On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic anions in Amazonian river water samples employing ion chromatography with conductivity detection

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ABSTRACT

An ion chromatography procedure, employing an IonPac AC15 concentrator column was used to investigate on line preconcentration for the simultaneous determination of inorganic anions and organic acids in river water. Twelve organic acids and nine inorganic anions were separated without any interference from other compounds and carry-over problems between samples. The injection loop was replaced by a Dionex AC15 concentrator column. The proposed procedure employed an auto-sampler that injected 1.5 ml of sample into a KOH mobile phase, generated by an Eluent Generator, at 1.5 mL min^{-1}, which carried the sample to the chromatographic columns (one guard column, model AG-15, and one analytical column, model AS15, with 250 x 4mm i.d.). The gradient elution concentrations consisted of a 10.0 mmol l^{-1} KOH solution from 0 to 6.5 min, gradually increased to 45.0 mmol l^{-1} KOH at 21 min., and immediately returned and maintained at the initial concentrations until 24 min. of total run. The compounds were eluted and transported to an electro-conductivity detection cell that was attached to an electrochemical detector. The advantage of using concentrator column was the capability of performing routine simultaneous determinations for ions from 0.01 to 1.0 mg l^{-1} organic acids (acetate, propionic acid, formic acid, butyric acid, glycolic acid, pyruvate, tartaric acid, phthalic acid, methanesulfonic acid, valeric acid, maleic acid, oxalic acid, chlorate and citric acid) and 0.01 to 5.0 mg l^{-1} inorganic anions (fluoride, chloride, nitrite, nitrate, bromide, sulfate and phosphate), without extensive sample pretreatment and with an analysis time of only 24 minutes.

KEY WORDS: On-line pre-concentration, inorganic anions, organic anions, ion chromatography, river waters

Pré-concentração em linha para a determinação simultânea de ácidos carboxílicos de baixo peso molecular e ânions inorgânicos em amostras de rios da Amazônia empregando cromatografia de íons com detecção por condutividade elétrica

RESUMO

A metodologia analítica foi desenvolvida empregando coluna pré-concentradora AC15 em linha na cromatografia iônica na determinação simultânea de ânions orgânicos e inorgânicos, com uso de coluna de guarda AG15 e analítica AS15, 250 x 4 mm i.d. (Dionex Corp.). O gradiente de concentração do eluente foi fixo em 10,0 mmol.l^{-1} KOH nos tempos de retenção de 0 até 6,5 min, seguido do aumento da concentração até 45,0 mmol.l^{-1} KOH a 21 min, imediatamente retornando e mantendo a concentração inicial até o tempo total de análise de 24 min. Os compostos foram separados com boa resolução e deslocados para uma cela de detecção de condutividade elétrica acoplada a um detector eletroquímico. O emprego da coluna pré-concentradora em linha apresentou vantagens analíticas na determinação de rotina dos íons na faixa linear de 0,01 até 1,0 mg l^{-1} (r=0,9989) de ácidos orgânicos (acético, propiônico, fórmico, butírico, glicólico, pirúvico, tartárico, ftálico, metanossulfônico, valérico, maleico, oxálico e cítrico) e 0,01 até 5,0 mg.l^{-1} (r=0,9987) de ânions inorgânicos (fluoreto, cloreto, nitrito, bromo, nitrato, sulfato, clorato e fosfato) sem pré-tratamento da amostra. Um tempo de análise de 24 min e limite de detecção de 5 μ.l^{-1} foram obtidos para os ânions orgânicos ácido ácetico, ácido fórmico, ácido butírico, ácido glicólico, ácido valérico, ácido cítrico e de 10 μg.l^{-1} para ácido propiônico, piruvato, ácido tartárico, ácido ftálico, ácido metasulfônico e ácido maleico. Para os ânions inorgânicos 2 μg.l^{-1} de fluoreto, cloreto, nitrato, bromo, sulfato e 10 μg.l^{-1} de clorato, nitrito e fosfato foram estimados, segundo metodologia sugerida por IUPAC.

PALAVRAS-CHAVE: Pré-concentração em linha, ânions inorgânicos, ânions orgânicos, cromatografia de ions, rio Amazonas.

