Dr Martyn J. Earle

THE UTILISATION OF IONIC LIQUIDS WITH IONIC LIQUID-LIQUID CHROMATOGRAPHY

ILLC

Dr. Martyn J. Earle (QUILL)

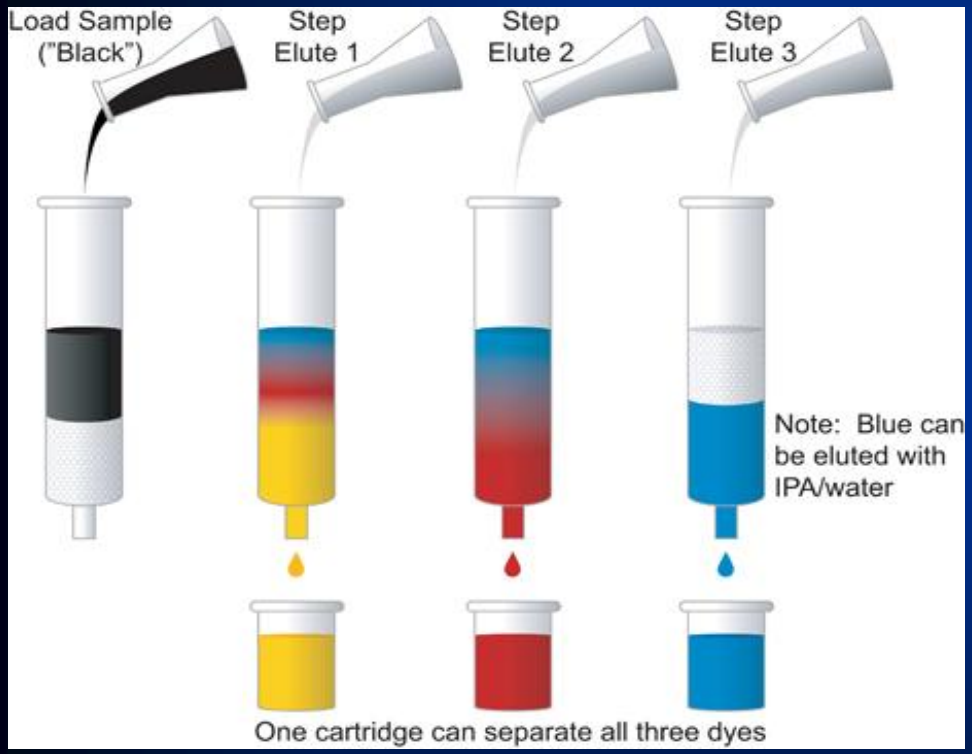
A New Form of Chromatography

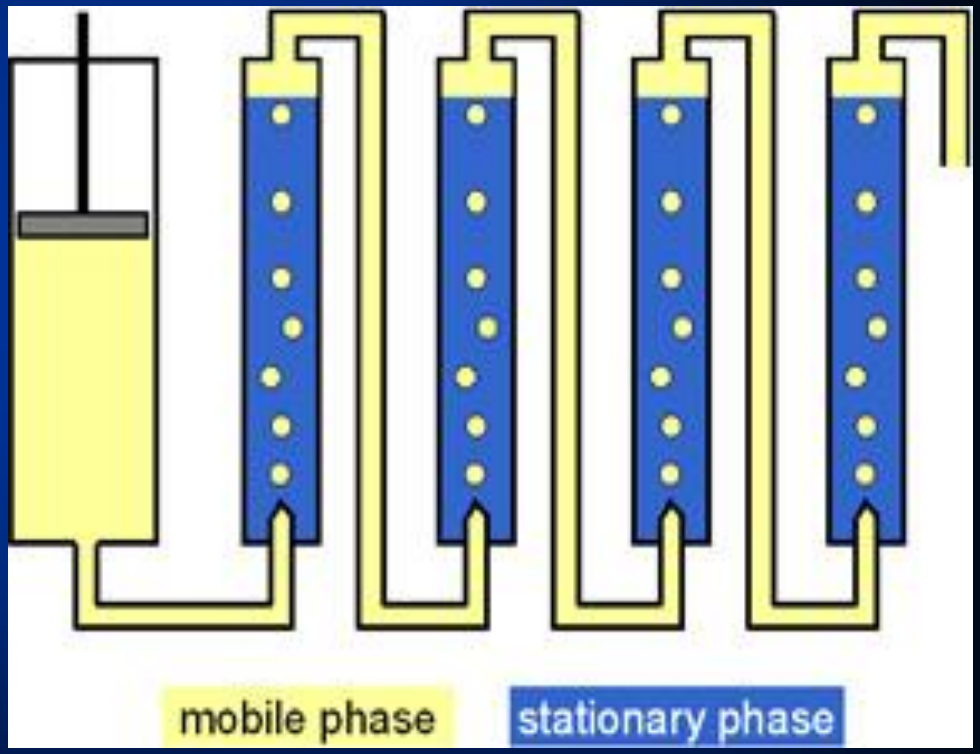
A general purpose method for the separation of practically all dissolvable compounds

