

Supplementary material: *Which aluminium fractionation method will give true inorganic monomeric Al results in fresh waters (not including colloidal Al)?*

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### ***Inorganic monomeric Al - PCV procedure***

#### ***- Pyrocatechol violet method for aluminium fractionation on AutoAnalyzer***

Aluminium was measured as total monomeric Al ( $Al_m$ ) and organic monomeric Al ( $Al_o$ ) by the colorimetric reaction of pyrocatechol violet modification of Al standard method<sup>1</sup>, combined with cation exchange using continuous flow analysis with a 2-channel AutoAnalyzer II system (®Bran Luebbe/Seal Analytical). The system is a continuous segmented flow analyzer and consists of sampler, pump and two chemistry manifolds with flowcell photometers linked to a computer. Standard transmission tubing of Tygon and glass coils is used for mixing reagents with samples.

On-line cation exchange with a high precision pump followed by automatic introduction and mixing of the reagents gives the high accuracy and repeatability which is needed for a complex analytical procedure. The samples were analyzed in duplicates at the same time simultaneously determining pre- and post-cation exchange aluminium on the two channels. The results were evaluated as peak-heights with AACE (AutoAnalyzer Control and Evaluation Software, Seal Analytical). The Al-Autoanalyzer II system manifold is shown in scheme 1. The cation exchange procedure distinguished the determination of  $Al_o$  from  $Al_m$ . Organic monomeric Al ( $Al_o$ ) passed through the column while the potentially toxic fraction, inorganic monomeric Al ( $Al_{im}$ ) was retained by the cation exchange resin (and hence could be calculated as the difference between  $Al_m$  and  $Al_o$ ).

#### ***Reagents and solutions***

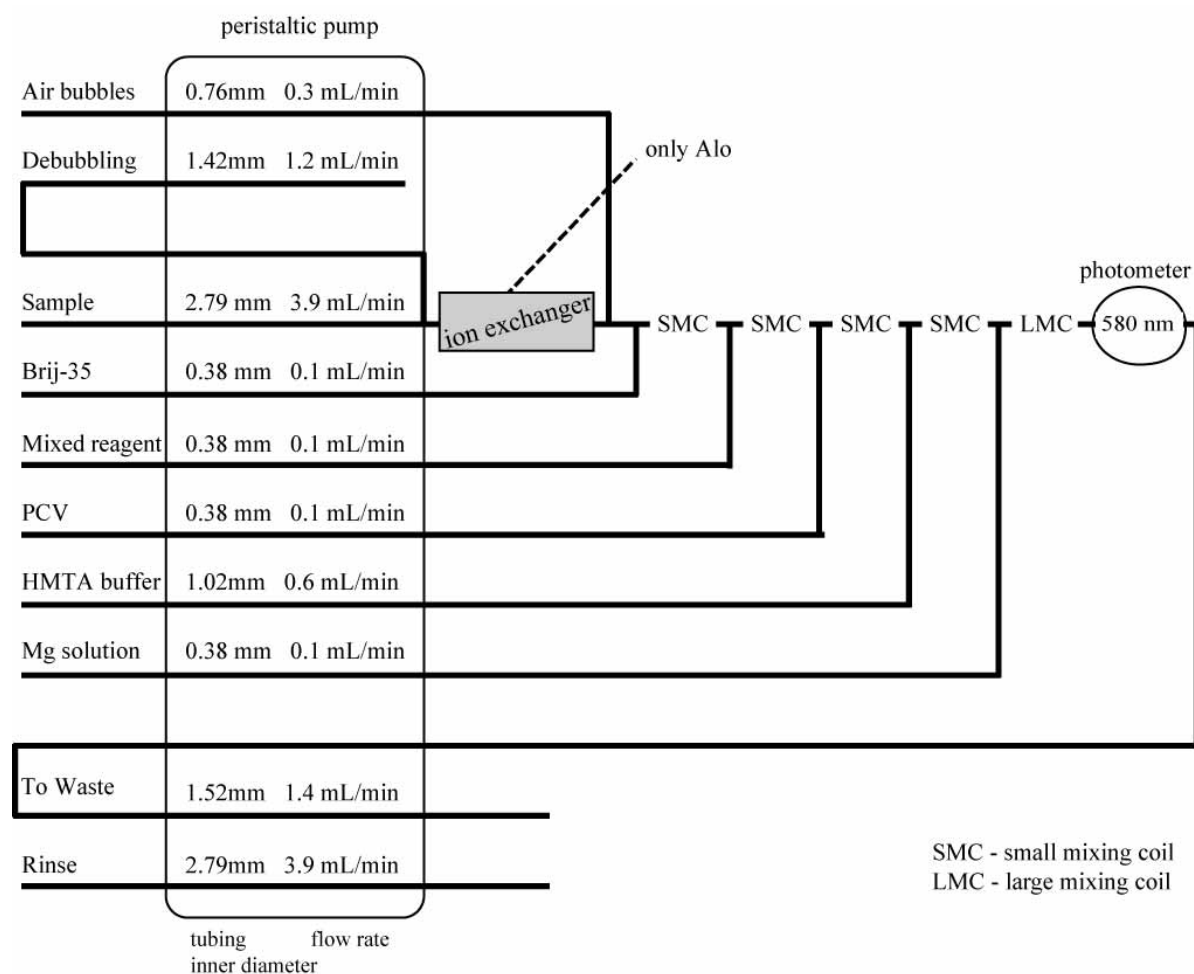
All water used is deionized. Reagents and solutions were prepared and kept in vessels of polyethene or polypropene (glass should be avoided) also pipettes of plastic were used.

##### Rinse water, 1mM NaCl:

Prepare rinse water by degassing water with a water aspirator in at least 10 minutes. Add 1 mL 1M NaCl per liter.