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ACTA AMAZONICA

On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

INTRODUCTION

In aquatic environments bacteria are primarily responsible for the biochemical decomposition of organic matter. The efficiency in which bacteria use dissolved organic carbon is an important factor governing the flow of carbon and energy through the microbial food chain. In this process complex materials can be converted to low-molecular-weight compounds (Vallino *et al.*, 1996). Recent studies have demonstrated that some low molecular weight compounds also result from photooxidation of humic substances as well as excretion by algae and cyanbacteria during carbon assimilation (Karlsson, 1999). In fact, although these labile organic acids are present at low concentrations, (at the µg.l^{-1} level), as a group they may account for approximately 5 to 8 % of the dissolved organic carbon (DOC) of natural waters (Thurman, 1985).

Experimental studies have been conducted to characterize the composition of dissolved organic matter, examine its production and utilization, understand its impact on microbial dynamics and determine the extent to which it supports higher tropic levels (Vallino *et al.*, 1996), several of those in aquatic environments (Findlay & Sinsabaugh, 2003). Low molecular weight organic acids (LMWOA) have been also identified and measured in a wide variety of environments, such as soil solution, atmosphere, rivers, snow, and sea waters (Thurman, 1985; Souza *et al.*, 1999; Albert & Martens, 1997; Strobel, 2001) and analyzed in other matrices (Toofan *et al.*, 1997; Ding *et al.*, 1997; Eiteman & Chastain, 1997; Morales *et al.*, 1998; Klampfl *et al.*, 2000; Sharma *et al.*, 1998).

Initially, analyses of low molecular weight carboxylic acids were determined by paper chromatography. For the last two decades, routine analysis often employ chromatographic techniques such as gas chromatography (Kuiters & Denneman, 1987), high performance liquid chromatography and suppressed and non-suppressed ion chromatography (Dahlén *et al.*, 2000; Strobel, 2001). More recently, capillary zone electrophoresis has also been used for these determinations (Dahlén *et al.*, 2000; Findlay, 2003).

The short chain carboxylic acids which can partly be dissociated to anionic forms in aqueous solution can also be separated by suppressed ion chromatography (IC) with conductivity detection. However, most published methods appear to be unsuitable for application to environmental samples with organic acid concentrations in the presence of inorganic anions because high concentration of inorganic anions interfere in the separation of low concentration of organic acids (Ding *et al.*, 1997; Fang, 1993). Nevertheless, sampling and sample preparation are often critical in the determination of trace constituents in natural waters due to, for example, hydrolysis, volatilization and biodegradation (Ding *et al.*, 1997). In the case of LMWOA, there is still a scarcity of procedures concerning the simultaneous determination of the organic and inorganic anions in river waters.

Ion chromatography allows adding the concentrator columns in replacement of sample loops, using a six port switching valve. The advantage of this option is the ability to perform routine analysis for ions at µg.l^{-1} levels without prior off-line sample treatment, increasing the throughput of determinations per hour. On another hand, there are several difficulties that must be investigated in order to evaluate the parameters that could affect the behavior of inorganic anions and organic acids during on-line pre-concentration (Fang, 1993).

In this work we present an analytical methodology for the simultaneous on-line pre-concentration, separation and determination of organic acids and inorganic anions in river waters using ion chromatography. Several parameters were tested, such as relationship between sample loading and injection flow-rate, sample volume, interferences, suppressor current setting and concentration of the elution gradient. After optimization, several river water samples were analyzed.

MATHERIAL AND METHODS

INSTRUMENTATION

The ion chromatograph used in this work consisted of a Dionex Corporation DX-500 system equipped with an AS50 Auto select Autosampler containing a 9126 Rheodyne 6-port injection valve, a GP50 gradient pump, an EG40 eluent generator system with EluGen™ EGC-KOH cartridge, an ASRS ULTRA II 4 mm self-regenerating suppressor and an ED40 conductivity detector. Dionex IonPac AS15 (250 x 4 mm i.d.), AG15 (250 x 4 mm i.d.) and AC15 (4 x 50 mm i.d.) were used, respectively, as guard, analytical and concentrator columns. The PeakNet 6.0 software was used for system control and data collection.

