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Rapid simultaneous analysis of oxyhalides and inorganic anions in aqueous media by ion exchange chromatography with indirect UV detection

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Abstract Simultaneous analyses of oxyhalides (BrO_3^-, ClO_3^-) and inorganic anions (Cl^-, Br^-, NO_3^- and SO_4^{2-}) have been achieved on metrosep anion dual1 Metrohm as polymer column (150×3 mm D.I.) with *ortho*-phtalic acid as a visualization agent and as ion developer constituent of the mobile phase. The separations have occured without interferences and any base line perturbation.

Best separations have also occured between (Cl^-/ClO_3^-) and (Br^-/BrO_3^-) with good a resolution. Detections limits (S/N = 3) of BrO_3^-, ClO_3^- and NO_3^- were 2 and 5 ppm for inorganic anions Cl^-, Br^- and SO_4^{2-}. The method had a good linearity ($r^2 > 0.995$) and high precision (relative standard deviation) $< 4\%$. The main reason for the detector choice was that UV detectors are widespread in educational and low level equipment laboratories. Indirect photometric detection is an attractive and inexpensive approach and the system is versatile.

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1. Introduction

In the last decade, we have developed many analytical chromatography technics for inorganic anions like chloride, nitrate, sulfate, phosphate (Mercier et al., 2000; El Haddad et al., 2006, 2002, 2003) and inorganic cations like sodium, potassium, magnesium, calcium (El Haddad et al., 2005, 2001a,b) by ion exchange chromatography (IEC) coupled with evaporative light scattering detector (ELSD). We have also analyzed inorganic anions using *ortho*-phtalic acid as ion developer by

IEC with UV indirect mode and conductimetric detections (El Haddad et al., 1999). In this case, it's recognized that inorganic anions can be analyzed by IEC with indirect UV detection using sodium salicylate, pyromellitate, potassium phthalate and 4-hydroxybenzoïque acid as visualization agents.

The main hazardous inorganic oxyhalide disinfection by-products are: chlorate and bromate. In this fact, chlorate is formed when chlorine, chlorine dioxide, hypochlorite or chloramine is used to disinfect raw water (Erdinger et al., 1999). Chlorine dioxide oxidizes the organic matter under the formation of chlorite, which can be oxidized to chlorate by ozone or hypochlorite if a combination of chlorine dioxide and these disinfectants is used. The ozonation of water containing bromide can cause the formation of bromate (Gun ten and Oliveras, 1998). Chlorate and bromate have potential harmful effects for human beings. The International Agency for Research on Cancer (IARC) has concluded that chlorate causes oxidative damage to red cells (WHO, 1998). So, bromate has been identified as a possible human carcinogen (Kurokawa et al., 1990).

Several analytical methods have been developed for the analysis and determination of oxyhalides (BrO_3^-, ClO_3^-, IO_3^- ...) with IEC. Hautman et al. have achieved the separation of BrO_3^- in a mixture of anions (Cl^-, CO_3^{2-}, NO_3^-) by the use of boric acid/tetraborate as the mobile phase (Hautman and Bolyard, 1992). Chloride was eliminated by pretreatment with a cation exchange resin based on silver by Joyce and Dhillon (1994). However, these methods are less selective for BrO_3^- because they used a conductimetric detection. Takeuchi et al. carried out a selective separation of IO_3^- and BrO_3^- in drinking water with a micro-column by IEC with a pre-enrichment column with UV as a detection system (Takeuchi and Kitamaki, 2004).

This work describes an isocratic separation of two oxyhalides (BrO_3^-, ClO_3^-) and four inorganic anions (Cl^-, Br^-, NO_3^- and SO_4^{2-}) on metrosep anion dual1 Metrohm as polymer column (150 × 3 mm D.I.) by IEC with UV indirect as detection system in order to achieve quantitative analysis of ionic species composition of some waters; tap, spring, thermal and mineral.

2. Experimental

2.1. Apparatus

The liquid chromatograph consisted of an isocratic pump Model 307 Gilson (Villiers-le-Bel, France), an injector Rheodyne 7725 (California, USA) equipped with a 20 μl sample loop. An integrator Hewlett Packard 3395 and spectrophotometer UV–Vis Model 118 Gilson were used in this study. All experiments were carried out with a metrosep anion dual1 Metrohm as polymer column (150 × 3 mm D.I.).

