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Thin layer coulometric determination of nitrate in fresh waters

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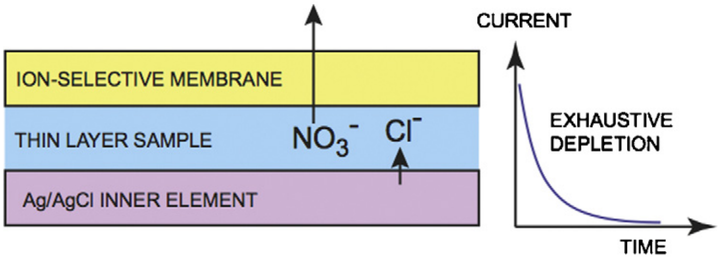
HIGHLIGHTS

- ► A tubular membrane nitrate ion-selective electrode is capable of the coulometric analysis of nitrate in lake water.
- ► Exhaustive nitrate electrolysis in an ion-selective coulometric sensor yielded a calibration free response.
- ► The coulometric nitrate ion-selective electrode possesses a comparable precision and accuracy to spectrophotometry.

GRAPHICAL ABSTRACT



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ABSTRACT

A nitrate ion-selective electrode (ISE) employing a permeable tubular membrane impregnated with a conventional ISE cocktail has been used successfully in the coulometric analysis of nitrate in fresh waters. The liquid ISE membrane comprising a nitrate ionophore [tridodecylmethylammonium nitrate (TDMAN)], lipophilic electrolyte [tetradodecyl-ammoniumtetrakis(4-chlorophenyl)borate (ETH 500)] and plasticizer [bis(3-ethyl-hexyl)sebacate (DOS)] was supported on a porous polypropylene tube. Coulometric analysis with the tubular membrane ISE showed that nitrate could be detected in the range 10–100 μM with a precision of 2.3% relative standard deviation (RSD), limit of detection of 1.1 μM and relative accuracy of 4.4% compared to a certified reference material (CRM) Lake sample.

1. Introduction

Nitrate (NO_3^-) finds its way into the environment from both natural and anthropogenic sources. It is ubiquitous in environmental, industrial and physiological systems, as well as foods, and is primarily present as the free anion [1]. Nitrate is one source of nitrogen in plants and phytoplankton, and is assimilated through the roots and converted into ammonia, based on its utilization in the Krebs cycle for the formation of amino acids [2]. Nitrate is also a well-known contaminant of ground and surface waters and, along with phosphate, is often implicated in the eutrophication of lakes and coastal waters [3]. High amounts of nitrate may be harmful to living species [4–10] through metabolic and physiological disorders in animals and plants [11].

Consequently, analytical methods for the determination of nitrate are critically important in both environmental and biological applications. An accurate and field deployable method for the measurement of nitrate in aquatic ecosystems and plants is very important since it will allow a monitoring of the impact of nitrate on the environment. It is important that analytical methods for the determination of nitrate are capable of determining reliably its concentration in various environmental matrices such as natural waters, as well as soil, sediment and plant solution extracts. In particular, the presence of nitrate in drinking water has been

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an area of major concern [12,13], so methods capable of real-time determinations of nitrate in natural waters are a high priority for maintaining the high quality of potable waters. Moreover, the World Health Organization (WHO) and US Environmental Protection Agency (EPA) have imposed a maximum permissible level of 44 ppm nitrate (10 ppm as nitrogen per litre) in drinking water [12,14].

Several analytical methods have been developed for the determination of nitrate in water samples, and there is a strong interest in the development of new techniques for the rapid, reliable and real time environmental monitoring of nitrate. When nitrate is determined by spectrophotometric and chromatographic methods, analysis times are lengthy and instrumentation requirements are costly, and these methods utilize toxic reagents and carrier solutions. Accordingly, there is a need for simple and low cost analytical methods such as ion selective electrodes (ISEs) or biological catalyst-based electrochemical sensors that do not perturb the sample or utilize toxic reagents or carrier solutions [1,15].

In recent years, ISEs have provided an attractive method for the analysis of nitrate due to their robustness, simplicity, specificity, low detection limits and capacity for use in field deployable instrumentation. On the other hand, the use of electrochemical sensing has been somewhat limited since, despite the thermodynamic feasibility of nitrate reduction, the kinetics of the charge transfer reactions at the electrode surface are slow, so the direct reduction of nitrate is characterised by poor sensitivity and reproducibility due to increased electrode passivation effects [1,16]. By contrast, the need for regular recalibration in real-time environmental monitoring is a major challenge with ISEs. Coulometry, on the other hand, is a unique electrochemical method that allows an absolute measurement of analyte based on Faraday's law. In coulometry, exhaustive electrolysis of the analyte is performed in a thin layer of sample and, according to Faraday's law, the quantity of charge consumed or liberated during electrolysis relates directly to the number of moles of analyte, as long as there are no side reactions and/or non-Faradaic processes such as background charging of the electrochemical device. In practice, coulometry is effective at high analyte concentrations, but is less successful at lower analyte concentrations due to high background compared to analyte currents that may not be subtracted or corrected effectively relative to the analytical signal [17].

