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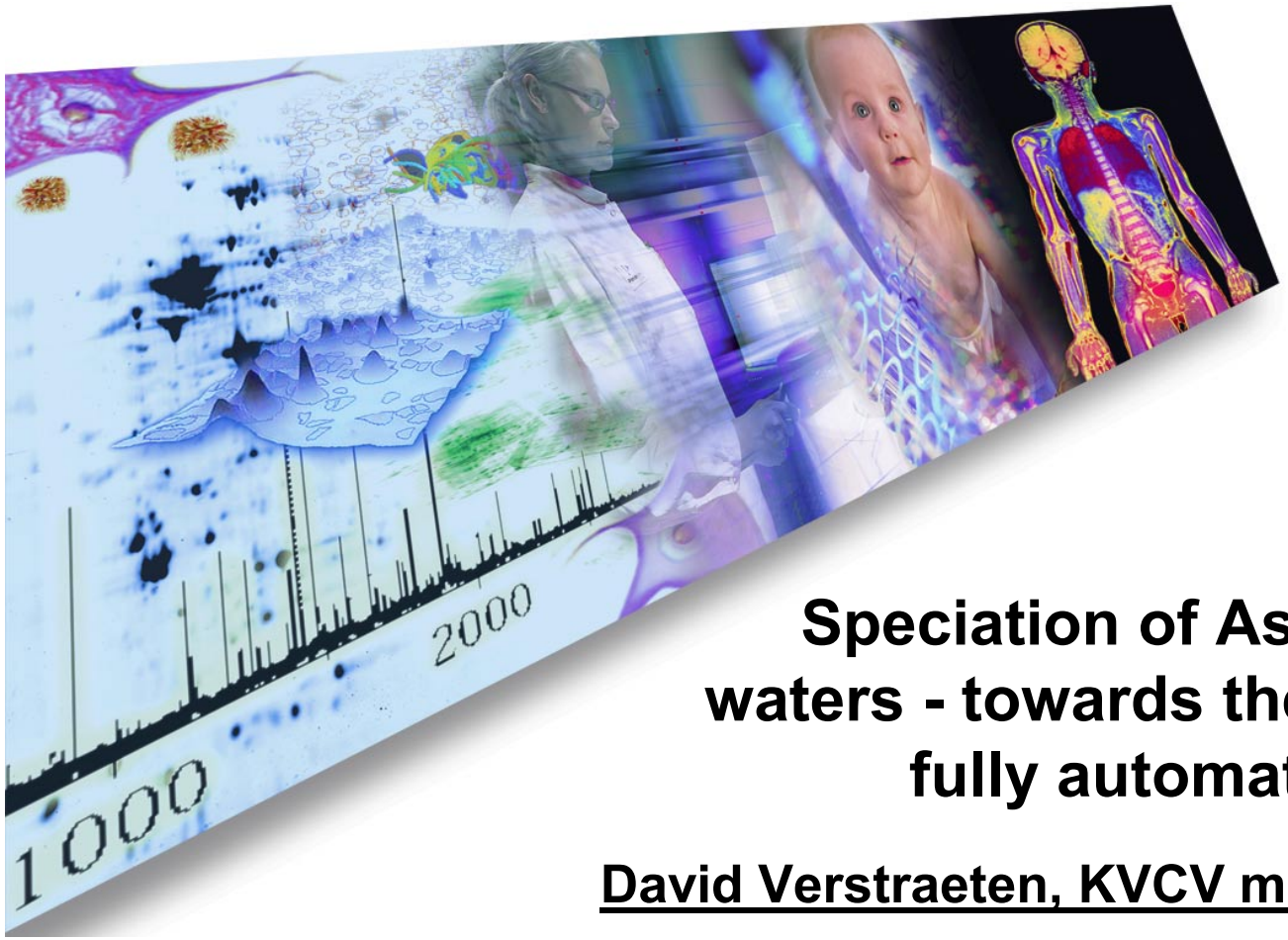
precisely.



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

David Verstraeten, KVCV meeting 12 october 2006

- 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).

Goals

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

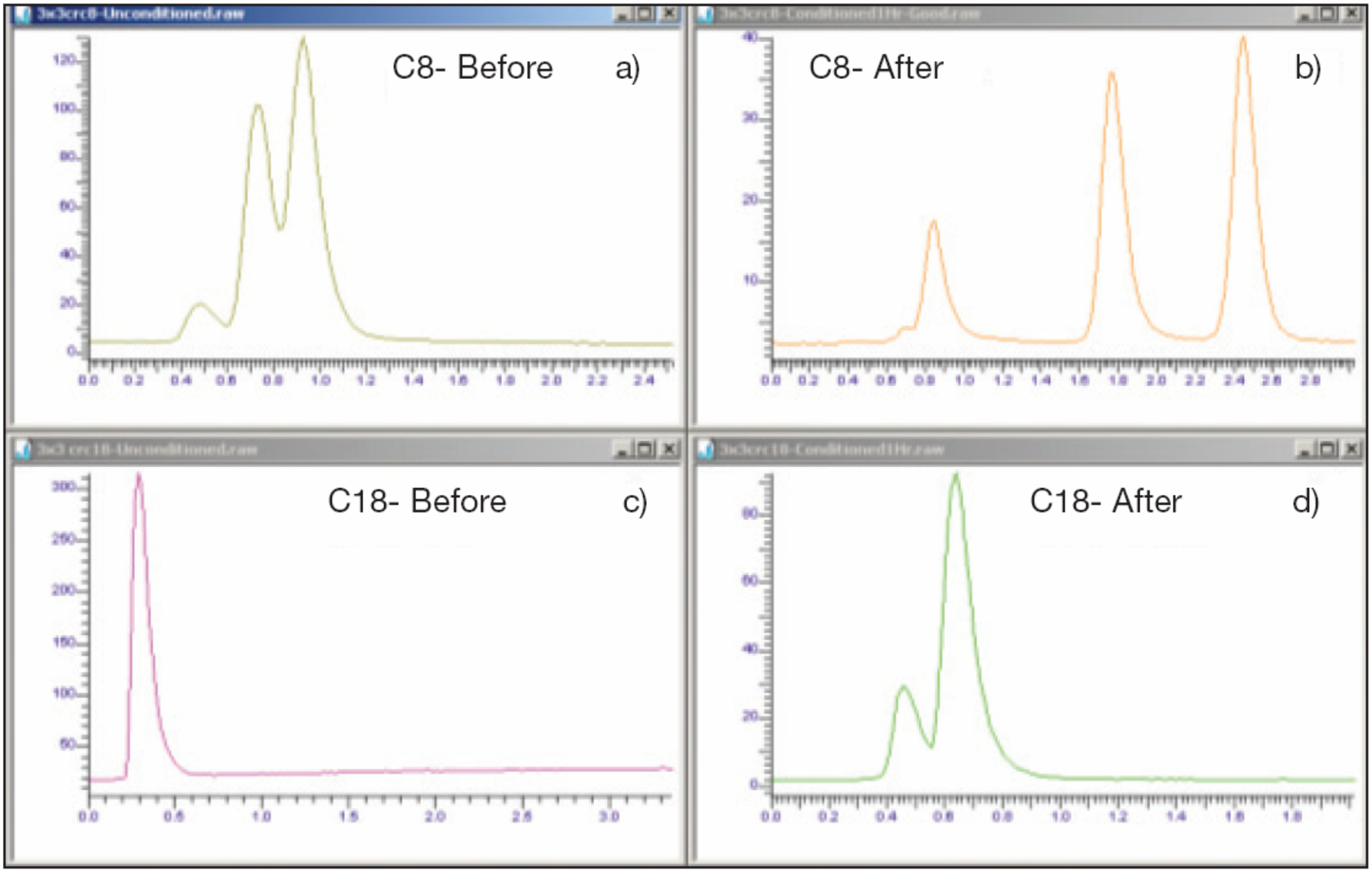
Method development - HPLC

HPLC System	PerkinElmer Series 200 Binary Pump, Auto Sampler and Vacuum Degasser
Column	C8; 3 µm particles; 3 cm (PerkinElmer)
Mobile Phase	1 mM TBAH + 0.5 mM EDTA (potassium salt) + 5% methanol
pH	7.2
pH Adjustment	Dilute HNO_3, NH_4OH
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.

