Water Research 39 (2005) 1887–1895

WATER RESEARCH

www.elsevier.com/locate/watres

Modification of a continuous flow method for analysis of trace amounts of nitrate in iron-rich sediment pore-waters of mine pit lakes

P. Herzsprung[a,*], A. Duffek[a], K. Friese[a], M. de Rechter[b], M. Schultze[a], W.v. Tümpling jr[a]

[a]*Department of Inland Water Research, UFZ Centre for Environmental Research Leipzig-Halle, Magdeburg, Brückstr. 3a, 39114 Magdeburg, Germany*

[b]*SKALAR analytic GmbH, Gewerbestr. Süd 63, 41812 Erkelenz, Germany*

Received 14 April 2004; received in revised form 2 February 2005; accepted 15 February 2005

Abstract

Nitrate was analysed in pore-waters with high ionic strength. Extremely high concentrations of dissolved ferrous iron interfere common analytical methods. The automatic photometrical procedure based on the cadmium reduction method is often used for analysis of nitrate in water samples (continuous flow analysis CFA). An integrated dialysis usually serves for sample dilution and (or) sample purification (from particles). Iron was precipitated as iron hydroxide due to the imidazole buffer system (pH 7.5). The dialysis membrane is an effective barrier for iron hydroxide particles to prevent interferences within the cadmium column or the flow-cell. However, dialysis membrane is blocked successively after analysis of several iron-rich pore-water samples by agglomeration of precipitated iron. The blocking of nitrate diffusion through the dialysis membrane is tantamount to a decrease of analytical sensitivity to recognise by decreasing photometrical extinction. Minimising the iron deposition within the dialyser solved the problem. A simple modification of the CFA apparatus was found to keep the analytical sensitivity nearly constant: The mixing coil for the imidazole buffer was considerably elongated. Nearly all iron hydroxide was deposited at the glass coil surface installed before the dialyser. At least 50 iron-rich samples could be analysed within one sample queue with a loss of sensitivity $<10\%$. The recovery of nitrate was about 95%, demonstrated by spiking experiments.

Keywords: Continuous flow analysis; Nitrate; Iron; Mine pits; Pore-water

1. Introduction

1.1. About the relevance of nitrate determination in the field of sediment investigations associated with acid mine drainage and lake remediation

The generation of acid-mine drainage from abandoned mine tailings and overburden dumps by chemical and microbial oxidation of sulfide minerals is a major

---

[*]Corresponding author. Tel.: +49 391 8109 330; fax: +49 391 8109 150.

E-mail address: peter.herzsprung@ufz.de (P. Herzsprung).

0043-1354/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2005.02.017

environmental concern worldwide (Colmer and Hinkle, 1947; Parsons, 1964; Davis and Ashenberg, 1989; Evangelou, 1995; Miller et al., 1996; Geller et al., 1998). For the remediation of acidic mining lakes, the characterisation of the geochemical balance and processes of a particular site is an important prerequisite. The sediment–water interface is the site where gradients in physical, chemical and biological properties are the greatest (Santschi et al., 1990). The upper sediment layer is the region where important geochemical and biogeochemical reactions take place like the microbial reductive dissolution of ferric minerals and the formation of secondary mineral phases (Levy et al., 1997; Peine et al., 2000). The analysis of pore-waters gives much information about transport and transformation processes in the sediment and about chemical exchange of substances between litoral or profundal water and the sediment (Lerman et al., 1995; Berg et al., 1998). Both chemical and microbiological transformation processes are responsible for cycling of elements between water and sediments. A lot of specific chemical, microbial, biological, and physical parameters have to be analysed from sediment and sediment pore-water for characterisation of kinetic and thermodynamic processes. The knowledge about concentrations of electron donors like ammonium and ferrous iron or electron acceptors like oxygen, ferric iron, and nitrate is essential to identify and quantify biogeochemical processes which are relevant for producing and broadening acidity (pyrite oxidation, ammonium oxidation) or alkalinity (sulphate reduction, nitrate reduction). In sediments, nitrate is an important electron acceptor in the decomposition of organic matter, and its presence (or absence) is an indicator of redox conditions (Froelich et al., 1979). Sediment investigations are part of accompanying research for acidic lake remediation by neutralization after flooding (Duffek and Langner, 2002; Schultze et al., 2002) or addition of organic substrate to enhance sulphate reduction (Herzsprung et al., 2002; Wendt-Potthoff et al., 2002; Koschorreck et al., 2002).