REAGENTS AND PROCEDURES

All carboxylic acid standards were prepared from analytical reagent grade chemicals (>99% pure) in 18.3 MΩ water, obtained from a Barnstead Nanopure Infinity water purification system. Individual stock solutions of 1000 mg.l^{-1} fluoride, chloride, nitrite, nitrate, bromide, sulfate, phosphate, acetate, propionic acid, formic acid, pyruvate, maleic acid, oxalic acid, chlorate and citric acid were prepared from their analytical reagent grade sodium salts (except for methanesulfonic acid, n-valeric acid, butyric acid, phthalic acid, glycolic acid, L-tartaric acid, oxalic acid, which were prepared from liquid standards). Each 250 ml of the standard solutions received 25.0 mg of thymol to protect carboxylic acids from bacterial decomposition, and were stored in amber glass bottles at 4°C. Working calibration standard solutions

ACTA
AMAZONICA

On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

0.0; 0.01; 0.025; 0.05; 0.1; 0.25; 0.5; 1.0; 2.5 and 5.0 mg.l^{-1} inorganic anions and organic acids were prepared daily by appropriate dilutions of the stock solution with water.

The mobile phase was produced by an EG40 Eluent Generator System with ElunGen™ EGC-KOH cartridge commercially available from Dionex Company.

Sample solutions were taken in separate polyethylene bottles and filtered through 0.45 µm membrane filter, spiked with thymol and kept refrigerated in amber polyethylene bottles at 4°C. This sample solution was injected into the ion chromatograph directly.

A Rheodyne 9126 valve with a rotor that converts the valve from 6 ports with a needle port to a 6 port valve can be used to configure a concentrator column in a sample injection system. The sample is introduced through port 6 rather than the needle port. In the load position, sample enters the valve at port 6, flows out of the valve at port 1 to the concentrator column, back into the valve through port 4, and out to waste through port 5. The eluent enters the valve at port 3 and flows to the analytical column through port 2 (Figure 1). In the inject position, the eluent is pumped into the valve at port 3 and out of the valve at port 4 to the concentrator column to elute the analytes to the analytical column. With this configuration, the analytes are concentrated in one direction on the concentrator column and eluted to the analytical column in the opposite direction. In general, reversed flow elution decreases the dispersion of the concentrate during elution and improves the enrichment factors (Toofan *et al.*, 1997).
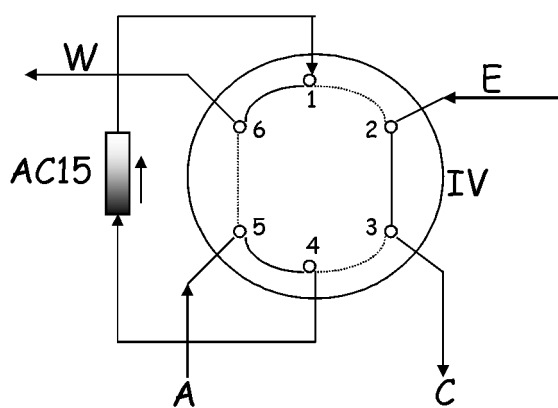

Figure 1 - Process for loading the Ion Pac AC15 concentrator column. IV-injection valve; C- to guard and analytical column; E- eluent in; W- waste; AC15- concentrator column; A- sample in. Solid and dashed lines indicate the flow pathways in the valve.

The effects of parameters, such as sample loading and injection flow rates, sample volume, interferences, suppressor current settings and gradient elution comprised the set of variables that were investigated to establish the best operational conditions. All samples were also preserved with thymol and kept frozen until analysis (Chen *et al.*, 1999). Before manipulation samples were equilibrated to the laboratory temperature. All sample measurements were performed in triplicates and the average peak area was used in these studies.

