An improved technique for the determination of oxidised nitrogen in natural waters with a sequential injection analysis (SIA) system

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Abstract

An SIA system is proposed for the determination of oxidised nitrogen (nitrate + nitrite as N) in natural waters. A cadmium reductor, made of cadmium granules closely packed in a glass column reduces the nitrate to nitrite. The reduced nitrate and the nitrite present in the water samples is diazotised in the SIA system with sulphanilamide and coupled with N – (1-napthyl) ethylene diammoniumdichloride to form a highly coloured azo dye which is detected at 540 nm with a UV/Vis spectrophotometer. The proposed system is fully computerised and is able to monitor total oxidised nitrogen as nitrite at a frequency of 36 samples per hour with a standard deviation of < 1.2%. The calibration curve is linear up to 5 mg/ℓ with a detection limit of 0.01 mg/ℓ.

Introduction

The oxidised nitrogen content (nitrate + nitrite) of lakes, rivers and streams usually arises from groundwater, sewage effluents or drainage and leaching from agricultural land (Foster et al., 1986). The determination of total oxidised nitrogen is a subject of interest in the routine laboratory analysis of potentially polluted waters.

Knowledge of nitrate concentrations in waters is important for many reasons; for example, their importance in eutrophication (Lund, 1972; Gauntlet, 1980) and their responsibility in methaemoglobinaemia of sucklings (Goodman, 1980; Schuster and Lee, 1987). Nitrate reduces itself to nitrite in the human body. Nitrites have also been shown to be an important precursor of N-nitrosoamines which are potential carcinogens (Lijinsky and Epstein, 1970; Wolff and Wasserman, 1972). On a better note nitrates and/or nitrites are used in the food industry in the curing of meat (West and Ramachandron, 1966; EUR Report, 1990). When nitrate is added to meat, nitrite is formed due to reduction by the organic matter in the raw meat. *Clostridium botulinum* grows only under anaerobic conditions and it is the nitrate rather than the nitrite which assures an aerobic environment. Meat cured with nitrate is a bright red, while nitrite imparts a darker colour to the meat; thus the latter's use is mainly to control colour, rather than the prevention of *Clostridium* infection *per se*. It is used for pigment and other colourants (Francis, 1998).

Hence, it is necessary to control the concentration of nitrate and nitrite in water. Several methods are available for the determination of nitrate in water, and may fall into the following categories:

- The reduction of nitrate to ammonia (Bremmer and Keeney, 1965; Keay and Menage, 1970)
- Photo-induced reduction of nitrate to nitrite (Takeda and Fujiwara, 1995)
- Direct spectrophotometry (Rennie et al., 1979; Huiro et al., 1991)
- Potentiometric methods using ion-selective electrodes (Keeney et al., 1970)
- Reduction of nitrate to nitrite (Lambert and Dubois, 1971; Davison and Woof, 1978; Gine et al., 1980).

The determination of nitrate is difficult because of the relatively complex procedures required, the probability that interfering constituents will be high and the limited concentration ranges of the various techniques. Consequently, the actual determination of total oxidised nitrogen as nitrate is not recommended for waters, but rather as nitrite where the nitrate is reduced to nitrite.

Many colorimetric methods have been proposed for the determination of micro-amounts of nitrite. The most pronounced method seems to be a modified version (Watson,1980; Chaube et al., 1982; Sunita and Gupta, 1984; Bashir and Flamez, 1981; Daspgupta, 1984; Norwitz and Kelliher, 1985; Tarafder and Rathore, 1988; Rathore and Tiwari, 1991) of the Shinn (1941) reaction which is based on a well-known Griess reaction. This is a reaction of nitrite with a primary aromatic amine to form a diazonium salt which is coupled with another aromatic compound to form the azo dye of which the absorbance is measured.

The strategy commonly adopted is based on the reduction of nitrate to nitrite which is then spectrometrically determined after diazotation and coupling reaction. Either homogeneous or heterogeneous reductors are used. The nitrite so produced is determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5.

When using the cadmium reducing method, nitrate is reduced almost completely to nitrite. The applicable range of the method is 0.01 to 1 mg NO_3^- - N/ℓ. The technique is especially recommended for nitrate levels below 0.1 mg/ℓ where other methods lack adequate sensitivity. A number of flow injection systems (Zagato et al., 1980; Anderson, 1980; Van Staden, 1982; McCormack et al., 1994; Van Staden and Makhafola, 1996; 1999) have been developed using this modification.

Sequential injection analysis (SIA) launched in 1990 (Ruzicka et al., 1990a; b) is a technique that has tremendous potential especially for on-line process measurements and in monitoring of the environment. It is simple and convenient to operate. This technique considerably decreases sample and reagent consumption

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