Harrar [18] reported nitrite determinations using a controlled coulometric detection regime employing a platinum electrode for the oxidation of nitrite to nitrate at the electrode surface under exhaustive electrolysis conditions. However, until recent times, progress with coulometric sensors has been limited due to difficulties with high background signals from interfering species and/or a failure to exhaustively and selectively extract the analyte over a short time-frame due to small electrode surface areas compared to the sample volume and the absence of selective chemistries and electrochemistries in such devices. Kihara and co-workers [19] designed a smart electrochemical cell and flow system for rapid coulometric determinations of calcium at the water/organic liquid interface using a porous Teflon tubular membrane. The tubular membrane was assembled via immersion in an organic phase, and water is forced to flow through a small gap between the Teflon tube comprising a silver/silver chloride wire as an inner working electrode. The organic phase exterior to the tubular membrane also contained an ionophore, which is capable of binding selectively calcium in the aqueous sample. Moreover, exhaustive electrolysis was undertaken by controlled potential electrolysis of the internal Ag/AgCl wire electrode. Buffle and co-workers [20–22] also developed a permeation membrane that purified and pre-concentrated analytes prior to analysis by spectrophotometry or atomic absorption spectrophotometry. This system also comprised a hydrophobic hollow fibre polypropylene permeation membrane separating two aqueous solutions. This permeation membrane was impregnated with an organic solvent containing an ionophore or a selective carrier for the analyte ion, noting that the test analyte was transported from the source (outer) solution to the strip (inner) solution by liquid–liquid extraction via diffusion in the membrane. The selectivity of this tubular membrane system was due to the presence of an ion carrier in the permeation membrane that is capable of generating a complex between carrier molecules and analyte species.

Extending the approach of Kihara and co-workers [17,19,23] as well as Buffle and co-workers [20–22], Bakker and Grygolowicz-Pawlak [24,25] revisited this coulometric mode of detection by using a thin layer liquid permeation membrane system coupled with a high surface area working electrode and a very small sample volume. A tubular membrane ISE comprising a porous polypropylene tube doped with a plasticizer along with dissolved ionophore and ion sites, an inner electrolyte together with an inner Ag/AgCl wire electrode was utilized in the coulometric and calibration-free sensing of calcium. The sample solution also containing background electrolyte was forced through the internal channel of the polypropylene tube, thereby creating a very thin layer of sample (about 50 μm) between the internal reference element and the tubular membrane. Notably, this system was submerged in an outer solution also containing the analyte and the same background electrolyte solution. A multi-pulse protocol was utilized to compensate for non-Faradaic processes during coulometric measurements [25]. This system was successfully employed in the potentiometric and controlled potential coulometric determination of calcium, as a model system, in aqueous samples [24,25].

In this study, the authors have utilized a similar approach to Bakker and co-workers [24,25] and Kasuno et al. [26] in the fabrication of a suitable nitrate ISE system, and successfully employed this sensor in the calibration-free, coulometric determination of nitrate in fresh waters. An ability to conduct calibration-free or intervention-free analysis of nitrate in environmental waters is a significant advantage of the coulometric sensing device, thereby making this sensor highly desirable in field deployment. This paper is the first report of a calibration-free and coulometric ISE analysis of nitrate in environmental waters.

2. Experimental

2.1. Reagents and instrumentation

Tridodecylmethyl ammonium nitrate (TDMAN), tetradodecyl ammonium tetrakis(4-chlorophenyl)borate (ETH 500), bis(3-ethyl-hexyl)sebacate (DOS) (1,6,10,15-tetraoxa-2,5,11,14-tetraazacyclooctodecane,1,7,11,17-tetraoxa-2,6,12,16-tetrazacycloeico-sane), nitrate ionophore V (9,11,20,22-tetrahydrotetrabenzo[d.f,k,m][1,3,8,10]tetraaza-cyclotetradecine-10,21-dithione), tetrahydrofuran (THF), sodium nitrate, sodium chloride, magnesium chloride, calcium chloride, calcium nitrate, sodium sulphate, potassium bicarbonate, sodium bicarbonate, all other chemicals and silver wire of 500 μm diameter were purchased from Sigma–Aldrich. All solutions were prepared in de-ionized water (18 MΩ cm) [Millipore Pty Ltd., North Ryde, NSW, Australia]. The polypropylene hollow fibre tube, Accural PP Q3/2 with 600 μM internal diameter, was supplied by Membrana GmbH (Wuppertal, Germany).

All potentiometric measurements were performed at room temperature using a 16-channel EMF monitor (Lawson Laboratories, Inc., Malvern, PA) against a double-junction Ag/AgCl/saturated KCl/1 M LiOAc double-junction reference electrode (Mettler-Toledo AG, Schwerzenbach, Switzerland). The coulometric measurements were performed using an Autolab PGSTAT128N instrument (Metrohm Autolab, Utrecht, The Netherlands) interfaced to a