Determination of low citric acid concentrations in a mixture of weak acid/bases

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Abstract

A titration approach was developed to measure low concentrations of citric acid ($C_6H_8O_7$) in a mixture of other weak acid/bases. Two methods were tested. The first and more practical method (a 4-point titration procedure) is applicable in conditions where volatile fatty acids (VFAs) are not normally present. The second method (a 5-point titration procedure) was developed for anaerobic environments where VFAs may be encountered. Generally, fairly accurate and repetitive results (precision >95%) were obtained for both situations although stability and accuracy were better in the absence of VFA. Both methods can be used for routine monitoring of biological reactors where citric acid is added as a carbon source and electron donor. Mg^{2+} and Ca^{2+} form complexes with citric acid and thus inhibit the use of the method. To overcome this, a sodium-saturated cationic ion exchanger was used to exchange these cations with Na^{+}. Following cation exchange, citric acid concentration was determined accurately using the method.

Keywords: citric acid measurement, acid titration, mixed weak-acid system, VFA

Introduction

Citric acid ($C_6H_8O_7$) is a natural component and common metabolite of plants and animals. It is the most versatile and widely used organic acid in foods, beverages, detergents and pharmaceuticals. Because of its functionality and environmental acceptability it is used in numerous industrial and research applications for chelation, buffering, pH adjustment, and also as a source of energy for controlled bacterial metabolism. The latter application is widely used in scientific research for the cultivation of both aerobic and anaerobic bacteria (Herzberg et al., 2003; Yoo et al., 2004). Often in these applications, process control depends on routine determination of the citric acid concentration.

Current determination of high concentrations of citric acid in the absence of "interfering" substances (other hydroxide-accepting species) is normally carried out by strong base titration (typically NaOH) to an endpoint pH of around 7.0 (*Standard Methods*, 1998). Low concentrations are currently determined by a spectrophotometric method based on a reaction with pyridine and acetic anhydrine (Hartford, 1962). Also, an enzymatic (Taraborelli and Upton, 1975) and HPLC methods (Guerrand, 1982) are in use. More recently, other methods based on ion chromatography (Saccani et al., 1995), gas chromatography (Chepurnoi and Bolbat, 1996), and fluorescence spectroscopy (Yedur and Berglung, 1996) have been proposed. All existing methods for determination of low citric acid concentrations lack simplicity, and some require relatively expensive equipment, and trained operators.

The work presented here was aimed at developing an accurate, simple, inexpensive, and rapid titration procedure for determination of relatively low citric acid concentrations (approximated range: 20 mg/ℓ to several hundred mg/ℓ) in a mixture of various weak acid species, primarily the carbonate system. The method was developed for two distinct situations. First, a mathematical algorithm and a matching titration procedure were developed for cases where the sole unknowns are the citric acid concentration and the total inorganic carbon concentration. This situation represents an aerobic environment in which volatile fatty acids (VFA) are normally not present, and the concentration of the other weak acid species (ammonia, phosphate, sulphide, etc.) is known. Second, the model is extended to solve a third unknown – the VFA concentration. The extended procedure can be used in the context of wastewater anaerobic reactors where VFA concentrations are normally encountered.

It is expected that the method will find use in bioreactor research where citrate is a popular carbon source for bacterial growth. The proposed method is not intended as a very accurate tool for citric acid determination, but rather as a fast and easy means of determining the concentration within an accuracy of ± 5 to 10 mg/ℓ. Such accuracy is in many cases sufficient in bioreactor operation practice.

In the following sections the equations comprising the mathematical algorithms for aerobic (VFA absent) and anaerobic (VFA present) conditions are described, and the corresponding titration procedures are developed and tested.

Model derivation

Apart from the carbonate system that is invariably present, other weak acid systems that affect the titration curve, and are thus considered in the "aerobic" model, are the phosphorus and the sulphide systems. In anaerobic environments, the volatile fatty acids (VFA) systems, that for practical purposes are simulated together by the acetic acid system (pK values of the acetic, propionic and butyric acids are all close to 4.75) are added. The ammonia system is not considered in the model because it has no buffering capacity at the proposed titration range.

A by-product of the model is the accurate determination of carbonate alkalinity, and also the VFA concentration in cases where it is present, the most important example being anaerobic biological reactors.

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