Presentation Order

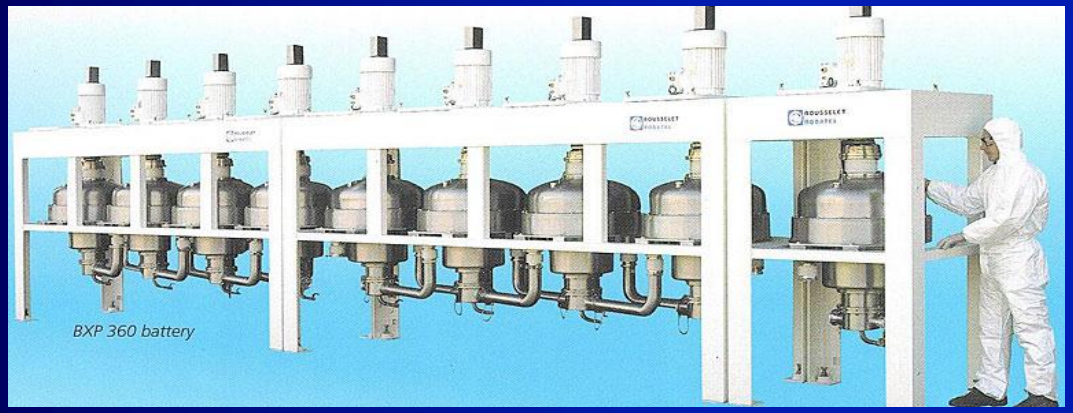
- Principals of Liquid-Liquid Separations
- Ionic Liquid – Liquid Separations (ILLC)
- Operation of ILLC Chromatography
- Metal Separations

What is Liquid-Liquid Chromatography ?





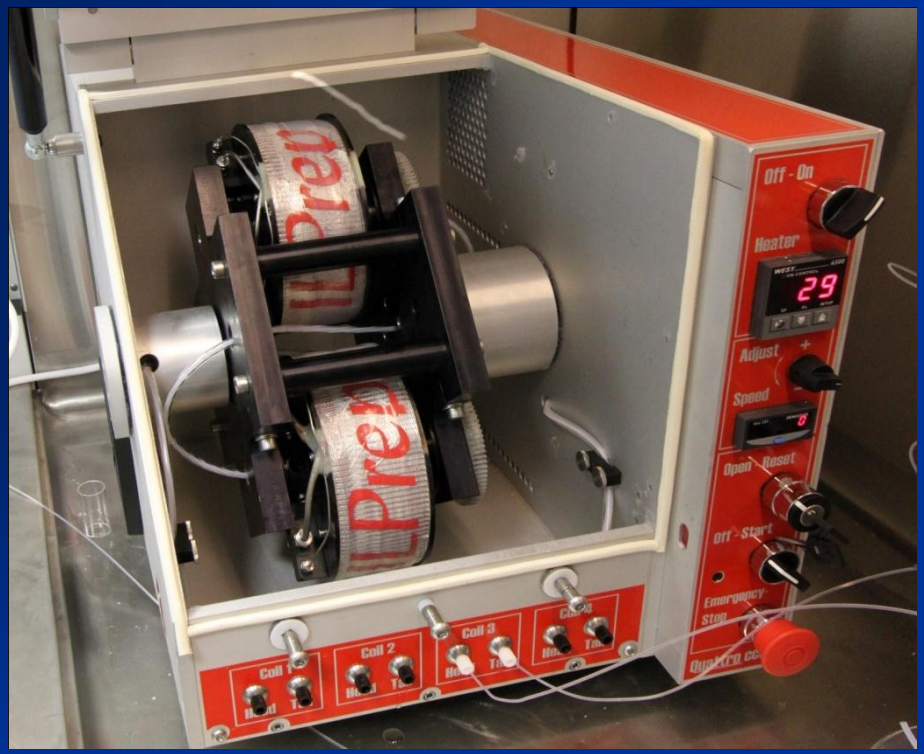
Industrial Countercurrent Extraction



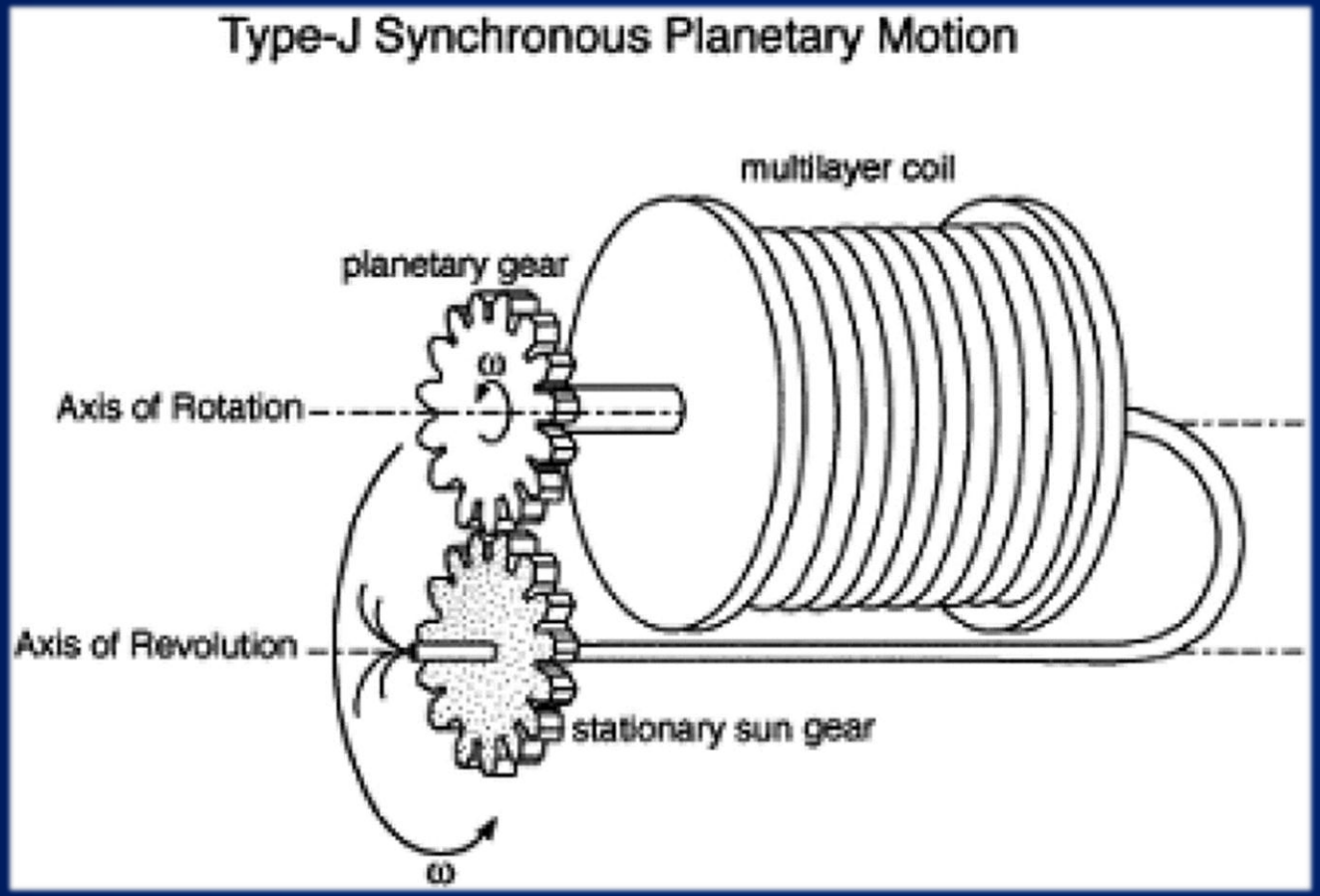
A wide range of industrial scale liquid-liquid, countercurrent (CC) extractors are available

