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ORIGINAL ARTICLE

Free fluoride determination in honey by ion-specific electrode potentiometry: Method assessment, validation and application to real unifloral samples

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Abstract Surprisingly, a reliable method for measuring the concentration of free fluoride ions in honey is still missing from the literature, notwithstanding the generally recognized importance of the analyte and the matrix. To fill this gap, this study proposes and validates a straightforward ion-specific electrode potentiometric method for this task. The method offers very low detection and quantification limits (6.7 μg kg^{-1} and 25 μg kg^{-1}, respectively), good linearity ($R^2 > 0.994$), good sensitivity (typically 55 ± 3 mV for an order of magnitude of concentration) in an unusually low concentration interval (between 0.020 and 1 mg L^{-1}), and acceptable precision and bias. The method was applied to 30 unifloral (thistle, eucalyptus and strawberry tree) honey samples from Sardinia, Italy. The amount of free fluoride ions found in these honeys appears to be lower than

Abbreviations: FISE, fluoride ion-selective electrode; TISAB, total ionic strength adjusting buffer; EDTA, ethylenediaminetetraacetic acid disodium salt; CDTA, 2-[2-[bis(2-hydroxy-2-oxoethyl)amino]cyclohexyl]-(2-hydroxy-2-oxoethyl)aminoethanoic acid; EC, external calibration method; MSA, multiple standard additions method; CRM, certified reference material; LOD, limit of detection; LOQ, limit of quantification

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the range usually found in the literature; indeed, early results suggest a possible dependence of the analyte concentration on the honey's botanical origin.

1. Introduction

Fluoride ion is ubiquitous in water, minerals, foods and tissues of animals and plants. It is included in the list of elements considered essentials for animal life, but, at concentrations slightly higher than those of physiological action, it is considered harmful to animals, humans, and plants. In particular, it is demonstrated as one of the most phytotoxic air pollutants (Fornasiero, 2001). The major natural sources of fluoride ion are airborne HF and other fluorine-containing species like SiF_4, present in volcanic activity, ocean spray, and dust from the weathering of fluoride-containing rocks or soils. Anthropogenic sources of gaseous and particulate fluorides are represented by the airborne emissions by industrial plants or by combustion processes, mainly from coal combustion.

Honey, the chief hive product, essentially consists of a supersaturated aqueous solution of sugars, mostly fructose and glucose, but its composition includes a series of minor organic and inorganic species. The variety and abundance of these compounds are often related to the botanical and geographical origins of honey, but, as in the case of inorganic components, sometimes they may also reflect the existence of an environmental issue in the production area (Bogdanov et al., 2007; Fermo et al., 2013; Lambert et al., 2012; Leita et al., 1996; Meyer et al., 1988; Przybyowski and Wilczynska, 2001; Rashed et al., 2009; Rashed and Soltan, 2004; Rodríguez Garcia et al., 2006; Tong et al., 1975; Yücel and Sultanoğlu, 2012).

In the past, scarce attention has been devoted to the determination of the fluoride ion in apiary productions. Early, Tong et al. (1975) evaluated the concentration of 47 elements (including fluorine) in 19 honey samples produced near highways, industrial and mining areas using spark source mass spectrometry methods. Later, Meyer et al., 1988 measured the amount of fluoride in a number of honey samples produced in three sites localized in the Puyallup Valley, Washington, USA, along a three-year period. Unfortunately, no detail concerning the nature of the potentiometric method was provided in the study. More recently, Rashed and Soltan (2004) evaluated the concentration of this analyte in three unifloral Egyptian honeys (sesame, orange and clover). The fluoride ion-selective electrode (FISE) measurement has been performed on a solution obtained by extracting the "dry sample" with 1 M $HClO_4$ and adjusting the pH to 5.2 with 1 M CH_3COONa. "Good precision" and recoveries between 93% and 103% were claimed by the authors. The fluoride level measured in these studies spanned over a quite wide range, between 300 and 12500 $\mu g\ kg^{-1}$ (Meyer et al., 1988; Tong et al., 1975; Rashed and Soltan, 2004) probably depending both on natural causes (e.g. different floral and geographical origin of the analyzed samples) and anthropogenic factors, like the presence of industrial activities in the proximity of the apiary (Tong et al., 1975). On the other hand, the adoption of analytical methods not completely validated for this matrix cannot exclude the possibility that literature data were bias affected.

Following these introductory considerations and pursuing our interest in the qualitative and quantitative determination of minority compounds in beehive products (Ciulu et al., 2011, 2013; Sanna et al., 2000; Spano et al., 2006, 2008, 2009a, 2009b), we assessed and validated a potentiometric FISE method to directly measure the free fluoride concentration in honey. The procedure was also successfully applied to a number of selected unifloral honeys produced in different parts of the island of Sardinia, Italy.

2. Experimental

2.1. Equipment and labware

Potentiometric measurements were performed using a Fluoride Ion Selective Electrode (mod. DX219, Mettler Toledo, Switzerland) connected to an Ag/AgCl reference electrode (mod. 373/SSG/6 J, Amel s.r.l., Milan, Italy) and an ion analyzer (pH 1500 CyberScan, Eutech Instruments, the Netherlands). In addition, a combined glass-electrode (LIQ-GLASS 238000/08, Hamilton, Switzerland) was used with the ion analyzer to measure pH. Appropriate fixed volume Eppendorf Research Series 2100 pipettes were used. Everywhere possible, glassware was replaced with polyethylene labware.

2.2. Chemicals and reagents

All reagents were of analytical grade (Fluka, Milan, Italy), except NaF (99.99%, Sigma–Aldrich, Milan, Italy) and CH_3COOH (100% extra pure, Riedel-de Haën, Milan, Italy). Ultra-pure type I water (Merck, Milan, Italy) was used to prepare all the solutions. NaF was dried at 110 °C for two hours and cooled in desiccator before the preparation of 1000 mg L^{-1} F^- standard solution, which was then used to prepare diluted solutions. Total ionic strength adjusting buffer (TISAB) solution used in our study closely resembles that early proposed by Frant and Ross (1968), with the only difference being by the replacement of citric acid with EDTA. Hence, 58.0 g of NaCl, 37.0 g of NaOH, 57.0 mL of CH_3COOH were dissolved in 300 mL of 0.1 mol L^{-1} ethylenediaminetetraacetic acid disodium salt (EDTA). The pH was adjusted to 5.5 with 5.0 mol L^{-1} NaOH, then water was added to the solution up to a final volume of 1 L.

2.3. Samples

Thirty monofloral honey samples (thistle, *Carduus* L.; eucalyptus, *Eucalyptus camaldulensis;* strawberry tree, *Arbutus unedo* L.) were collected in different areas of Sardinia, Italy

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