RESULTS AND DISCUSSION

CHOICE OF THE ANALYTICAL COLUMN AND EFFECTS OF SAMPLE VOLUME

The IonPac AS11-HC and AS15 analytical columns in combination with the AG11 and AG15 guard column, respectively, are designed for the trace analysis of inorganic anions and low molecular weight organic acids in complex matrices using potassium hydroxide gradient elution. The first study consisted of testing the effects of the sample volume in the available columns AS11-HC and AS15 (250 x 4 mm i.d.) in order to monitor the organic acid and inorganic anion responses without any previous optimizations in the method. In general, the companies suggest that low sample volume should be inserted into AS11-HC column because of the overloading effect, while the AS15 column did not have this restriction. In this sense, different sample volumes were inserted varying from 200 to 500 µl with 5 µl cut volume into AS11-HC and full injection type varied from 500 to 2000 µl into AS15 column. Volumes above 2000 µl were not available because sample could contaminate the flush bottle through the transfer line, which had a volume of 2200 µl volume. Peak area results were observed using a reference solution containing 1.0 mg.l^{-1} organic and inorganic anions. This parameter control was performed to attain a better combination of selectivity and sensitivity. The result of these studies shows (Figure 2) that the area signals for all analytes increase up to *c.a.* 80% when the aliquot volume was increased from 200 µl to 300 µl with 5 µl cut volume with AS11-HC column. However, this area signal increase was not observed when aliquot volumes above 300 µl were inserted because this column showed overloading problems for large injections volume. Nevertheless with this column, we did not detect any of the organic anions such as pyruvate, glycolate, propionate, tartrate and maleate. Although good results with the AS11-HC were obtained, only some organic and inorganic anions could be determined in the linear range from 0.05 to 5.0 mg.l^{-1} such as fluoride, acetate, formate, butirate, MSA, valerate, proprionate, nitrite, nitrate, chloride, bromide, sulfate and phosphate.

On another hand, when AS15 column was employed better results were obtained in selectivity and sensitivity for
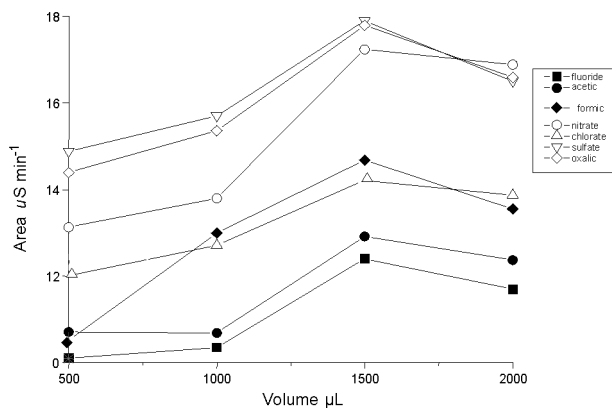
ACTA
AMAZONICA

On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic
anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

Figure 2 - Effect of the sample volume. A 1.0 mg l⁻¹ organic and inorganic anions solution (fluoride, acetic acid, formic acid, nitrate, chlorate, sulfate and oxalic acid) was used maintaining the AS15 analytical column, 100 mA current output level and 3.0 ºC temperature.

all organic and inorganic anions in linear range from 0.05 to 5.0 mg.l⁻¹. With this column, a relationship between sample volume and 33% signal area increase for all organic and inorganic anions was observed when sample volume was increased from 500 to 1500 μl into analytical column. Between 1500 and 2000 μl of aliquot sample, no significant differences were observed in the signal. Volumes above 2000 μl were not available because samples could contaminate the flush bottle through the transfer line. These results show that the volume of sample could be used to increase sensitivity for this typical low linear concentration range. Thus, the AS15 analytical column and 1500 μL were selected for further experiments.

EFFECTS OF PRE-CONCENTRATION VOLUMES AND FLOW RATES

The relationship between sample volumes and flow rates are very important factors that affect the pre-concentration step. In this sense, we investigated the best condition for the relationship between sample volume and flow rate into the AC15 concentrator column during the pre-concentration step. First, in order to investigate the effect of sample volume, different volumes of a solution containing 1.0 mg.l⁻¹ of all analytes were pre-concentrated with the AC15 concentrator column. Volumes of 500 to 2000 μl organic and inorganic anions were pre-concentrated using a fixed sample loading flow-rate of 1.8 ml.min⁻¹. Similar to the results obtained in the tests for choosing the type of analytical column, in this case increasing the injection volumes from 500 to 1500 μl resulted in higher peak areas for both organic and inorganic anions. When 2000 μl was inserted no significant differences in peak areas were observed. Peak areas were similar to those obtained when 1500 μl was pre-concentrated with the AC15 concentrator column.