Dr Les Brown with IL-Prep™ Machine

AECS's IL Prep™ ILLC Machine Installed in QUILL



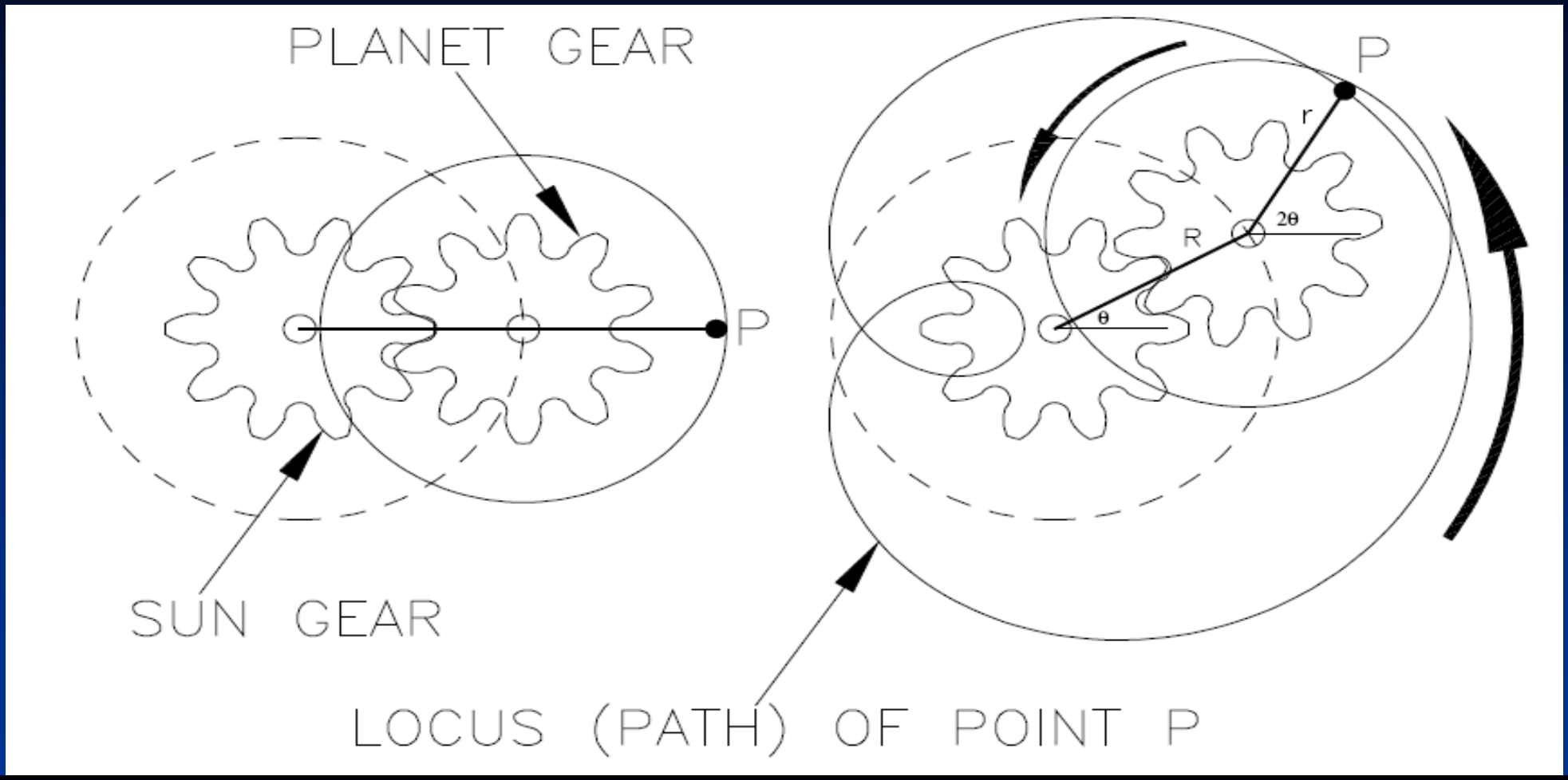
The J-Type Centrifuge



The flying leads go through both the axis of rotation and the axis of revolution

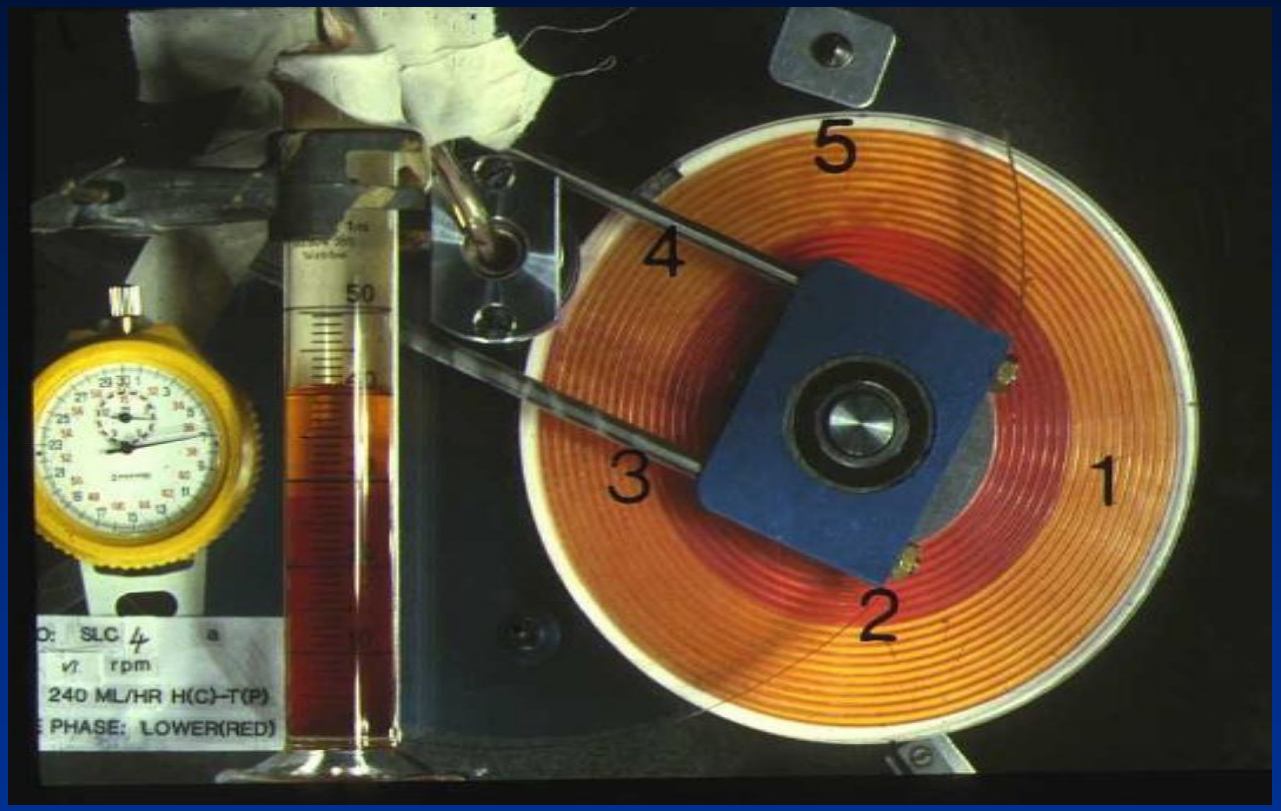
No overall rotation of the flying leads

Hydrodynamic ILLC



The coils are subject to double rotation in what is known as planetary motion (like Earth rotation, it rotates own axis as rotates around the sun, this is defined as "J" type.

