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Determination of free nitrilotriacetic acid in environmental water samples by ion chromatography with potentiometric and amperometric detection with a copper electrode

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ABSTRACT

An ion-chromatographic method is described for the analysis of free nitrilotriacetic acid in water samples. Separations are achieved on a polymer-based anion-exchange column with 6 m*M* nitric acid as eluent. Both potentiometric and amperometric detection have been applied using metallic copper as the indicator electrode. Detection limits are at about 500 ng injected in the potentiometric mode and 100 ng in the amperometric mode. On-line sample preconcentration is possible for volumes up to 2 ml of river water samples. The response of the detector to other aminopolycarboxylic and aminopolyphosphonic acids has been investigated.

INTRODUCTION

To an increasing degree, nitrilotriacetic acid (NTA) is used in industry and as a substitute for phosphates in detergents. After release to the environment it may affect the distribution of metals within aquatic ecosystems. Therefore, efficient analytical methods are necessary for monitoring NTA, both in its free form and in the form of complexes with metals.

Several analytical techniques exist for the determination of NTA, among them gas chromatography [1–4] after derivatisation of the carboxylic groups, polarography [5,6] and ion-interaction high-performance liquid chromatography following formation of the Cu(II)–NTA complex [7,8]. Unfortunately, these methods do not meet all the requirements of differentiation between free and complexed NTA. More recently, ion chromatography has been used to separate free NTA and other complexing agents [9,10]. Detection is generally by UV-absorbance after post-column reaction with Fe(III) ions; furthermore, the applicability of amperometric detection at carbon paste electrodes has been reported [11].

In this paper the combination of ion chromatography with an electrochemical detector containing a copper wire electrode is described. The detector can be used in the potentiometric mode [12–14] as well as in the amperometric mode [15,16] and should exhibit high selectivity for strong chelating compounds such as NTA. As a consequence, extensive clean-up of environmental samples might be avoided.

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EXPERIMENTAL

The ion-chromatographic instrumentation consisted of a Waters (Milford, MA, U.S.A.) M510 pump, a Rheodyne (Berkeley, CA, U.S.A.) 7010 injection valve with a 20 μl loop or a Waters IC Pak A Guard-Pak precolumn (5.0 × 6.0 mm I.D.), a Waters IC Pak A separation column (50 × 4.1 mm I.D.) and a Waters NRC-1094 mixing device for post-column mixing of the eluent with buffer delivered by a Waters M45 pump.

The electrochemical cell fitted with a copper wire electrode has been described previously [13] and was used in the potentiometric mode with a Beckman (Fullerton, CA, U.S.A.) Φ34 pH-meter or in the amperometric mode with a Bioanalytical Systems (West Lafayette, IN, U.S.A.) LC4A amperometric detector. Chromatograms were recorded using a home-made analog-to-digital converter, interfaced with an Apple IIe computer. Nitric acid (6 m*M*) was used as mobile phase and 100 m*M* phosphate buffer at pH 7 was employed for post-column pH adjustment. The flow-rates of the mobile phase and of the post-column buffer were each 1 ml/min.

River water samples were passed through a Millipore (Bedford, MA, U.S.A.) 0.45 μm Millex filter and then through a Waters C18 SepPak cartridge before injection. Spiked river water samples were prepared by the addition of 500 μl of an NTA stock solution in Milli-Q water to 100 ml of sample. NTA standard solutions were prepared in Milli-Q water by appropriate dilution of a stock solution.

Flow-injection analysis experiments were performed with a home-made metal-free instrument fitted with a wall-jet type electrochemical cell (Ag/AgCl/3 *M* KCl as reference electrode, gold as auxiliary electrode) in combination with a Metrohm (Herisau, Switzerland) E510 pH-meter or a Metrohm E612 potentiostat.

RESULTS AND DISCUSSION

In the potentiometric mode, the potential of the copper electrode is governed by the concentration of free copper ions existing at the electrode surface. This concentration depends on, among other things, the oxygen content and the complexation properties of the eluent. When the electrode is conditioned with an eluent of constant composition at a steady flow-rate, a stable background potential results. Eluted solutes which form very stable complexes with copper ions, such as NTA, will cause a change in the level of copper ions at the electrode surface, thereby producing a decrease in the electrode potential (potential values given in Fig. 2 indicate relative mV changes only and the peak shown for NTA represents a *decrease* in potential).

In the amperometric oxidative mode, a potential of about +100 mV *versus* Ag/AgCl is applied to the electrode. Under these conditions metallic copper becomes oxidised but the oxidative current will be limited due to the formation of passivating layers if the pH is kept in the neutral range [17]. NTA will dissolve these passivating films and increase the current.

In order to develop a chromatographic separation which was compatible with the copper electrode detector both in the potentiometric and in the amperometric mode, we first examined the use of neutral mobile phases. Unfortunately even very strong eluents, such as 1 *M* sodium sulphate, failed to elute NTA in a reasonable time. Under these conditions, NTA carries a double negative charge and is retained strongly.

Therefore an acidic mobile phase such as 6 m*M* nitric acid was employed in order to partially protonate the NTA and thereby reduce the effective charge. Under these chromatographic conditions, NTA was eluted at a retention time of approximately 8 min. These conditions also necessitated a post-column pH adjustment to permit the use of the copper electrode detector, since high background potentials resulted when the nitric acid eluent was passed directly to the detector. Post-column pH adjustment was accomplished by mixing the eluent with 100 m*M* phosphate buffer at pH 7, prior to passage to the detector. Detection limits (measured for a signal-to-noise ratio of 3) were about 500 ng injected in the potentiometric mode and 100 ng injected in the amperometric mode. The linearity of the response, determined for peak heights in a range up to 12 μg injected, was good for the amperometric mode (Fig. 1) with $r = 0.9995$. On the other hand, potentiometric detection showed a non-linear response, as could be expected from the Nernst equation, but within a small concentration range linearity can be assumed.