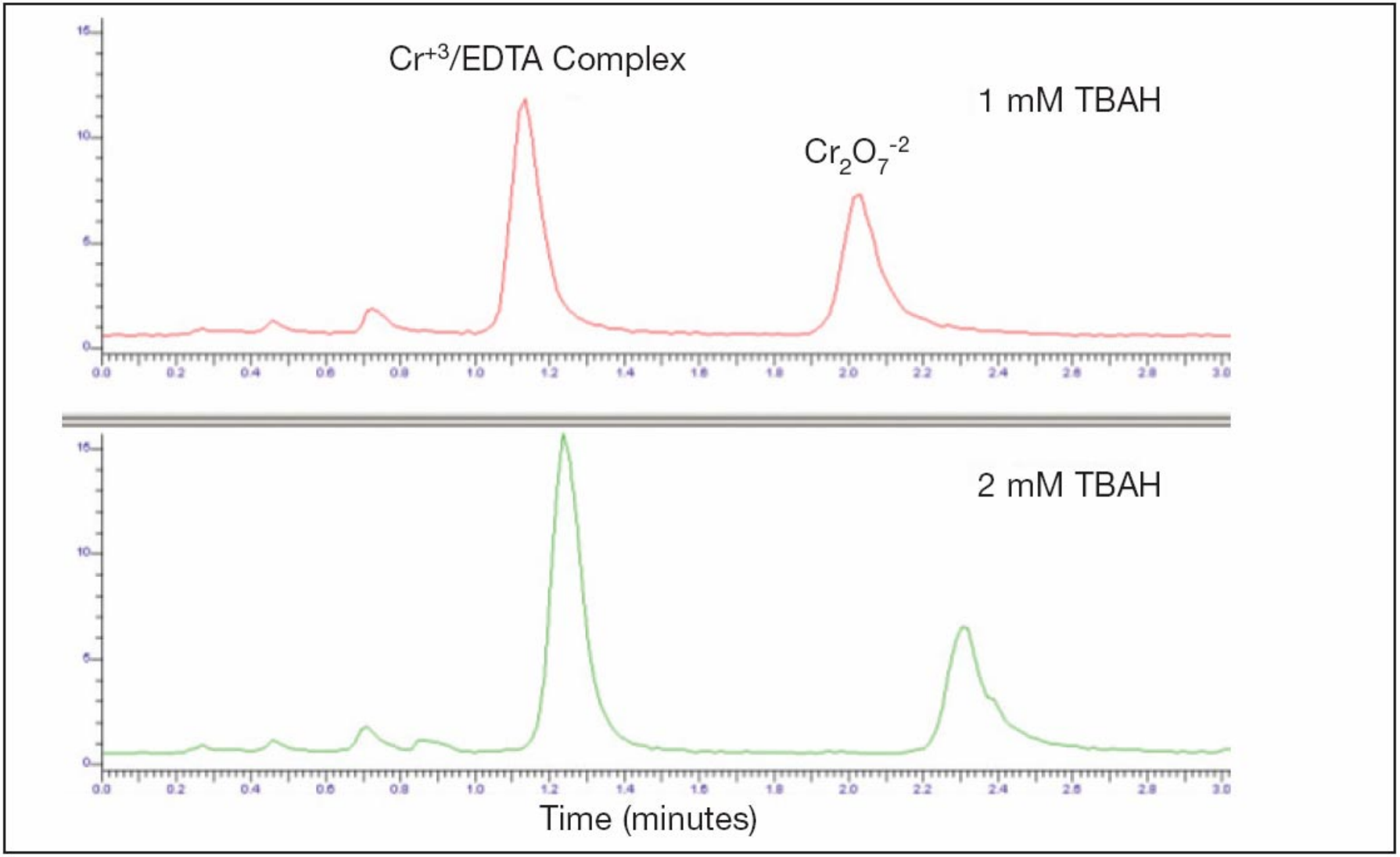
➢ Choice of chromatographic separation.