Hydrodynamic L-LC Mixing in Coils

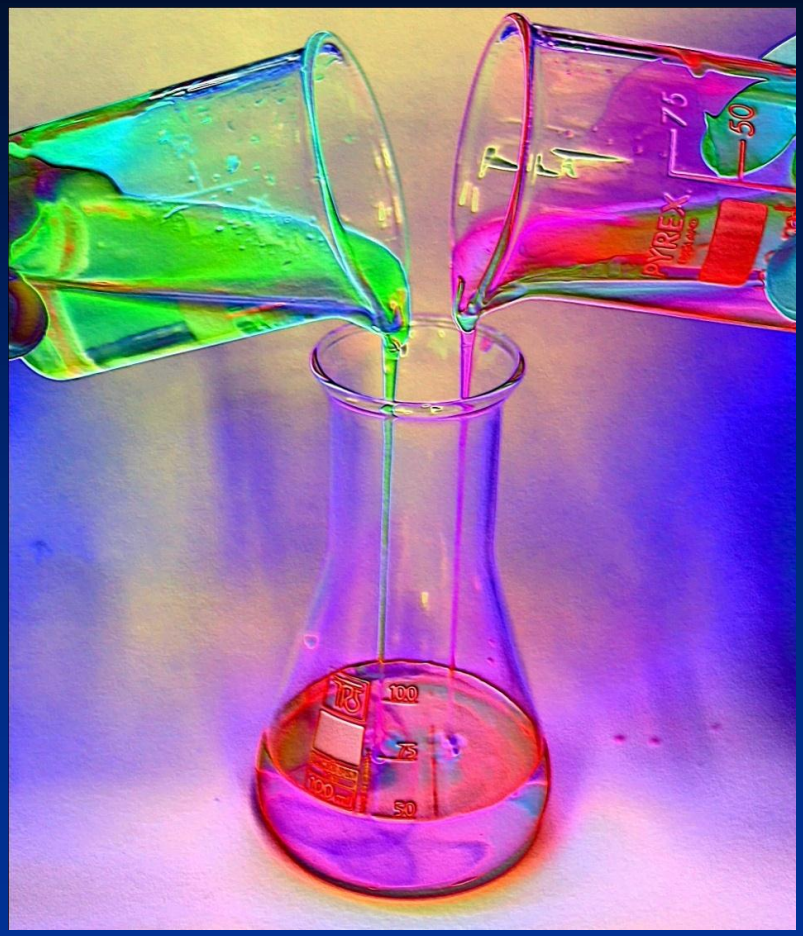


LOW
"G" = MIXING OF THE TWO LAYERS

HIGH
"G" = SETTLING OF THE TWO LAYERS

Imagine on Earth, at 1 "G" fixed wind causes 10 foot wave in ocean / water interface. Imagine same wind, same ocean, **BUT** 200 "G"? NO WAVE / NO MIXING. At 0.1 "G" FORCE OCEAN & AIR RAPIDLY MIXED.

Ionic Liquid-Liquid Chromatography



Ionic Liquid-Liquid Chromatography = ILLC
Ionic Liquid-Liquid Extraction = ILLE

QUILL Statement

No ionic liquids were harmed during the making of the films and in all separation processes carried out

Current State of the Art

Ionic liquids have not been significantly tested in most forms of liquid-liquid chromatography


Use of Coils

Coil Volume (cm^3)	Ionic Phase Needed (cm^3)	Comments
12	20	Feasibility testing
34	55	Small separations
133	175	General separations
236	300	Extractions and prep scale

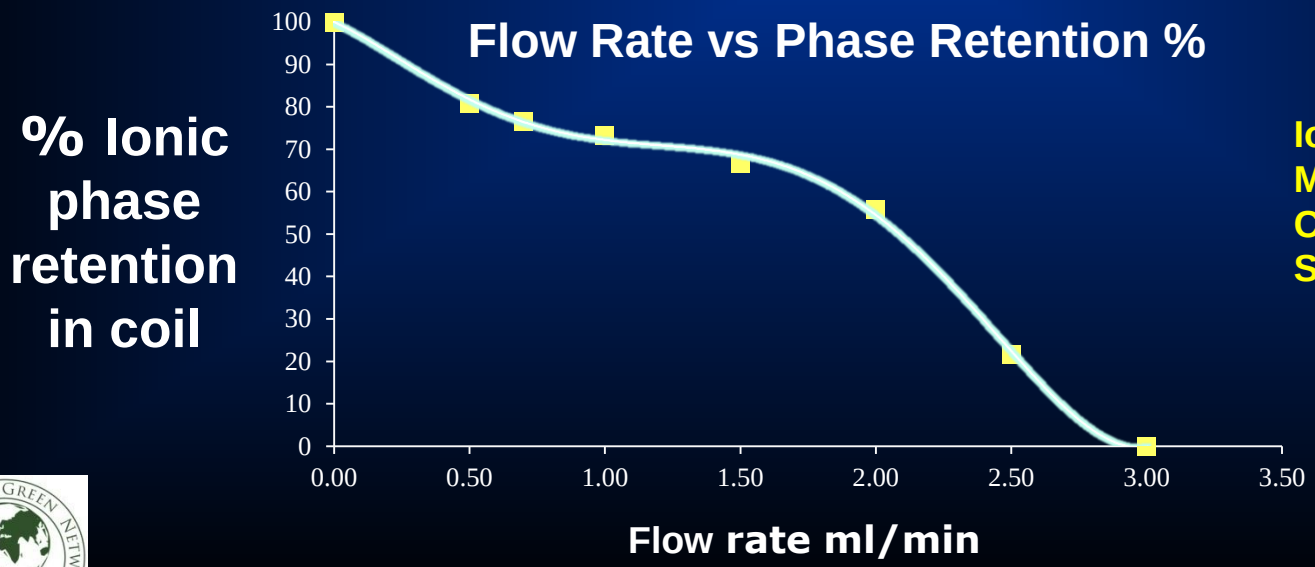
The ionic phase is the combination of materials that make up the ionic phase, and not the amount of ionic liquid needed

For a full test and scale up of a separation, at least 0.5 Kg of ionic phase may be required

All ionic liquids are recycled and reused

Example of Operation

- Pump ionic liquid phase into coil (stationary phase)
- Start the rotation of the machine
- Pump organic or water phase into coil until no more ionic phase comes out



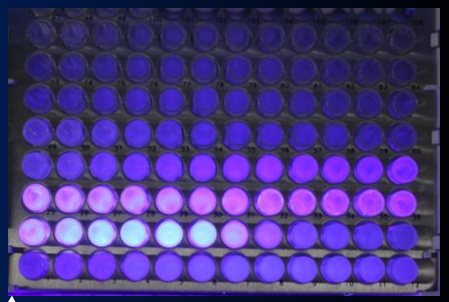
Ionic liquid = $[C_{12}mim][NTf_2]$
Mobile phase = hexane
Coil = 34 ml, 1.0 mm diameter
Speed = 865 rpm

