in some fermentations such as bioethanol production (Lin et al., 2011; Zaky et al., 2014). Hence, there is a need for an accurate and rapid method for NaCl determination during the manufacturing processes.

Classical titration methods, Mohr (Doughty, 1924) and Volhard (modified) (Schales and Schales, 1941), which are based on the use of silver nitrate ($AgNO_3$), are still widely used for the determination of NaCl (Leong et al., 2014; Rajković et al. 2010). However, those methods are associated with several limitations such as: a) time consuming, b) results are sensitive to the pH and the presence of heavy metals in the sample, c) they can have false end points, d) difficult to automate, and e) the safe disposal of silver compounds after testing (Wolfbeis and Hochmuth, 1984). Silver nitrate is considered as a very toxic and corrosive compound even at very low concentrations (Zhao and Wang, 2011). Hence, the chloride analyser has been suggested as a method, this is a rapid test but still requires $AgNO_3$ to operate (Johnson and Olson, 1985).

In general, use of HPLC is a convenient and accurate analytical method suitable for a variety of samples including the quantification of organic and inorganic compounds. However, obtaining an accurate quantification of NaCl using HPLC in samples containing sugars has proven difficult due to similar retention times for Cl^- and sugars especially glucose and sucrose (Sims, 1995). As those two sugars are most abundant in food products, the use of HPLC for measuring sugar content is limited in many food samples because they contain salt. In addition, the hydrolysis of cellulosic materials

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to monomeric sugars for second generation biofuel generates a considerable amount of salt during the neutralisation, so using HPLC for sugar quantification requires a method that separates sugars from salts in order to obtain an accurate analysis for both sugars and salts.

Chromatographic methods are the best analytical techniques for the quantification and identification of mono and oligosaccharides in food products (Duarte-Delgado et al., 2015). In fact, HPLC is the preferred method for sugar quantification according to the guidelines of the Association of Official Analytical Chemists (AOAC, 1993; Sims, 1995).

During HPLC analysis of a bioethanol fermentation sample, an unexpected peak appeared with a retention time (R_t) of 10.90 min (Fig. 1). The fermentation experiment was carried out using a medium that was prepared using natural seawater instead of freshwater. Further investigation revealed that this unexpected peak correlated with the concentration of chloride salts present in seawater. This study was thus carried out to validate this observation with an aim of introducing a new rapid and accurate HPLC method for the determination of chloride salts in the presence of sugars.

2. Materials and methods

2.1. Chemicals

Chemicals and solvents used in this study were HPLC or analytical grade purchased from authorized manufacturers and suppliers. Distilled water was used as a solvent for preparing the mobile phase and samples.

2.2. Chromatography

The HPLC system consisted of a JASCO AS-2055 Intelligent auto sampler (JASCO, Tokyo, Japan) and a JASCO PU-1580 Intelligent HPLC pump (JASCO). Chromatographic separation of sodium chloride (NaCl) as well as all other components under investigation in this study (organic and inorganic salts, sugars, organic acids and alcohols) was achieved at 35 °C using a Hi-Plex H column (7.7 × 300 mm, 8 μm) (Agilent Technologies, Inc., UK) and a Jasco RI-2031 Intelligent refractive index detector (Jasco). The mobile phase was 0.005 N H_2SO_4 at a flow rate of 0.4 mL/min. The mobile phase solution was also used for flushing the syringe of the auto sampler. The injected volume was 10 μL and the analysis was completed in 12 min for determination of Cl^- salts only, 16 min for determining Cl^- salts and sugars and 32 min to include the determination of organic acids and ethanol. A blank sample of distilled water was used to verify the purity of the water being used as solvent. The goodness-of-fit of various calibration models were evaluated by visual inspection and the correlation coefficient as well as intra and inter-run accuracy and precision values.

2.3. Preparing a stock solution of NaCl for peak identification

Stock solutions at the concentration of 40.00 g/L from 3 different NaCl grades (analytical grade from Fisher 99.85%, rock salt Lab grade from Fisher and salt food grade from SAXA) were prepares at 4 levels (40.00, 20.00, 10.00, 5.00 g/L) to identify the peak under investigation.

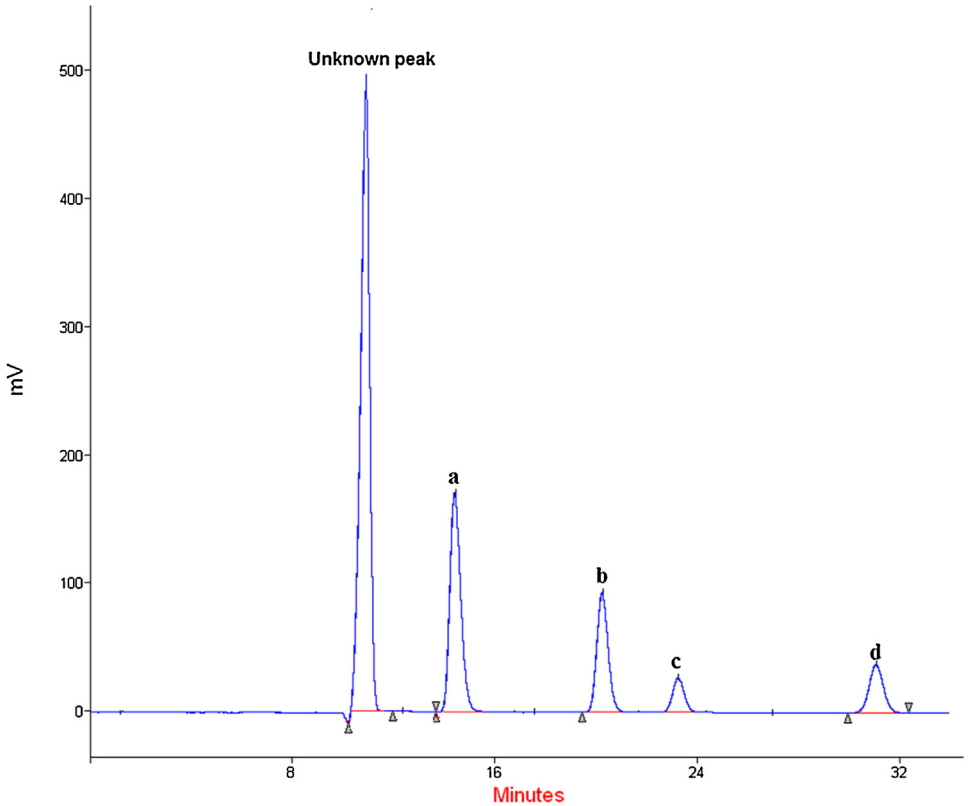

Fig. 1. Peaks present on a HPLC chromatogram from fermentations media using seawater based media.
Peaks analogous to standards for glucose (a), glycerol (b), acetic acid (c) and ethanol (d) are labelled along with an unknown peak which was eluted after 10.90 min.