Investigation of capillary ion chromatography (Cap-IC) for nuclear prospects

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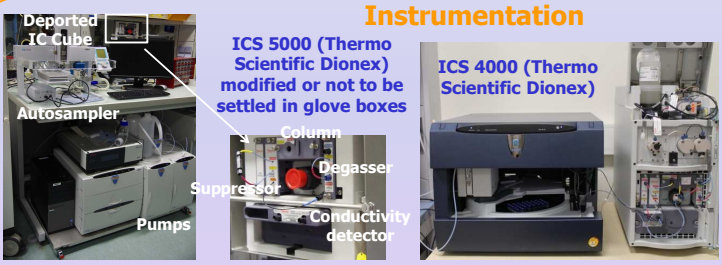
The recent development of commercial capillary ion chromatography (Cap-IC) systems [1-4] provides a major opportunity to increase the reactivity of laboratories and to reduce the amount of radioactive effluents produced from the chromatographic analyses in the nuclear field. As the column replacement in a radioactive environment is tedious, the retention behavior of IC columns was investigated at capillary scale to anticipate this operation.

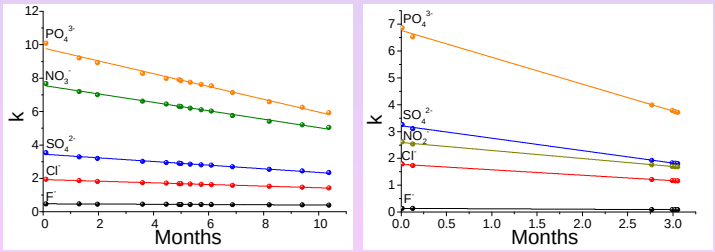
Instrumentation



Capillary column	Bead diameter (µm)	Hydrophobicity according to Thermo's manuals	Presence of latex	Capacity of capillary column (µequiv)	Flow rate (µL/min)	Eluent concentration
AG15/AS15 (0.4 x 250 mm)	6.5	medium high	no	2.25	12	38 mM KOH
AG11-HC-/AS11-HC-4µm (0.4 x 250 mm)	4	medium low	yes	2.9	15	30 mM KOH
AG10/AS10 (0.4 x 250 mm)	8.5	low	yes	1.7	10	85 mM KOH
CS12A (0.4 x 250 mm)	8	medium	no	9.4	10	20 mM MSA

Evolution of retention behavior of Cap-IC columns

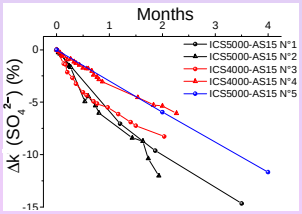
Evolution of retention factors over several months for AS15 and AS10 capillary columns (a) AS15/AG15 0.4 x 250 mm N°1, commercial ICS-5000 system, 38 mM KOH, 12 µL/min, 30 °C (b) AS10/AG10 0.4 x 250 mm, modified ICS-5000 system, 85 mM KOH, 10 µL/min, 30 °C



→ **Linear decrease of retention factors as a function of the operating time of the Cap-IC columns whatever the type of columns and the studied anions**

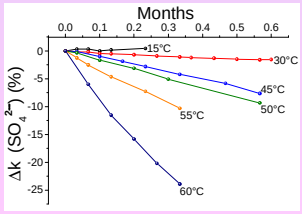
≠ **no decline for cation-exchange Cap-IC columns**

Relative variation of sulphate retention factor for AS15 capillary columns (N°1 and N°2 on ICS-5000 system, N°3 and N°4 on ICS-4000 system, N°5 on another ICS-5000 device), 38 mM KOH, 12 µL/min, 30 °C



→ **Monthly decrease between 2.5 % and 5 % when using AS15 Cap-IC columns**

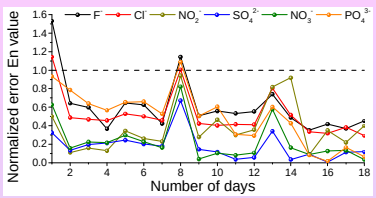
Relative variation of the retention factor of sulphate as a function of time for AS15 column temperature ranging from 15 °C to 60 °C



→ **Application of a limited column temperature (<20°C) when no analysis is performed in order to preserve the Cap-IC column retention capabilities at long term**

Validation of Cap-IC

Quality Control (QC) charts obtained for QC standards analyzed with the same calibration curve during 18 days

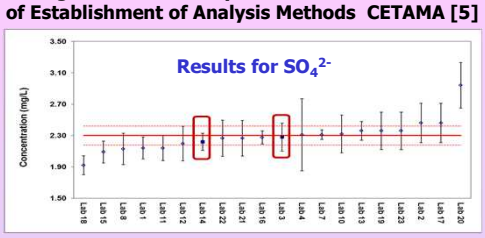


$$with\ E_n = \frac{|x_{d_i} - X_{ref}|}{\sqrt{U_{d_i}^2 + U_{ref}^2}}$$

where x_{d_i} is the measurement result obtained the day i (d_i), X_{ref} is the reference value, $U_{d_i}^2$ is the expanded uncertainty (k=2) of x_{d_i} ($U_{d_i}/x_{d_i} = 5\ \%$), U_{ref}^2 is the expanded uncertainty (k=2) of X_{ref}, ($U_{ref}/X_{ref} = 1\ \%$)

→ **Accurate quantification of all anions by using the same calibration curve during 18 days**

Participation to an interlaboratory comparison exercise (EQRAIN IONS 1) organized in 2014 by the French Committee of Establishment of Analysis Methods CETAMA [5]



→ **No bias observed for the two laboratories using Cap-IC whatever the analyzed anions**

Novel aspect

Despite the linear decrease of retention factors observed for anions, the analytical performance of capillary ion chromatography was validated with an interlaboratory comparison exercise, which makes this technology convenient for applications to radioactive samples. This work is of prime interest for nuclear analysts but also for IC users who intend to increase the flexibility and the reactivity of their laboratories.

[1] PR Haddad et al. (2008) Recent developments and emerging directions in ion chromatography. J Chromatogr A 1184:456-473.
[2] CA Lucy et al. (2013) Advances in High-Speed and High-Resolution Ion Chromatography. LC GC Europe 31:38-42.
[3] H Eghbali et al. (2012) Performance evaluation of ion-exchange chromatography in capillary format. J Sep Sci 35:3461-3468.
[4] ES Rodriguez et al. (2015) Capillary ion chromatography with on-column focusing for ultra-trace analysis of methanesulfonate and inorganic anions in limited volume Antarctic ice core samples. J Chromatogr A 1409:182-188.
[5] C Gautier et al. (2016) Are analytical standards and reagents really reliable? Accred. Qual. Assur. 21:41-46.