ION Chromatography – a better tool to analyse ions in wet deposition and passive samples



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Theory of IC

History

Definition

«An analytical method where a substance mixture appearing in just one colour is separated in a way that different colours become visible. The method is used to separate chemical substances which are chemically quite similar and though difficult to separate»



Greek *chroma* = colour *graphein* = to write

Going back to school

A simple experiment from school

take a piece of paper make a little drop with «black» ink just add water to it's center







see the colors that make up the black» ink





Physico chemical

Definition

«The term «chromatography» is the general name for a wide range of physico-chemical separation processes in which the components to be separated are distributed between a stationary and a mobile phase.»



mobile phase stationary phase gaseous liquid liquid \rightarrow GLC, LLC solid \rightarrow GSC, LSC (HPLC - IC) **Column interactions**

Types of chromatography

Mobile phase dissolves and transports the analyte Stationary phase retains the analyte

adsorbing ⇒ adsorption chromatography





dissolving ⇒ distribution chromatography

reacting ⇒ ion exchange chromatography



Polarities

Methods of chromatography

Based on the polarities of the stationary and mobile phases a distinction is made between the following methods:

Group 1 – traditional TLC + HPLC

normal phase chromatography
 reversed phase chromatography

Group 2 – Ion Chromatography 4. ion exchange chromatography 3. ion pair chromatography 5. ion exclusion chromatography



Traditional methods

Group 1 – traditional TLC + HPLC 1. Normal phase chromatography

Stationary p. = polar (e.g. SiO_2) – mobile p. = non polar (e.g. n-hexane)

2. Reversed phase chromatography Stationary p. = non-polar (e.g. C₁₈) – mobile p. = polar (e.g. acetonitrile or methanol / water)



Group 2 – IC 4. Ion exchange chromatography

Cations and anions form a weak ionic binding with the stationary phase. C: Stationary p. = polar (e.g. $R-SO_3^-$) – mobile p. = polar (e.g. HNO_3 aq.) or A: Stationary p. = polar (e.g. $R-NR_3^+$) – mobile p. = polar (e.g. Na_2CO_3 aq.)

Ion exchange chromatography retains <u>analyte</u> molecules based on <u>coulombic</u> (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge.

- Cation exchange chromatography
- Anion exchange chromatography.

Cation exchange chromatography retains positively charged <u>cations</u> because the stationary phase displays a negatively charged functional group

Anion exchange chromatography retains anions using positively charged functional group

Note that the ion strength of either C+ or A- in the mobile phase can be adjusted to shift the equilibrium position and thus retention time.

Definition

«Ion chromatography includes all chromatographic methods that separate ionic substances and substances that dissociate easily. These methods are ion pair chromatography, ion exchange chromatography and ion exclusion chromatography. Analyte and mobile phase are initially always polar and/or ionic. Ion exchange chromatography is the most important separation mechanism in ion chromatography.»

Most popular set up





Where does it actually happen?



Eluent Pump Injector Column Detector

Ion exchange

The stationary phase

Cations need a cation exchanger and anions need an anion exchanger How a stationary phase is built



Ion exchange

Composition of the stationary phase

substrate / resin carrier a spacer group a group that carries the separating capacity —

Substrates

Polystyrene/divinylbenzene Polymethacrylate Polyalcohol Hydoxyethylmethacrylate (HEMA) Silicate Anion exchanger quaternary ammonium groups alkyl amines hydroxy-alkylamines alkyl amines with acrylate type crosslinking

Cation exchanger sulfonates carboxylates

Spacer alkyl chain

NR⁺₃

SO3

Ion exchange

Mobile Phase

The mobile phase dissolves and carries the sample The mobile phase is usually aqueous

anions (I)

- Phthalic acid
- Salicylic acid
- p-Hydroxybenzoic acid
- Benzoic acid
- Borate

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- Borate/Gluconate
- Potassium hydroxide

anions (II)

- Carbonate/bicarbonate
- Potassium hydroxide

cations (I)

- Borate
- Nitric acid
- Tartaric acid

. . .

- Tartaric acid/dipicolinic acid
- Tartaric acid/citric acid
- Sodium dihydrogen phosphate
- oxalic acid/ethylene diamine/acteone

Ion exchange

Cation separation mechanism

Stationary phase and mobile phase compete for the analyte



Ion exchange

Cations



Ion exchange

Anion separation mechanism

Stationary phase and mobile phase compete for the analyte



Ion exchange

Anions