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

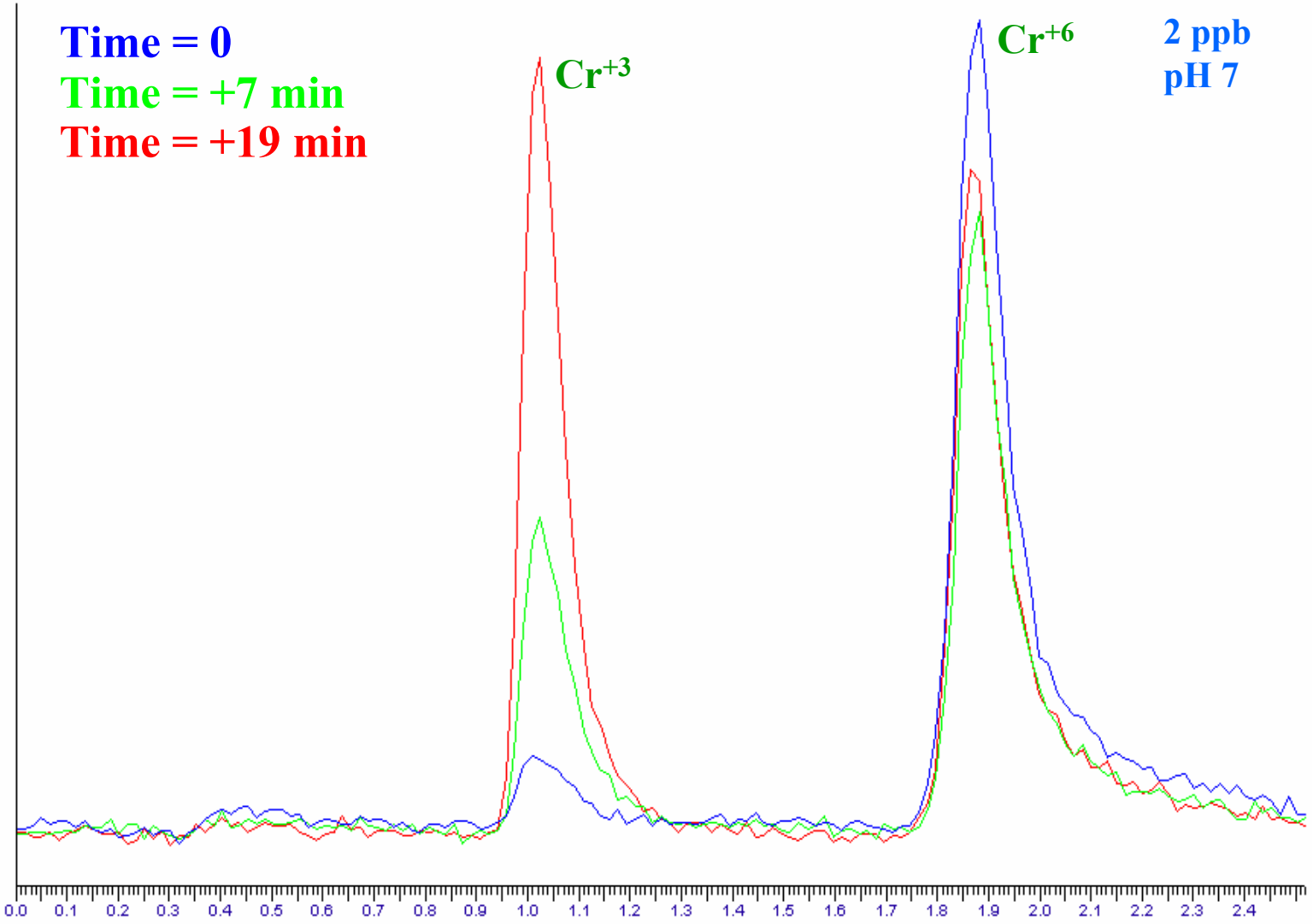
Method Development – Choice of column



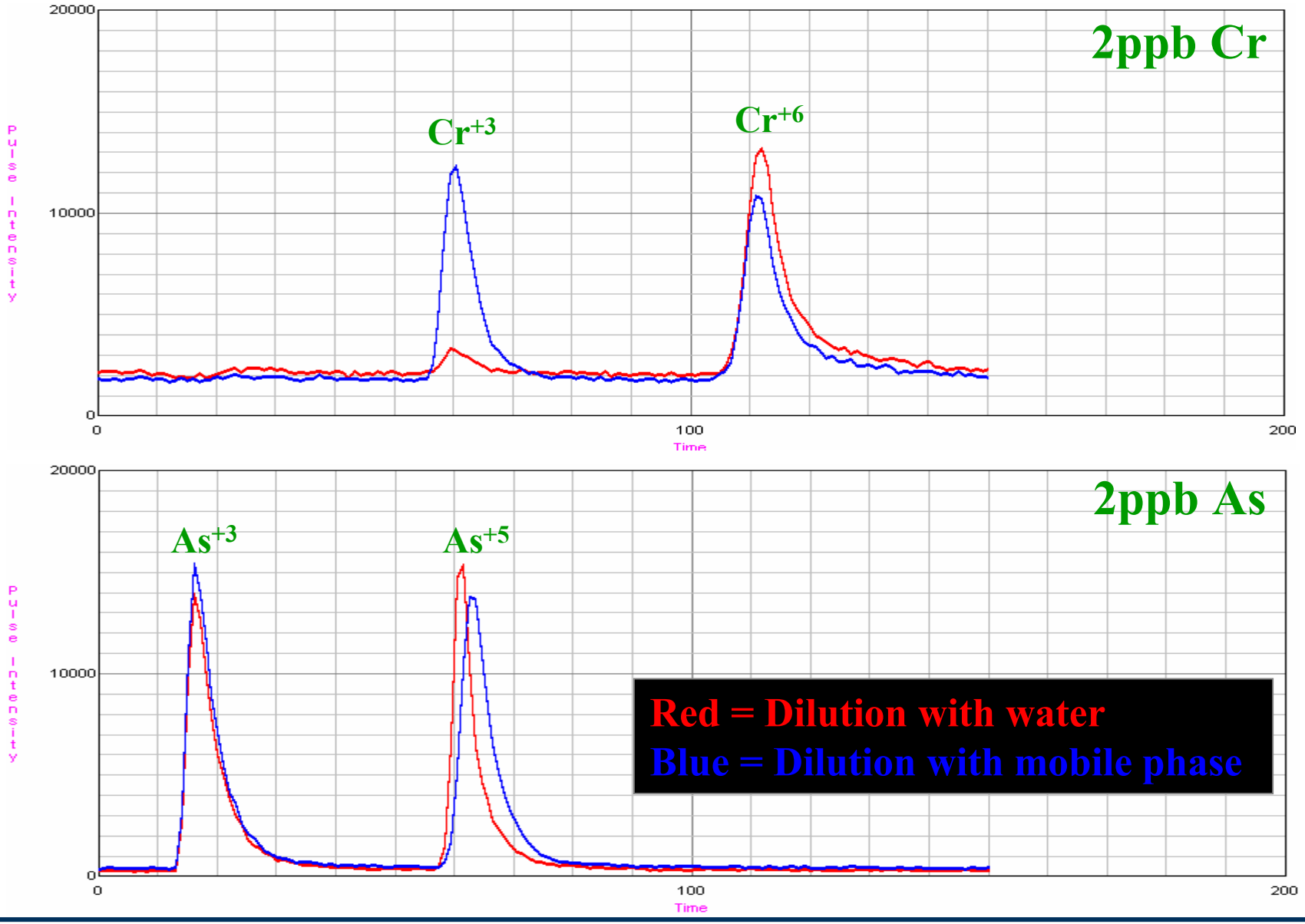
Method Development – Concentration of the ion pair reagent