After establishing the 1500 μl sample volume on the AC15 concentrator as the best alternative, we investigated the influence of flow-rate on the pre-concentration process. In this case, we tested the pre-concentration of 0.025 mg.l⁻¹ organic and inorganic anions at flow rates of 1.5; 1.8; 2.0 and 2.5 ml.min⁻¹ maintaining a current of 100 mA at the suppressor, 30 ºC temperature at the conductivity cell and a gradient elution. The gradient started at a KOH concentration of 10.0 mmol.l⁻¹ KOH, with retention time of 0 to 6 min, gradually increasing to 45.0 mmol.l⁻¹ KOH from retention times of 6 to 14 min and finalizing with 10 mmol.l⁻¹ KOH between 20 and 29 min of retention time. The chromatograms showed that when flow rate is increased from 1.8 to 2.5 ml.min⁻¹ a decrease in sensitivity was observed. Low resolution occurred between near residence time peaks of, for example, glycolate and acetate. The speed of elution was a crucial factor for the efficiency of on-line pre-concentration, with the best results attained at a flow rate of 1.5 ml.min⁻¹, which was employed in further experiments. This rate was also used in the reversed flow elution which decreased the dispersion of the concentrate during elution and improved the enrichment factors (Toofan et al., 1997).

GRADIENT ELUTION AND SUPPRESSION SETTINGS

Traditionally, acid or base eluents are prepared off line by dilution from reagent grade chemicals. This process can be tedious, prone to operator errors, and often introduces contaminants. The use of EG40 eluent generator modules in ion chromatography offers significant advantages over traditional procedures. Separations can be performed using only deionized water as the carrier while the EG40 module is placed between the outlet of the pump and the inlet of the sample injector. The eluent preparation step is eliminated, since the high purity base or acid eluent is generated on line at the point of use. Another advantage of eluent generators is the convenience of eluent generator control. Gradient separations can be performed using electrical current to generate gradients with minimal delay, instead of mixing eluents with different concentrations using gradient pumps. For trace level anion determinations, an anion trap column (ATC-1) was placed at the pump outlet to remove dissolved carbon dioxide and other anionic contaminants from the deionized water.

Finally, to complete the system parameter optimization the best combination of speed and selectivity was tested using three different gradient programs. In the first program, the elution concentration gradient started at a KOH concentration of 10.0 mmol.l⁻¹ from 0 to 3 min, followed by a gradual increase to 45.0 mmol.l⁻¹ KOH from 3 to 20 min and finished with 10 mmol.l⁻¹ KOH from 20 to 24 min of retention time. The second elution program, started with the same concentration KOH, but kept until 6.5 min, followed by a gradual increase to 45.0 mmol.l⁻¹ KOH at 21 min and returned to 10 mmol.l⁻¹

ACTA
AMAZONICA

On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic
anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

KOH between 21 and 24 min of retention time. For the last gradient elution program, KOH concentrations also started at 10.0 mmol.l^{-1} until 3 min., increased gradually to 45 mmol.l^{-1} at 14 min, and then were decreased to 10.0 mmol.l^{-1} from 14 to 24 min of retention time.

The first and third gradient elution programs showed low separation efficiency for organic anions with short retention times (from 0.0 to 3.0 min) employing 10 mmol.l^{-1} KOH eluent concentration, such as acetic and glycolic acids, formic and propionic acids. Therefore, adjustments were necessary to attain the proper eluent concentrations at the correspondent residence times. Problems with co-elution were minimized when the second gradient elution was used, keeping initial low concentration eluent from 0.0 to 6.5 min retention time. This interval of time has an eluent weak enough to retain, for example, fluoride well out of the void volume and separates several weakly retained monoprotic organic acids from inorganic anions. Also, the adjusts made on the final eluent concentration with retention time was capable of eluting triprotic phosphate and citrate. Thus, adjustment of the retention time allows better selectivity among analytes. The optimum conditions for a gradient elution were obtained with 10.0 mmol.l^{-1} KOH from 0 to 6.5 min, followed by a gradual increase to 45.0 mmol.l^{-1} KOH from 6.5 to 21 min and a 10 mmol.l^{-1} KOH between 21 and 24 min of retention time.