1.2. *Nitrate analysis—analytical difficulties in iron-rich pore-waters*

The automatic photometrical procedure based on the cadmium reduction method (continuous flow analysis, CFA) is often used for analysis of nitrate in water samples (Walinga et al., 1989; Garside, 1993; Stewart and Elliot, 1996; Zhang, 2000; ISO–13395, 1996). The advantage of CFA is the possibility to measure many samples automatically within a short time by a relative small sample volume demand (6 mL are necessary for one analysis).

The available sample volume of sediment pore-water is generally low if high resolution of concentration gradients is required. If additional chemical, biological or microbial parameters are required besides nitrate determination, the rare sample volume has to be partitioned to different analysis apparatus/methods. Using a dialysis sampler (Hesslein, 1976; Bufflap and Allen, 1995a, b; Jacobs, 2002) about 5 mL sample can be extracted (per sample chamber). Usually between 10 and 50 mL (strongly dependent on the porosity of sediment) pore-water can be extracted with the centrifugation technique (Herzsprung et al., 2002; Bufflap and Allen, 1995a, b; Jacobs, 2002) after slicing sediment cores in 1 or 2 cm thick layers.

Acidic surface waters from mining areas (Davis and Ashenberg, 1989; Miller et al., 1996; Herzsprung et al., 1998; Klapper and Schultze, 1995) or from volcanic origin (Geller et al., 1998; Varekamp et al., 2000; Koschorreck et al., 2003) are often characterized by high concentrations of dissolved iron and $\mathrm{pH} < 4$. The corresponding pore-waters from these areas can contain elevated concentrations of total dissolved iron (up to 5 g L) compared to the surface water (Levy et al., 1997; Peine et al., 2000; Herzsprung et al., 2002; Friese et al., 1998; Blodau et al., 2000). The dominating lake water species is ferric iron (Herzsprung et al., 1998), the dominating pore-water species is ferrous iron (Herzsprung et al., 2002). Depending on geochemical conditions pore-water pH ranges from acidic to circum neutral values (Blodau et al., 2000).

Little is known about automated photometrical analysis of nitrate in iron-rich waters. Elbaz-Poulichet et al., (1999) have reported about nutrient (nitrate, phosphate, silica) monitoring in extremely acidic river water. There the phosphate and silica analysis was cited using the automatic segmented flow techniques according to Whiteledge (nutrient analysis in sea water) (Whiteledge, 1981). Nitrate concentrations were reported but neither the nitrate analysis technique was described in the experimental part nor possible difficulties with iron precipitation were mentioned.

Because of the recommended addition of a neutral buffer solution within the nitrate analysis manifold iron precipitation is inevitable when analysing iron-rich water samples. Dissolved ferric iron and dissolved ferrous iron (after quick chemical oxidation) form iron hydroxide precipitates after addition of imidazole buffer (pH 7.5). Any precipitate will be a severe interference for photometrical analysis by light scattering within the flow cell. Furthermore, the precipitate might interfere the flow-through of the cadmium column. Dialysis usually serves for sample dilution and/or sample purification, as shown for extracts from vegetables (Beijaars et al., 1994) or soils (Adamowicsz et al., 1980). Employing the common manifold for nitrate analysis with integrated dialysis for those samples containing moderate amounts of dissolved ferric or ferrous iron ($< 0.2\,\mathrm{g\,L^{-1}}$) purification from fines (precipitated iron) was successful in our laboratory. However, in situations such as those present