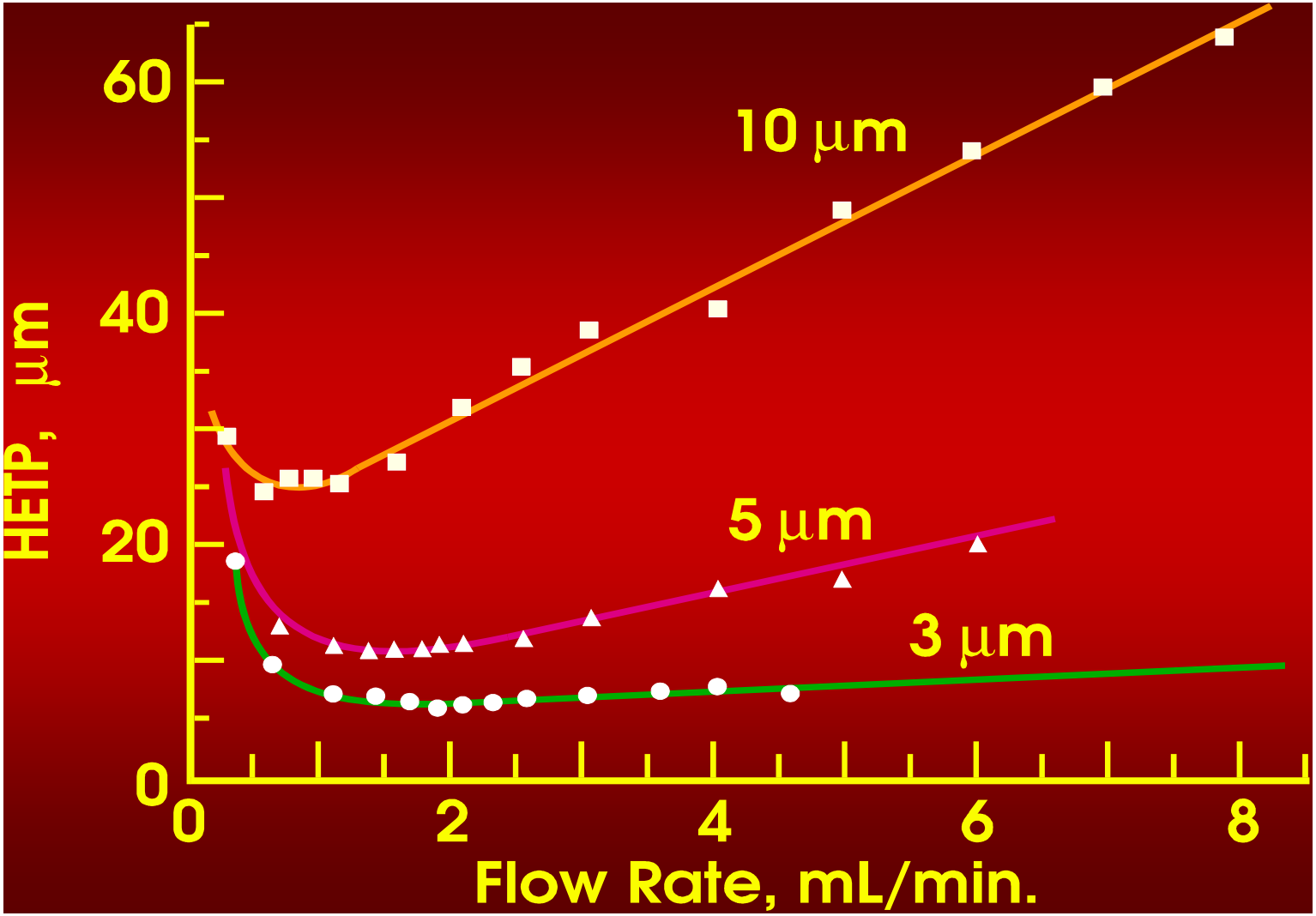
Method Development – Stabilisation time



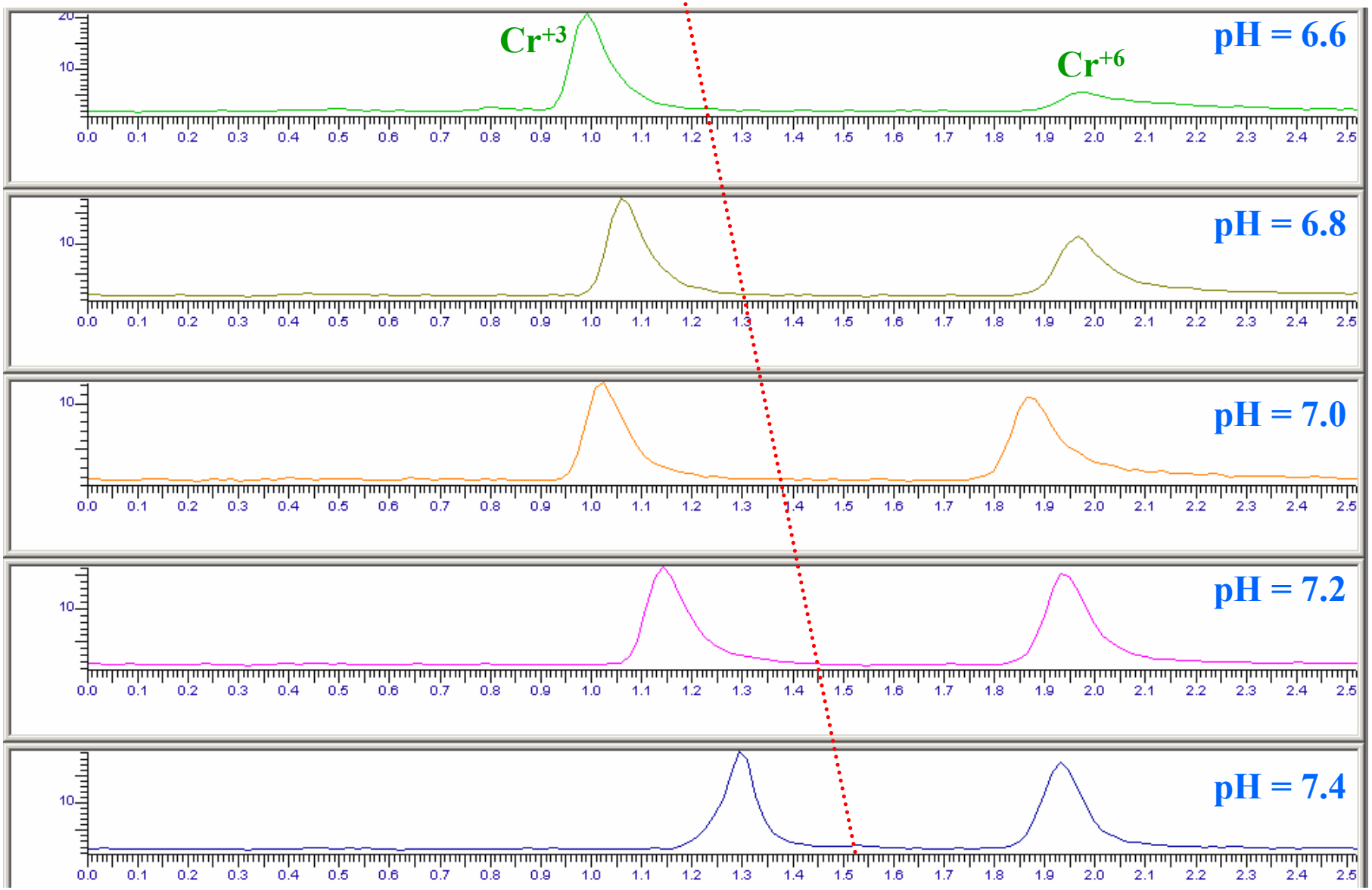
Method Development – Effect of Sample Diluent