2.2. Reagents

All solutions were prepared from analytical reagent grade chemicals in 18 MΩ water obtained from an Elgast UHQ II system from ELGA (Antony, France). All eluents were prepared by dissolution of different amounts of *ortho*-phtalic acid provided from Merck (Darmstadt, France) and TRIS (trihydroxyethylaminomethane) from Fluka (St. Quentin Fallavier, France). All solutes solutions: sodium chloride (NaCl), sodium bromide (NaBr), sodium bromate (NaBrO₃), sodium chlorate (NaClO₃), sodium nitrate (NaNO₃) and sodium sulfate (Na₂SO₄) were purchased from Merck (Darmstadt, France).

The mobile phase was delivered at a flow rate of 1 ml/min. Standard solutions were injected at a concentration of 100 mg/ml during the measurement of the retention factors.

3. Results & discussion

3.1. Simultaneous analysis of oxyhalides and inorganic anions

To achieve accurate single run analysis and simultaneous separation of inorganic anions (Cl^-, Br^-, NO_3^- and SO_4^{2-}) and oxyhalides (BrO_3^-, ClO_3^-) on metrosep anion dual1 Metrohm as polymer column (150 × 3 mm D.I.), we have used *ortho*-phtalic acid as ion developer as constituent of mobile phase using UV indirect as detection system. Solutes are detected by absorbance chute of base line of *ortho*-phtalic absorption (λ = 273 nm). Fig. 1 reports the variation of retention factors, k, for oxyhalides (BrO_3^-, ClO_3^-) and inorganic anions (Cl^-, Br^-, NO_3^- and SO_4^{2-}) studied versus the variation of *ortho*-phtalic acid concentrations (1, 2, 3, 4, 5 and 6) in the mobile phase. As observed in Fig. 1 retention factor, k, decreases for all inorganic anions and oxyhalides when increasing *ortho*-phtalic concentrations. Different profil separations are found, and the selectivities between two adjacent solutes are good when using a concentration of *ortho*-phtalic acid inferior or equal to 3 mM. For the following study, we have used *ortho*-phtalic acid 1 mM to make up the separation between (Br^-, BrO_3^-) and (Cl^-, ClO_3^-). The use of low concentration of *ortho*-phtalic acid allows the use of lower wavelength without saturation of the UV detector (favorable to indirect UV detection). The use of low concentration allowed setting the UV detector at 273 nm where spectrum slope is around zero and the absorbance is 0.7–0.8 AU. Good profil separation was obtained as depicted in Fig. 2. A simultaneous separation of halides (Cl^-, Br^-) and oxyhalides (ClO_3^-, BrO_3^-) was realized with best resolution of all ionic species as shown in Fig. 3.

In order to achieve the determination of oxyhalides in water, it's necessary to make the analysis in standard solutions containing the principal inorganic anions (Cl^-, Br^-, NO_3^- and SO_4^{2-}). Fig. 4 shows the simultaneous separation of oxyha-
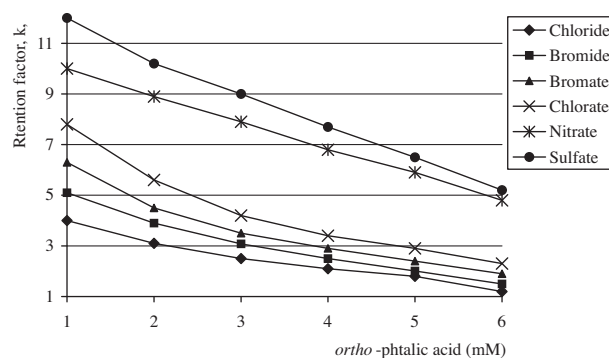

Figure 1 Effect of *ortho*-phtalic acid concentrations on the variation of retention factors of oxyhalides and inorganic anions. Column: metrosep anion dual1 Metrohm column (150 × 3 mm D.I.). Flow rate: D = 1 ml/min. Detection: indirect UV at 273 nm.