analysis. When high concentration elution was used, such as 45.0 mmol.l^{-1} KOH, during gradient elution, 300 mA output levels were better, because lower background conductivity could be achieved. Therefore, for the remaining experiments we used a gradient elution program started and kept at 10.0 mmol.l^{-1} for 6 min., then gradually increased to achieve 45.0 mmol.l^{-1} KOH at 21 min. and immediately returned to 10 mmol.l^{-1} KOH until 24 min. of retention time, with a fixed current of 300 mA at the suppressor column.

SAMPLE ANALYSIS

Once the experimental variables were optimized, a set of river water samples were processed in order to verify the feasibility of the proposed system, yielding the results of Tables 1 and 2. Although several compounds were identified in these waters, proving the method suitable for the simultaneous analysis of both organic and inorganic compounds, according to Souza (1998), certain species interact similarly with exchange resin sites and may not always be detected, misleading the interpretation of environmental data sets. Typical examples include co-elution of acetate/lactate peaks. To test if that was the case with the method proposed here, we added to the samples standard solutions containing 0.25 and 0.50 mg.l^{-1} lactate, both with 0.25 mg.l^{-1} acetate. Peak area results showed no significant interference during co-elution of acetate and lactate. Added lactate concentration was two-fold of that usually found in river water. Nevertheless, in natural

Table 1 - Determination of organic anions in Amazonian rivers samples.

Anions Organic	River samples			
(mg l^{-1})	Ji-Paraná	Comemoração	Igarapé Boa Vista	Urupá
acetic acid	0.282 ± 0.002	nq	nq	0.254 ± 0.002
Glycolic acid	0.054 ± 0.002	nq	nq	nq
propionic acid	nq	nq	0.013 ± 0.001	0.013 ± 0.001
formic acid	0.761 ± 0.002	0.631 ± 0.002	nq	nq
butyric acid	0.090 ± 0.002	0.235 ± 0.002	0.159 ± 0.002	0.355 ± 0.002
pyruvate	nq	nq	0.037 ± 0.002	0.075 ± 0.002
tartaric acid	nq	0.327 ± 0.002	0.263 ± 0.002	nq
phtalic acid	nq	nq	nq	nq
methanesulfonic acid	nq	nq	nq	nq
valeric acid	0.368 ± 0.002	0.261 ± 0.002	0.259 ± 0.002	nq
maleic acid	nq	nq	0.169 ± 0.002	nq
citric acid	0.193 ± 0.002	0.331 ± 0.002	0.591 ± 0.002	0.392 ± 0.002

Results expressed as means ± S.D. from triplicate measurements.
nq = no quantitated

The chemical suppression technology allows the increase in analyte conductivity and the decrease in the background eluent conductivity, resulting in an improvement in analyte detection limits. Different current output levels such as 50; 100 and 300 mA could be used in this module. Choosing the right current depends on the elution concentration during the

water samples, acetate determination is considered to be more important than lactate (Dahlén et al., 2000).

The set of samples from Amazonian rivers was analyzed by ion chromatography and results are presented in Tables 1 and 2. Figure 3 shows the chromatograms typical obtained with blank solution and sample solution, demonstrating that no

ACTA
AMAZONICA

On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

Table 2 - Determination of inorganic anions in Amazonian rivers samples.

Anions Inorganic	River samples			
(mg l⁻¹)	Ji-Paraná	Comemoração	Igarapé Boa Vista	Urupá
fluoride	0.066 ± 0.001	0.081 ± 0.001	0.089 ± 0.001	0.014 ± 0.001
chloride	0.341 ± 0.001	0.553 ± 0.001	1.616 ± 0.001	1.378 ± 0.001
nitrite	nq	nq	nq	nq
nitrate	0.478 ± 0.001	0.123 ± 0.001	0.111 ± 0.001	0.055 ± 0.001
bromide	0.141 ± 0.001	0.132 ± 0.001	1.043 ± 0.001	0.774 ± 0.001
sulfate	0.089 ± 0.001	0.065 ± 0.001	0.087 ± 0.001	0.068 ± 0.001
phosphate	0.153 ± 0.001	0.215 ± 0.001	0.515 ± 0.001	0.285 ± 0.001
chlorate	nq	0.022 ± 0.001	0.018 ± 0.001	0.024 ± 0.001