Example of Operation

Solution of mixture in ionic liquid phase and a second non-ionic phase

Mixture to be separated

Sample vials



Organic or Water Phase

Ionic Phase

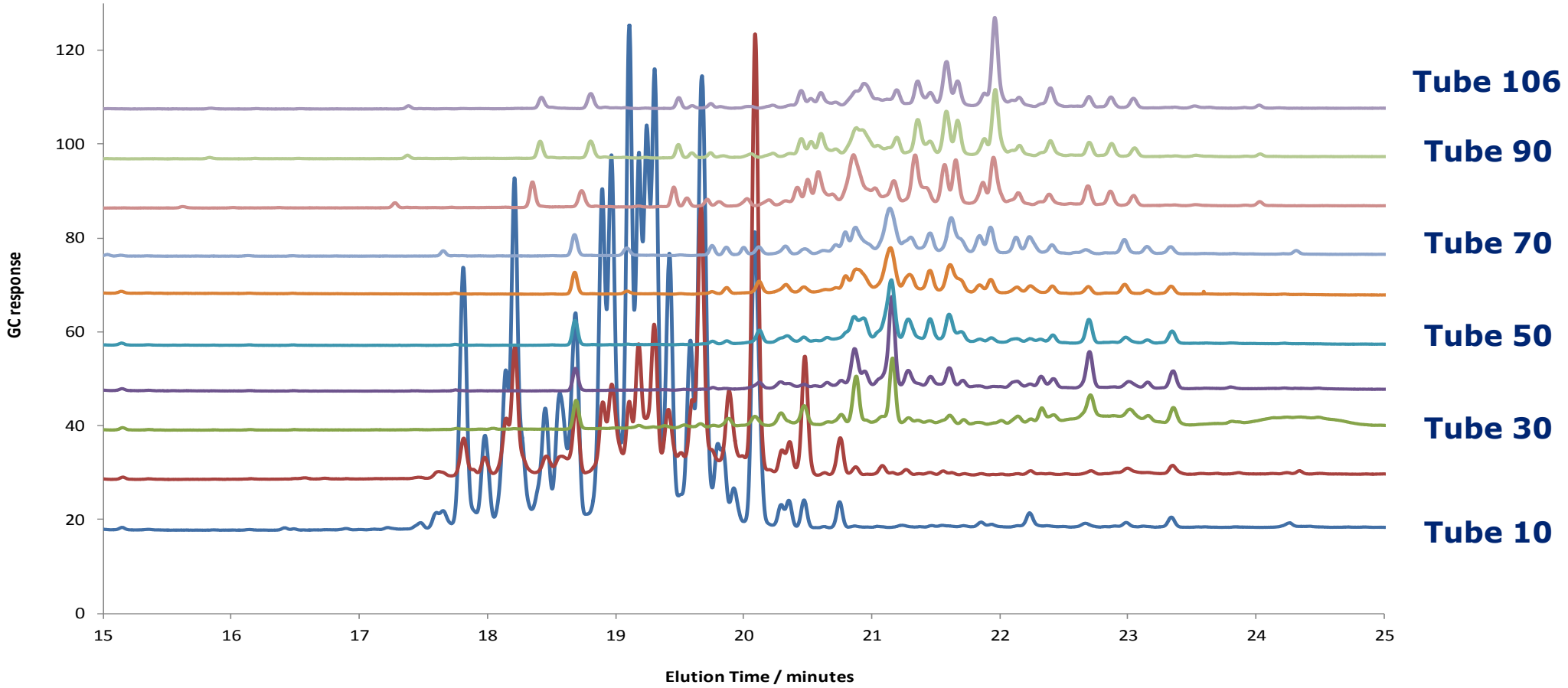
Pump

Pump

Fraction Collector

Separation of a Natural Plant Oil

Carried out on Coil 4 (236 cm^3), 30 C, @ 2 ml/min
Solvent system = $[C_{12}mim][NTf_2]$ / Hexane with ionic phase as stationary phase