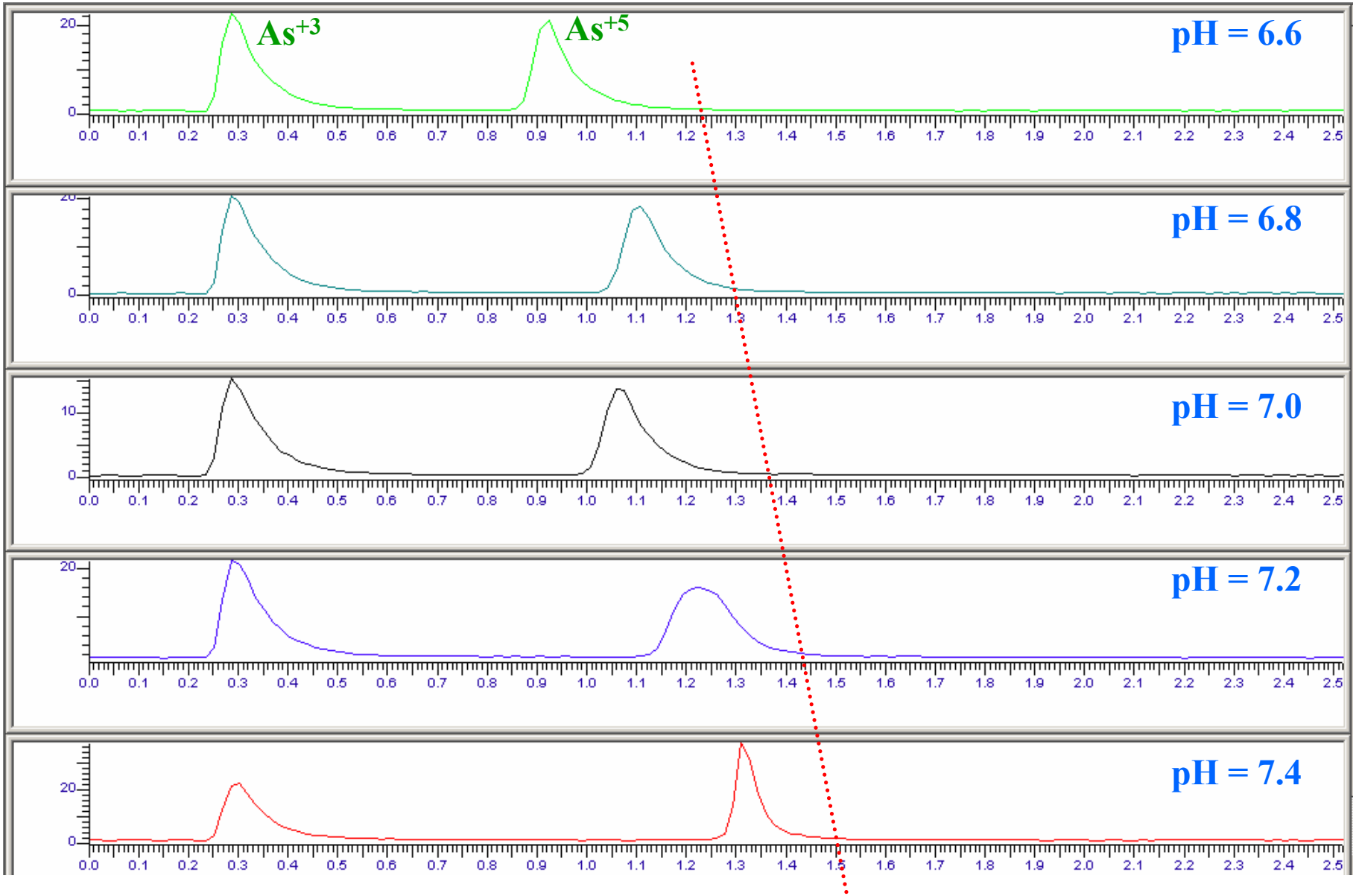
Method Development – Choice of flow rate



Method Development - Effect of pH on Cr



Method Development - Effect of pH on As



Method Development - Column preparation/maintenance

- 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.

Method development – ICP-MS

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

ICP-MS Optimisation for As

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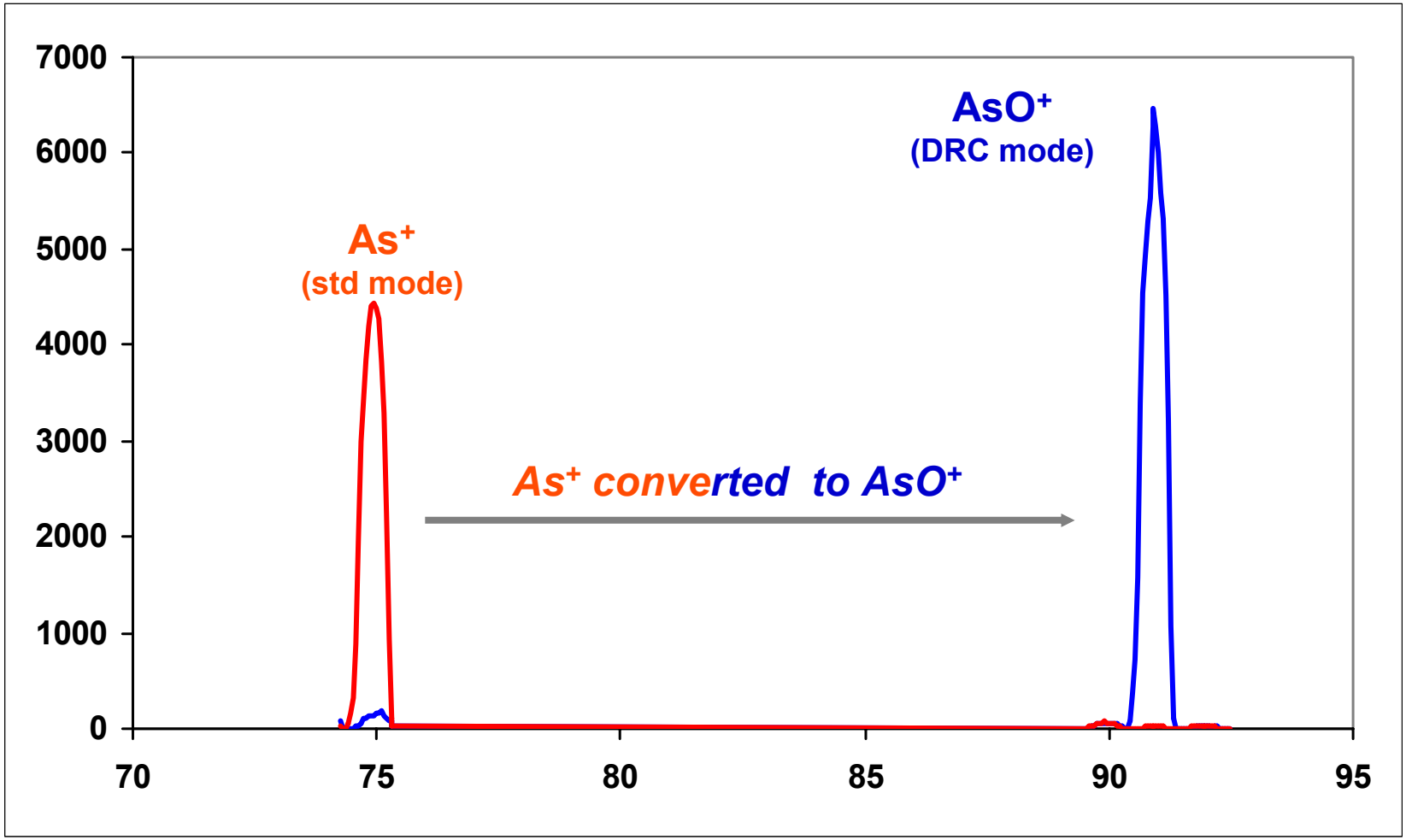
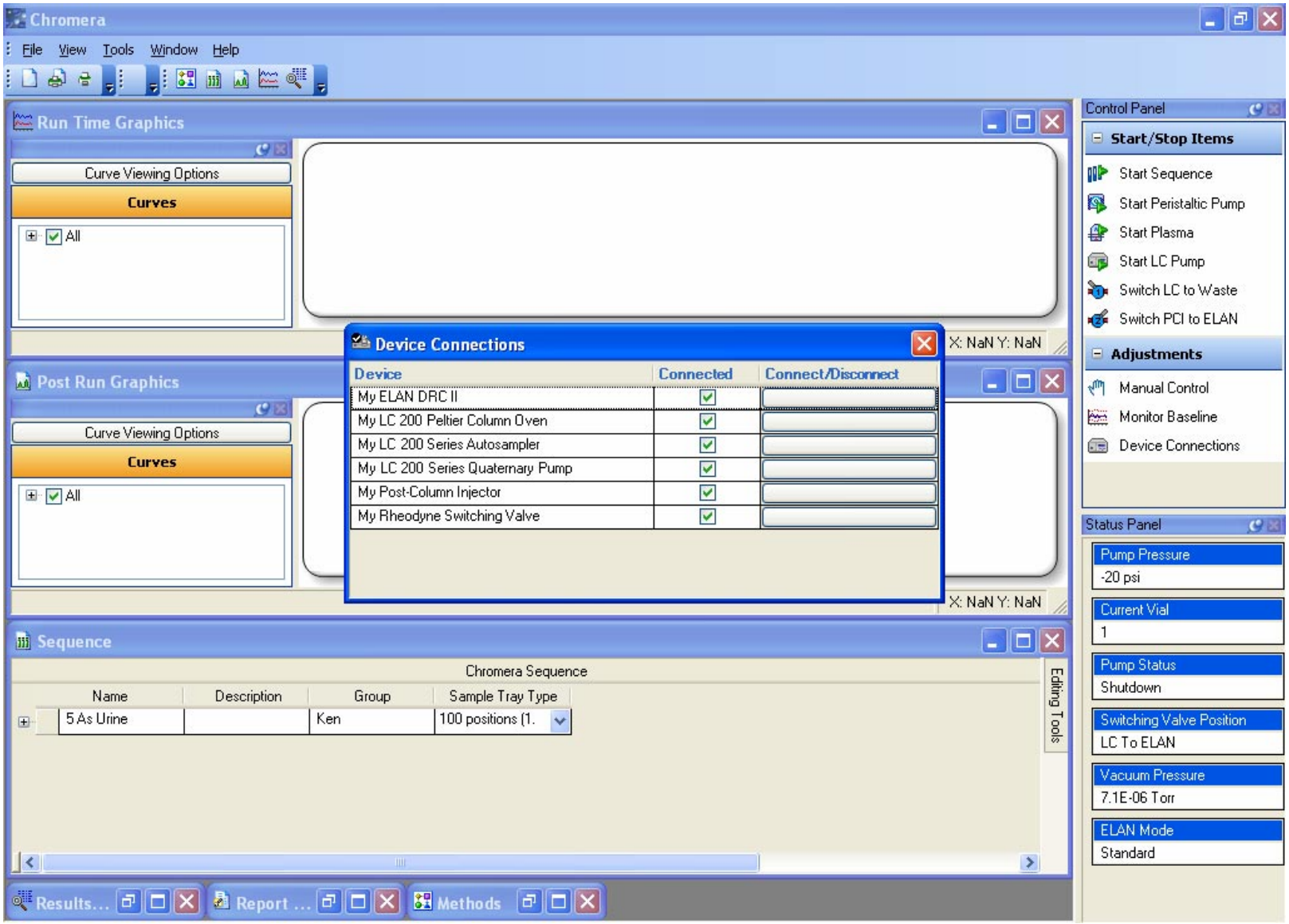
Sample: 1 ppb As in 1% HNO_3

