

Speciation of As and Cr in drinking waters - towards the development of a fully automated routine method

David Verstraeten, KVCV meeting 12 october 2006

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- Chromium and arsenic are two naturally occurring elements whose toxicity depends on their chemical form/oxidation state.
- Trivalent chromium (Cr III) is an essential nutrient, while hexavalent chromium (Cr VI) is toxic, not naturally occurring, and results only from anthropogenic activities.
- Arsenic exists in a variety of forms with the trivalent form (As III) being the most toxic, followed by the pentavalent form (As V).



The goals of this work were:

- Simultaneous separation of As and Cr inorganic species in environmental water samples using HPLC-ICP-MS.
- > Develop a very rapid separation method (less than five minutes).
- Eliminate potential interferences so that lower levels can be determined.
- Fully automate the process

Automation – Setup







HPLC System	PerkinElmer Series 200 Binary Pump,
	Auto Sampler and Vacuum Degasser
Column	C8; 3 μ m particles; 3 cm (PerkinElmer)
Mobile Phase	1 mM TBAH + 0.5 mM EDTA (potassium salt) + 5% methanol
рН	7.2
pH Adjustment	Dilute HNO ₃ , NH ₄ OH
Injection Volume	50 μL
Flow Rate	1.5 mL/min
Samples	Various waters (non-acidified)
Sample Prep	Dilute with mobile phase let sit 30 min.



> Choice of chromatographic separation.

- Ion pair separation on a "reverse-phase" type column (C8 or C18).
 - Lower cost
 - Flexible configuration (particle size, pore size, dimensions,...)





Method Development – Concentration of the ion pair reagent PerkinElmer







Method Development – Effect of Sample Diluent















Method Development - Effect of pH on As





- Prior to analysis, the column was conditioned for 30 minutes with the mobile phase flowing at 1.5 mL/min; this was required to properly equilibrate the column.
- Upon completion of analyses at the end of each day, the column was washed with a 5/95 mixture of methanol/water to remove the buffer/salts from the column, followed by a 15 minute wash with a 70/30 methanol/water mixture to prevent the column from drying out.



Instrument	ELAN DRC II (PerkinElmer SCIEX)
Nebulizer	Quartz Concentric
Spray Chamber	Quartz Cyclonic
RF Power	1500 W
Analytes	Cr+ (m/z 52); AsO+ (m/z 91)
Reaction Gas	O ₂ @ 0.6 mL/min
RPq	0.55
Dwell Time	500 ms (per analyte)
Analysis Time	210 seconds





Sample: 1 ppb As in 1% HNO₃



- Having an automatically controlled switching allows the user to:
 - run the automatic tuning of the ICP-MS whilst the column is being conditioned.
 - Switch off the plasma whilst the column is being washed out
 - If need be avoid loading the plasma with unretained species.

Automation – Software control of all devices



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Chromium Results										
Sample	Cr (III) (μg/L)	Cr (VI) μg/L)	Total Cr (μg/L)							
Connecticut River	_	—	0.07							
Lake Mohegan	0.08	—	0.09							
Shelton Water	0.14	—	0.38							
Glendale Water	0.56	3.7	3.2							
Well Water	_	_	0.003							
Bottled Water - A	0.12	_	0.38							
Bottled Water – B	0.31	_	0.58							
Bottled Water – C	0.25	—	0.34							

-- = None detected



Arsenic Results										
Sample	As (III) (μg/L)	As (V) (μg/L)	Total As (μg/L)							
Connecticut River	—	0.15	0.13							
Lake Mohegan	—	0.17	0.26							
Shelton Water	—	0.19	0.21							
Glendale Water	—	0.65	0.57							
Well Water	—	40	42							
Bottled Water - A	—	0.45	0.45							
Bottled Water – B	0.23	1.5	1.8							
Bottled Water – C	—	1.9	1.6							

-- = None detected



It was possible to rapidly separate and detect Cr³⁺, Cr⁶⁺, As³⁺ and As⁵⁺ ions in drinking waters.

Measured speciated data agreed with total elemental content for elements in the samples under investigations

Using a state of the art software it is possible to automate the whole process in order to provide a rapid routine method for conducting this analysis

The use of an automated switching valve improved productivity by ensuring that both the HPLC column and the ICP-MS instrument can be optimised independently.