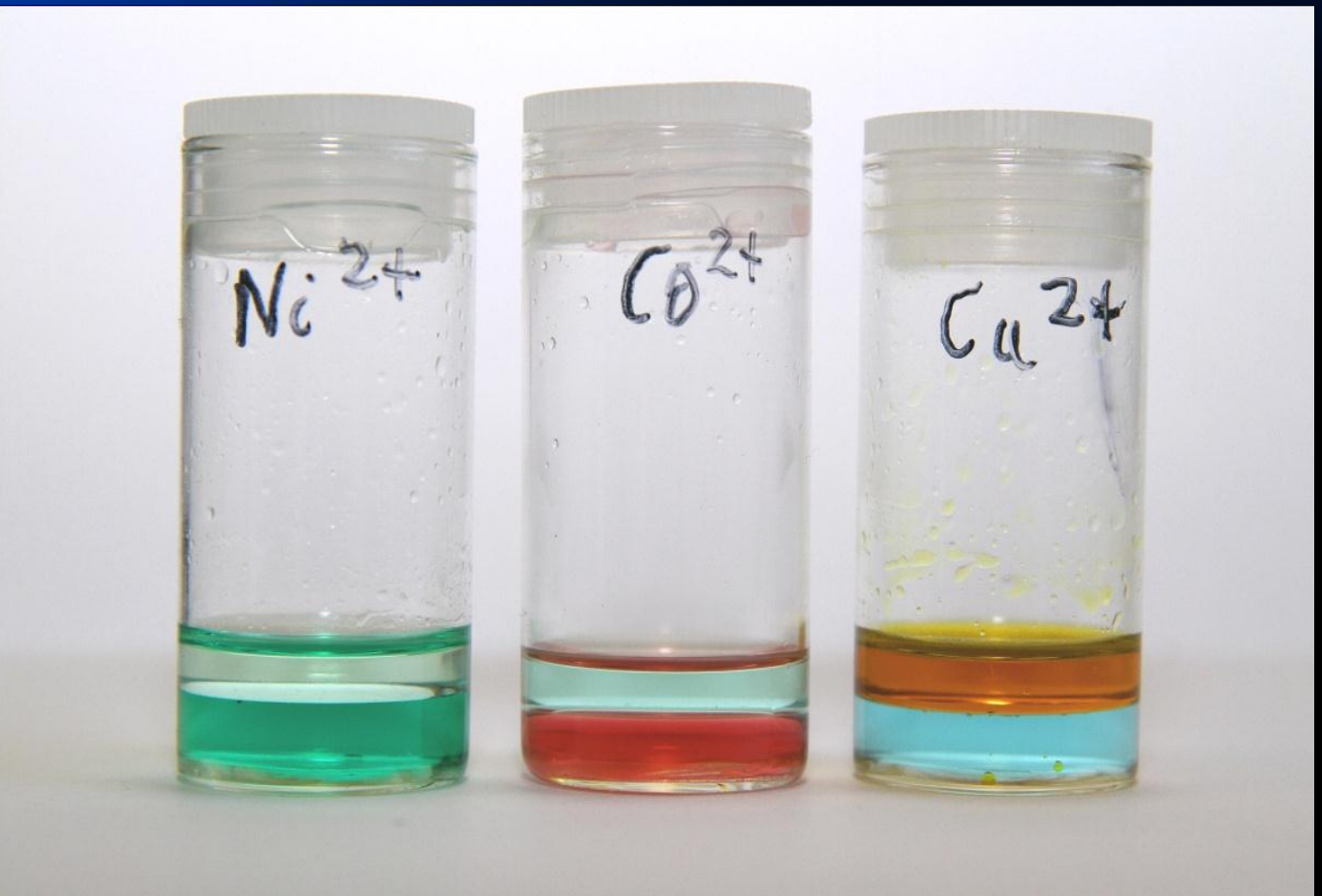



Metal Separations

Copper, Nickel and Cobalt Separations

The equilibrium is $[M(H_2O)_6]^{2+} + 4\ X^- = [MX_4]^{2-} + 6\ H_2O$ X = halide M = Cu, Ni, Co

The dihalides of Cu, Ni, and Co partition differently in a [Phosphonium][Halide] / Water mixture