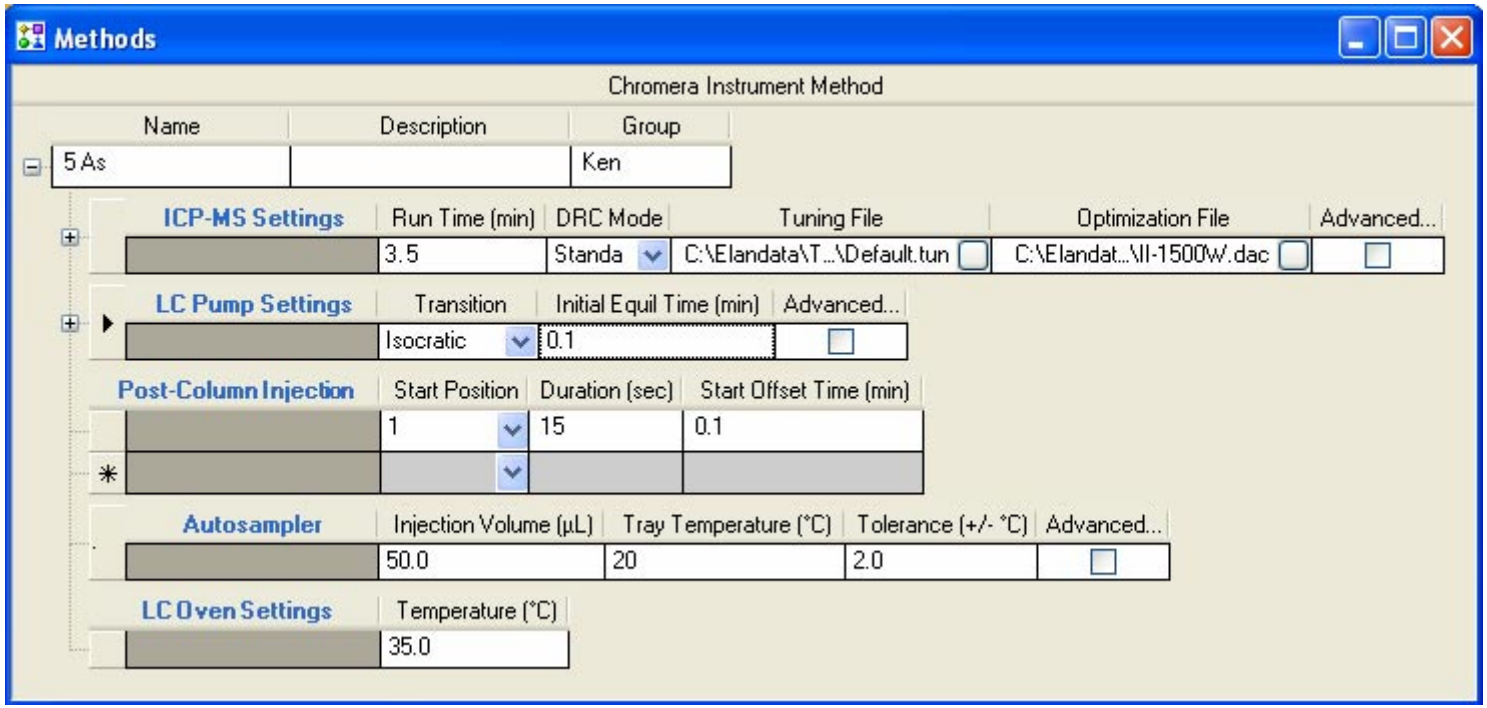


- **Having an automatically controlled switching allows the user to:**
  - **run the automatic tuning of the ICP-MS whilst the column is being conditioned.**
  - **Switch off the plasma whilst the column is being washed out**
  - **If need be avoid loading the plasma with unretained species.**