For application to environmental water samples, on-line sample preconcentration was employed by replacing the injection loop with a small precolumn. Sample volumes of several millilitres were loaded, and the bound NTA was then backflushed onto the analytical column by the eluent. With standard solutions, 20 ml of sample (higher volumes were not tried) could be preconcentrated without loss. In river water samples, the recovery of the preconcentration step was affected mainly by the amount of sulphate present, since sulphate competes with NTA for ion-exchange sites on the concentrator column. Up to 2 ml of samples containing up to 25 μg/ml sulphate could be preconcentrated with quantitative recovery. In such cases, it proved to be advantageous to wash the precolumn with 1 ml of 2 m*M* sodium nitrate after loading the sample in order to strip-off ions, such as chloride, which could give a response at the electrode. The recovery was not affected by this washing step as long as the wash volume did not exceed 1 ml.

In Fig. 2 chromatograms of NTA standards and river water samples (Lane Cove River, Sydney) are shown for the potentiometric and amperometric mode. The performance of the method (expressed as the percentage recovery ± the standard deviation for five replicates) when applied to a 2-ml injection of spiked river water was

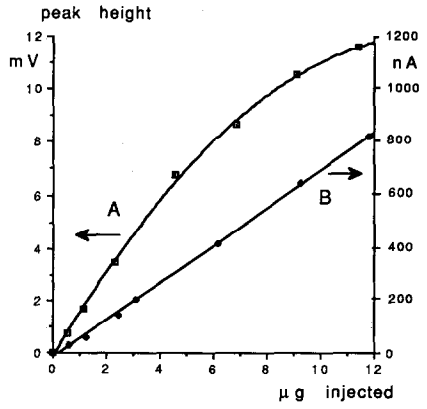

Fig. 1. Calibration plots for NTA obtained with a copper electrode in (A) the potentiometric mode and (B) the amperometric mode. Injection volume: 20 μl.

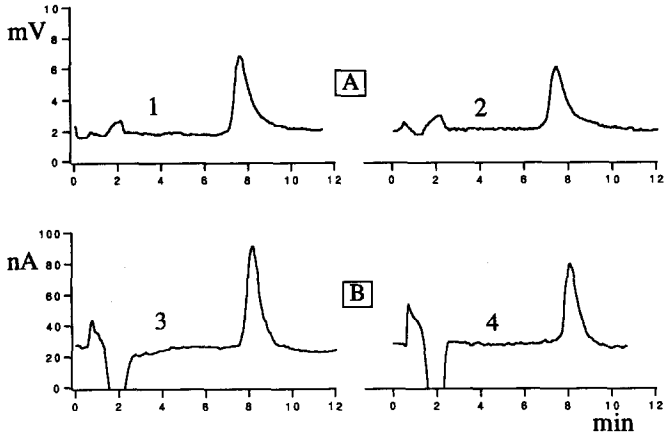

Fig. 2. Chromatograms of (1) standard containing 3.1 ppm NTA, (2) river water spiked with 2.2 ppm NTA, (3) standard containing 0.62 ppm NTA, (4) river water spiked with 0.49 ppm NTA, using (A) potentiometric detection and (B) amperometric detection. On-line preconcentration of 2 ml of sample was used.

97.2 ± 3.8% at a 2.46 μg/ml level for the potentiometric mode, and 95.6 ± 3.1% at a 430 ng/ml level for the amperometric mode. Whilst it is possible that poor recoveries might be encountered in samples of low pH, the results of the above spiking experiments suggest that it is not necessary to adjust the pH of the sample prior to preconcentration.

Similar chromatographic conditions can be used for the separation of other aminopolycarboxylic acids as well as organophosphonic acids, which may be present in detergents [9,10]. We therefore investigated the response of such compounds at a copper electrode by flow-injection analysis. The responses relative to NTA obtained by injecting 100 ng of each compound in 10 m*M* phosphate buffer pH 7 are listed in

TABLE I

RESPONSE OF DIFFERENT AMINOPOLYCARBOXYLIC ACIDS AND ORGANOPHOSPHONIC ACIDS RELATIVE TO NTA (DETERMINED BY FLOW INJECTION ANALYSIS OF 100 ng)

Compound	Relative response	
	Amperometry	Potentiometry
NTA	1	1
EDTA	0.71	1.20
Dequest 2060 (Diethylenetrinitrilopentamethylenephosphonic acid)	1.52	2.33
Dequest 2041 (Ethylenedinitrilotetramethylenephosphonic acid)	1.55	2.49
2-Phosphonobutane-1,2,4-tricarboxylic acid	1.07	1.11
Dequest 2010 (1-Hydroxyethane-1,1-diphosphonic acid)	2.57	2.14
Dequest 2000 Aminotris(methylenephosphonic acid)	1.26	2.10

Table I. Since all compounds tested gave similar response, we tried in a series of experiments to analyse both NTA and EDTA using ion chromatography with potentiometric or amperometric detection. Unfortunately, some of the injected EDTA becomes lost when the amounts injected are less than 15 μg. The most probable cause of this behaviour is the complexation of EDTA with Fe(III) ions arising either as a contaminant of the nitric acid eluent or from stainless-steel parts of the chromatographic system. Similar problems occurred in the analysis of organophosphonic acids, but were not observed with NTA, presumably because of the lower formation constant for the complex of Fe(III) with NTA. A metal-free instrumentation might help to overcome the difficulties encountered with EDTA and organophosphonic acids.

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