Results expressed as means ± S.D. from triplicate measurements.
nq = no quantitated

problems with carry-over occurred. Accuracy was ascertained by standard addition techniques of the 0.00; 0.05; 0.01 and 0.025 mg.l⁻¹ organic and inorganic anions and achievement of recoveries ranging from 97 to 107%. By applying the student *t*-test to the average recoveries, no significant difference at the 95% confidence level was observed.

response range from 0.01 to 1.0 mg.l⁻¹ for organic anions (acetic acid, propionic acid, formic acid, butyric acid, glycolic acid, pyruvate, tartaric acid, phthalic acid, methanesulfonic acid, valeric acid, maleic acid, oxalic acid, chlorate and citric acid) and 0.01 to 5.0 mg.l⁻¹ for inorganic anions (fluoride, chloride, nitrite, nitrate, bromide, sulfate and phosphate); glycolic acid (r=0.997), acetic acid (r=0.997), formic acid (r=0.997), propionic acid (r=0.997), methanesulfonic acid
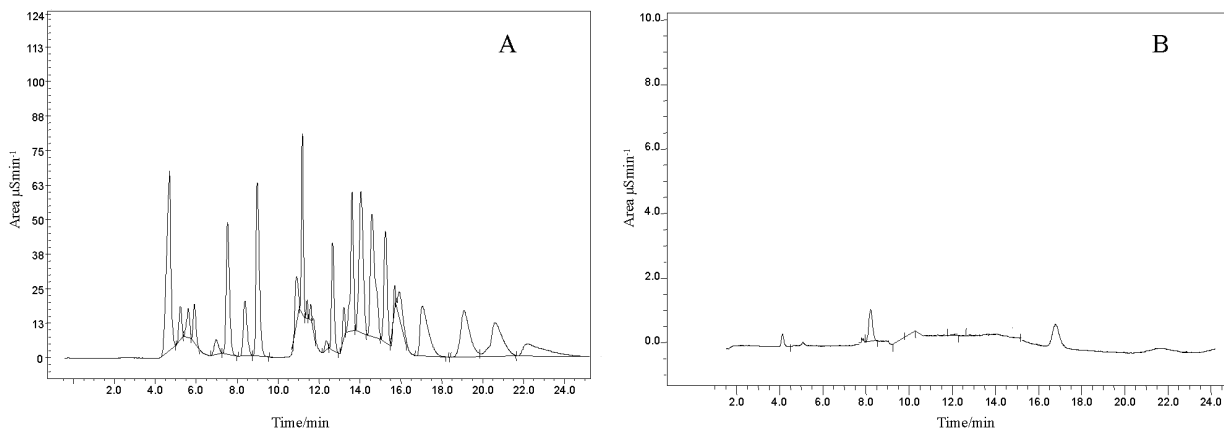

Figure 3 - Chromatograms typical obtained of the run system with preconcentration process. **A-** Sample solution; **B-** Blank solution.

Figure 4 shows the chromatograms typically obtained with 1.5 ml sample volume without and with pre-concentration steps of a standard solution containing 0.025 mg.l⁻¹ organic and inorganic anions. This figure also illustrates the advantages in sensitivity achieved with the use of the concentrator in LMWOA determination.