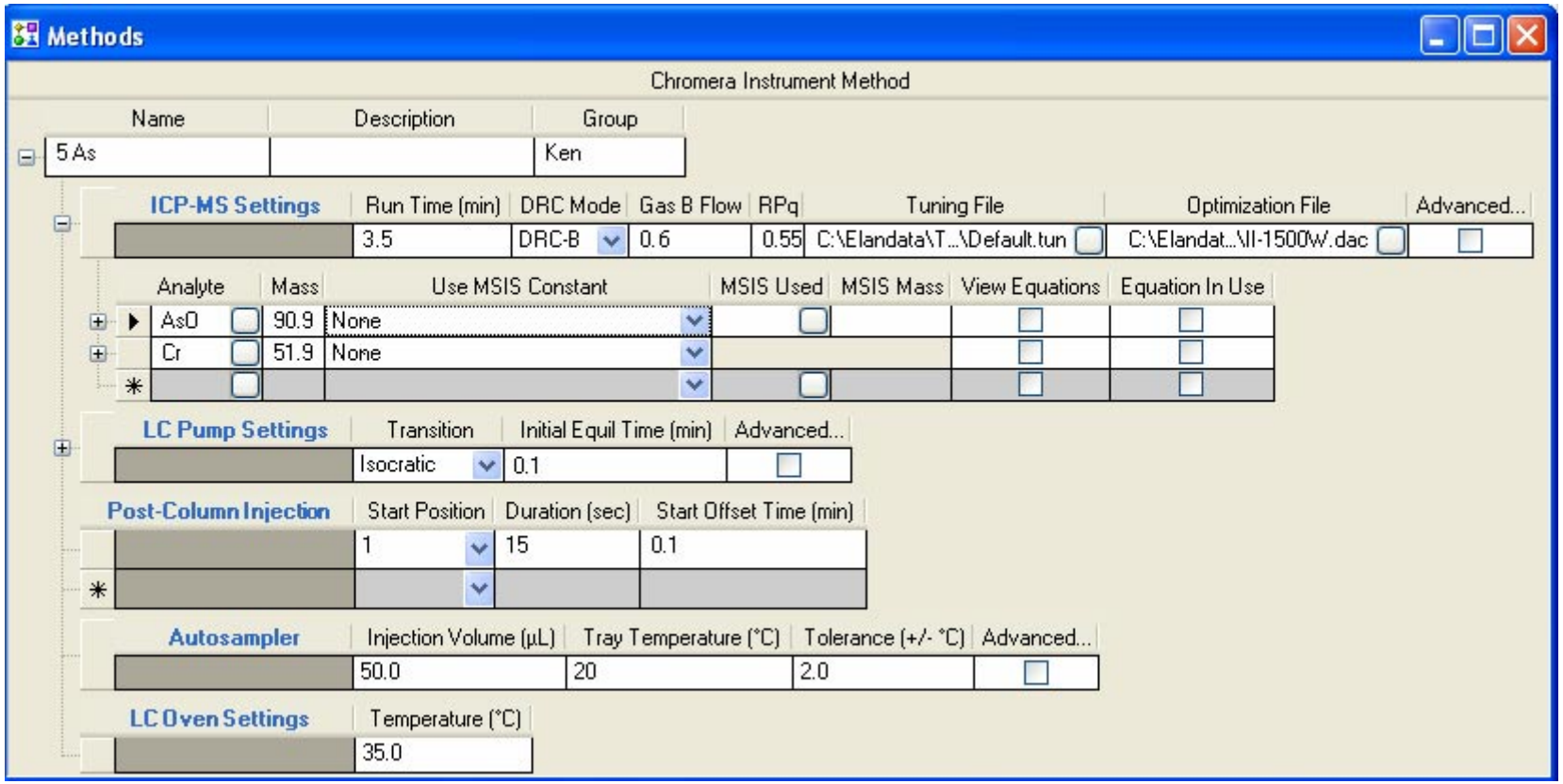
Automation – Software control of all devices