##### Wetting agent (Brij 35):

Add a few drops of 30 % Brij 35 to 200 mL water. Prepare fresh every day.



*Scheme 1. Al fractionation AutoAnalyzer manifold with on-line cation exchange Amberlite IR 120 and colorimetric pyrocatechol violet complexation measured in flowcell photometer. Two parallel setups were made following the scheme, with and without cation exchanger (rendering organic monomeric aluminium, Al<sub>o</sub> and total monomeric aluminium, Al<sub>m</sub>). The noted inner diameter of tubing used on an AutoAnalyzer pump gives the flow rates shown and correct reaction times and reagent concentrations.*

#### Mixed reagent:

First solve 10.8 g hydroxyl ammonium chloride HO/NH<sub>3</sub>Cl in water. Then add 0.54 g 1,10-phenantroline-monohydrate C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>·H<sub>2</sub>O and mix. After that add 7.7 mL of a 10 mg Al/L solution (=77 µg Al) and fill up the solution to 200 mL with water. Durability is about 1 month if refrigerated.

#### Pyrocatechol violet (PCV):

Dissolve 0.108 g pyrocatechol violet C<sub>19</sub>H<sub>14</sub>O<sub>7</sub>S (brand Fluka) and dilute to 200 mL with water. Durability is about 2 months if refrigerated.

#### HMTA-buffer:

Dissolve 706 g hexamethylenetetraamine (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> in deionized water and add approximately 40 mL 4M H<sub>2</sub>SO<sub>4</sub>. Dilute to 2000 mL with water. Filtrate the buffer with GF/C -filter by a water-

suction. Control pH in the Autoanalyzer photometer drains every time a new batch of buffer is prepared, the pH should be 6.1 – 6.2. Adjust buffer pH if needed by adding 4M H<sub>2</sub>SO<sub>4</sub> or NaOH. Durability is about 1 month.

Mg-solution:

Dissolve 54.26 g Magnesium sulphate heptahydrate MgSO<sub>4</sub>·7H<sub>2</sub>O and dilute to 200 mL with water. Durability is about 1 month.

Cleaning solution for Auto-analyzer, NAOH/EDTA:

Dissolve 65 g NaOH and 5 g Na<sub>4</sub>EDTA in 1000 mL water.

Aluminium standard solutions:

Stock solution 1 g Al/L: (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 2-5% HNO<sub>3</sub> – commercial).

Intermediate solution 10 mg Al/L:

1000 µL stock solution is diluted with water to 100 mL in an acid washed 100 mL volumetric flask. Durability is about 1 month if refrigerated.

5 mM HNO<sub>3</sub>:

Add 25 ml 0.1M HNO<sub>3</sub> 500 mL water.

Working standard solutions:

Take 250, 500, 1000, 1500, 2000 and 3000 µL of the intermediate solution and add reciprocal amounts of 5 mM HNO<sub>3</sub> (2750, 2500, 2000, 1500, 1000 and 0 µL) and dilute with water in acid washed 100 mL volumetric flask.

The final working Al concentrations are 25, 50, 100, 150, 200 and 300 µg/L. Prepare fresh solutions daily.

Drift, 200 µg Al/L:

Mix left over standard solutions to an approximate concentration of 200 µg/L, this is used to estimate instrument drift.

*Analytical procedure*

The unpreserved sample (3.9 ml/min) was de-bubbled (-1.2 ml/min) directly after the pump and then introduced to the cation exchange column and/or sent directly into to the analytical system. The cation exchange procedure was done according to Driscoll<sup>2</sup> with an optimal column flow rate of 2,7 ml/min\* ml resin. The column (Teflon tubing 13 cm x 3 mm i.d.) was placed immediately after de-airing following the peristaltic pump of the AutoAnalyzer on one of the channels. The column ends were covered in nylon net (25 µm) and connected to the system by thin Teflon tubing and a flow switch valve. The resin (99% sodium form Amberlite IR120

mixed with 1% hydrogen form)<sup>3</sup>, was rinsed with 1 mM sodium chloride (NaCl) between the samples and regenerated by storing in 1 M NaCl in between use.

In the AutoAnalyzer the sample was mixed successively with; Brij 35, Mixed reagent, PCV, HMTA-buffer and Mg solution (tubing dimensions in Scheme 1). After six minutes reaction and transfer time in the coils the colored Al-complex was measured at 580 nm in a 15 mm flowcell. The sampling rate was 30 samples per hour with one minute for sampling and one minute for washing. When the glass coils gets discolored or if the output is changed (lower and disproportional standard curve, pike- instead of plateau- shaped peaks) cleaning is needed. Put all tubing (except the rinse) and the sampling needle in the cleaning solution for five minutes and rinse liberally with water afterwards.

### *Comments*

There were three main differences compared to the procedure of Rogeberg and Henriksen<sup>3</sup>; a) no acid was added to the sample before the color reaction (which took place at each sample's individual pH), b) a known amount of aluminium was added in order to get a linear calibration-curve at concentrations below 50 µg Al/l and c) magnesium was added to minimize the fluoride interference.

To use the AutoAnalyzer pump for on-line cation exchange reduces random errors introduced by inadvertent flow variations. Overall, to automate aluminium fractionation on AutoAnalyzer minimizes variations in the analytical practice which increases the reproducibility and accuracy of the analysis.

### *References*

- 1 Swedish Standard, *SS 028210, Water analysis - Determination of acid soluble aluminium in water - Photometric method*, 1992.
- 2 C. T. Driscoll, *Int. J. Environ. Anal. Chem.*, 1984, **16**, 267-283.
- 3 E. Rogeberg and A. Henriksen, *VATTEN*, 1985, **41**, 48-53.