Ni^{2+} strongly prefers the water phase

Co^{2+} is more soluble in the water phase than ionic phase

Cu^{2+} prefers the ionic phase

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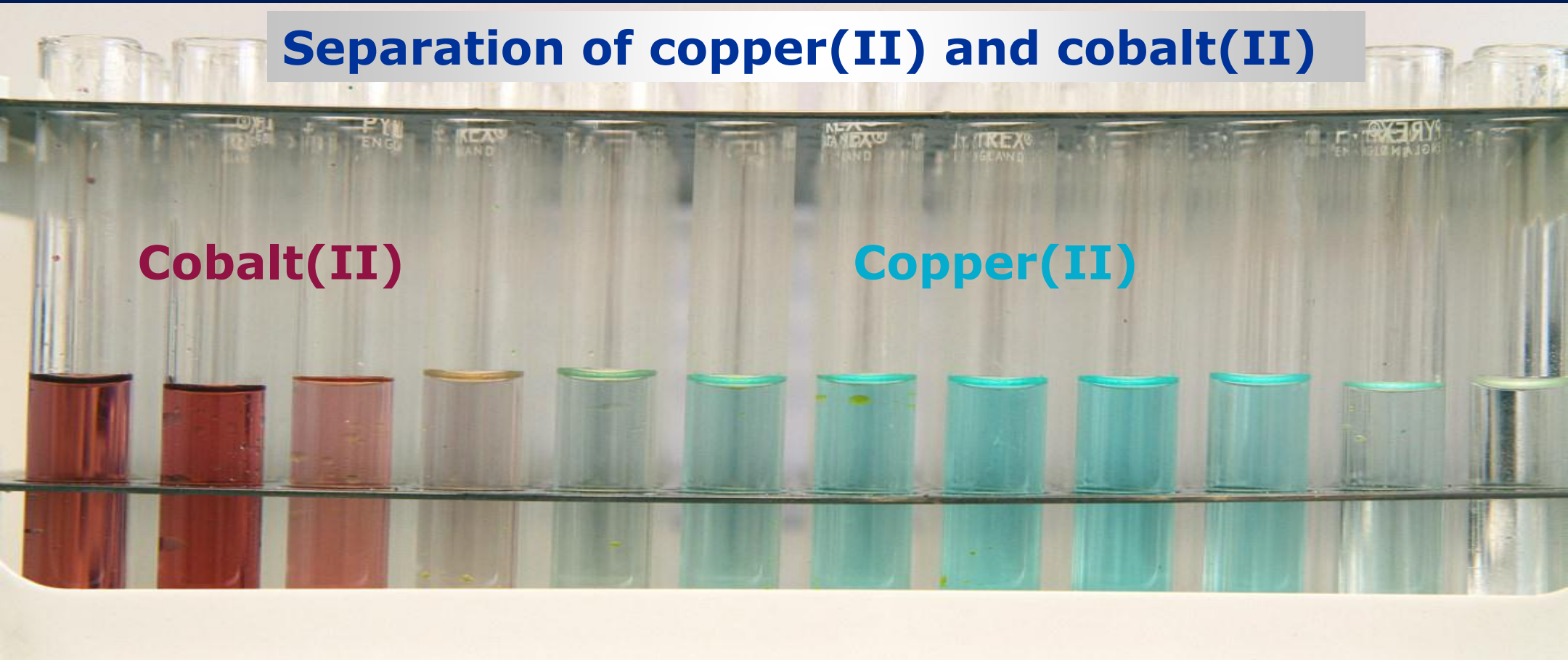
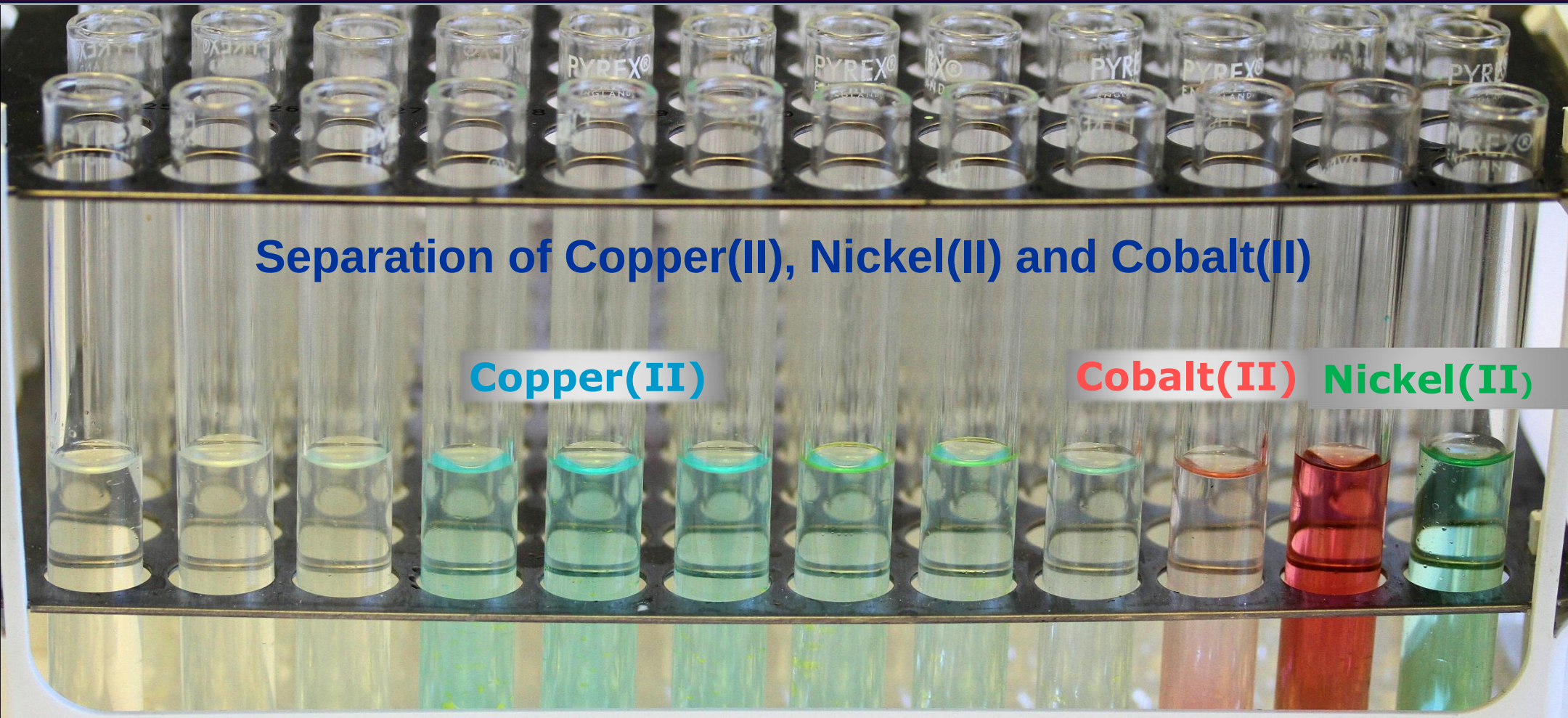
[Phosphonium][Halide] / H_2O / CH_2Cl_2

- Most dense stationary phase = [Phosphonium][Halide] / CH_2Cl_2
- Least dense mobile phase = H_2O



[Phosphonium][Halide] / H_2O / Ethyl Ethanoate



- Least dense stationary phase = [Phosphonium][Halide] / Ethyl Ethanoate
- Most dense mobile phase = H_2O

Summary

- ILLC is a new form of chromatography
- Unlike HPLC, there are no off the shelf columns or ionic liquids for specific separations
- The most difficult part of separations is choosing the best solvent system to use
- This requires test tube experiments to determine the solvent distribution ratios of dissolved solutes

ILLC™

- A general purpose methodology for the separation of practically all dissolvable compounds
- CCC can even be used to separate sand, grit and powders provided they can fit inside the piping used

Acknowledgments

- Professor K. R. Seddon (QUILL)
- Dr Leslie Brown (AECS)
- Dr Manuela A. Gîlea
- Dr Natalia V. Plechkova
- QUILL and Invest NI for funding

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Thank You for Listening

Questions ?