The proposed method includes several other favorable features, such as relative standard deviation of 2.0% (n=5) for a typical sample presenting 0.5 mg.l⁻¹ of all analytes; a linear

(r=0.999), butyric acid (r=0.997), tartaric acid (r=0.999), maleic acid (r=0.997), oxalic acid (r=0.997), phthalic acid (r=0.996), citric acid (r=0.996), fluoride (r=0.997), chloride (r=0.999), nitrite (r=0.999), chlorate (r=0.999), nitrate (r=0.998), sulfate (r=0.998), bromide (r=0.997) e phosphate (r=0.996). Also an analysis time of only 24 minutes and limit of detection of 5 µg.l⁻¹ for acetic acid, formic acid, butyric acid, glycolic acid, valeric acid, oxalic acid, citric acid and 10 µg.l⁻¹ for propionic acid, pyruvate, tartaric acid, phthalic acid,
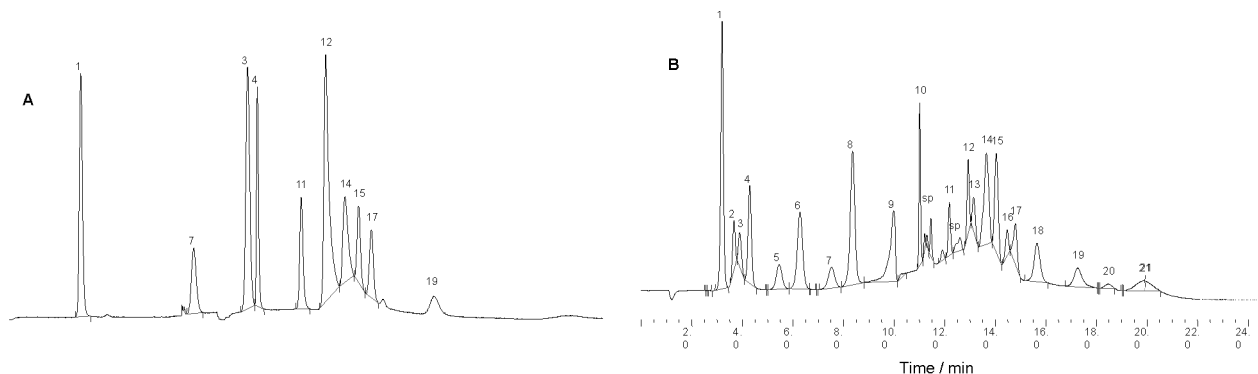
ACTA
AMAZONICA

On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

Figure 4 - Chromatograms of standard solution 0.025 mg l⁻¹ organic and inorganic anions. **A-** without preconcentration process; **B-** with preconcentration process. Conditions: AC5 concentrator column; AS15 and AG15 analytical and guard column; temperature 30 °C; flow rate 1.5 ml min⁻¹; conductance detector; 300 mA current output level and gradient elution. Peaks: sp = system peak; 1 = fluoride; 2 = glycolate; 3 = acetate; 4 = formate; 5 = propionate; 6 = MSA; 7 = pyruvate; 8 = chloride; 9 = nitrite; 10 = butyrate; 11 = chlorate; 12 = bromide; 13 = nitrate; 14 = valeric; 15 = tartaric; 16 = maleic; 17 = sulfate; 18 = oxalate; 19 = phosphate; 20 = phthalate; 21 = citrate.

methanesulfonic acid, maleic acid were obtained. A detection limit of 2 µg.l⁻¹ for fluoride, chloride, nitrate, bromide, sulfate and 10 µg.l⁻¹ for chlorate, nitrite, phosphate, estimated as suggested by IUPAC (1987), were also achieved.

CONCLUSIONS

On line sample pre-concentration coupled with auto suppression ion chromatography can be employed to increase the selectivity and sensitivity for the analyses at low concentration levels of anions without sample pretreatment. This association is an excellent tool for the quantitative determination of low molecular carboxylic acids (acetic acid, propionic acid, formic acid, butyric acid, glycolic acid, pyruvate, tartaric acid, phthalic acid, methanesulfonic acid, valeric acid, maleic acid, oxalic acid, chlorate, citric acid) and inorganic anions (fluoride, chloride, nitrite, nitrate, bromide, sulfate and phosphate) in river water and analysis time of 24 minutes. The AS15 selectivity and high capacity allow the determination of low levels of inorganic anions and low molecular weight organic acids using large volume loop injection. Furthermore, the method offers the advantages of good linearity, high precision, accuracy and easy operation. This method does not require any complicated sample preparation, allowing its use on a routinely basis.

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On line pre-concentration for simultaneous determination of low molecular weight organic acids and inorganic anions in Amazonian rivers waters samples employing ion chromatography with conductivity detection

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