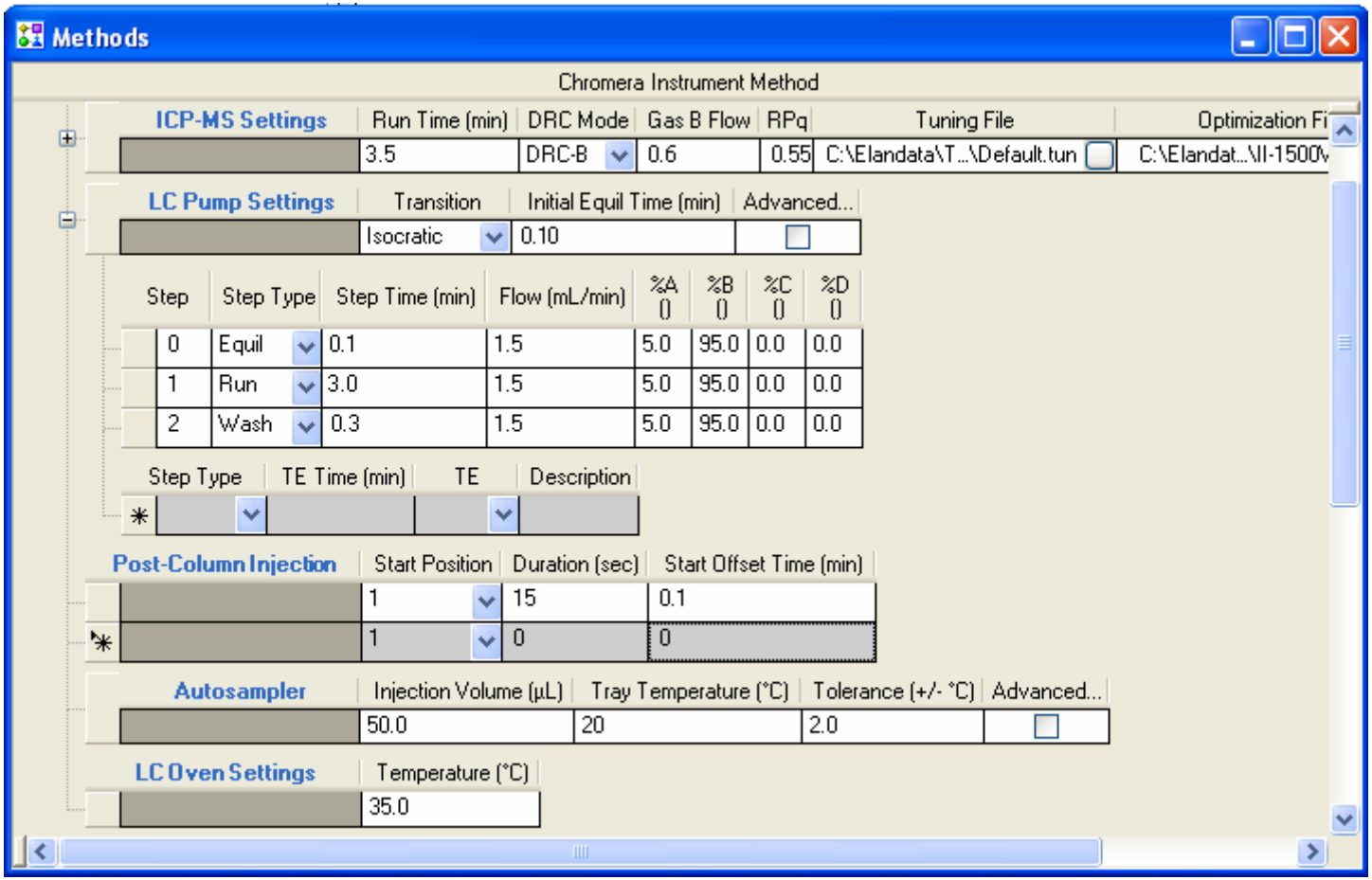
Automation – Method setup



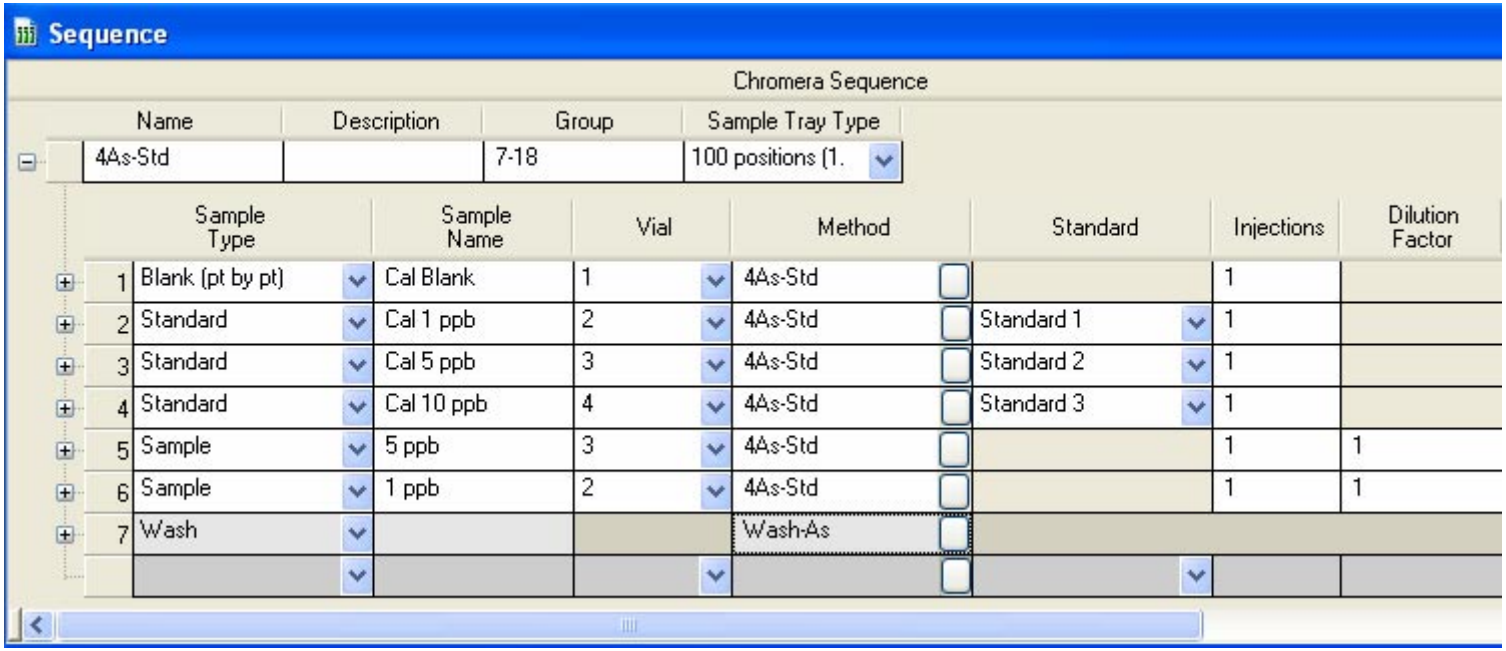
Automation – Method setup



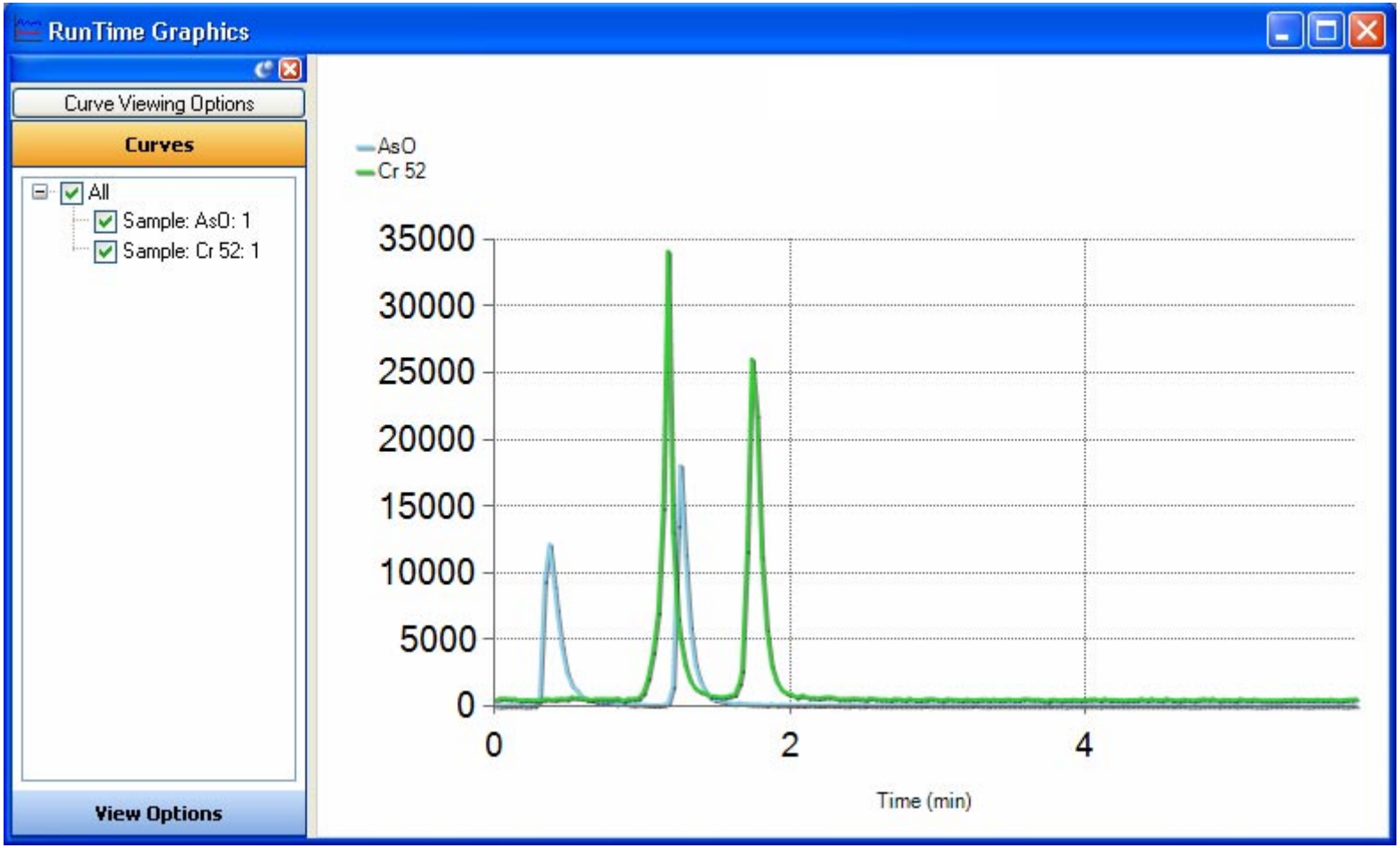
Automation – Method setup



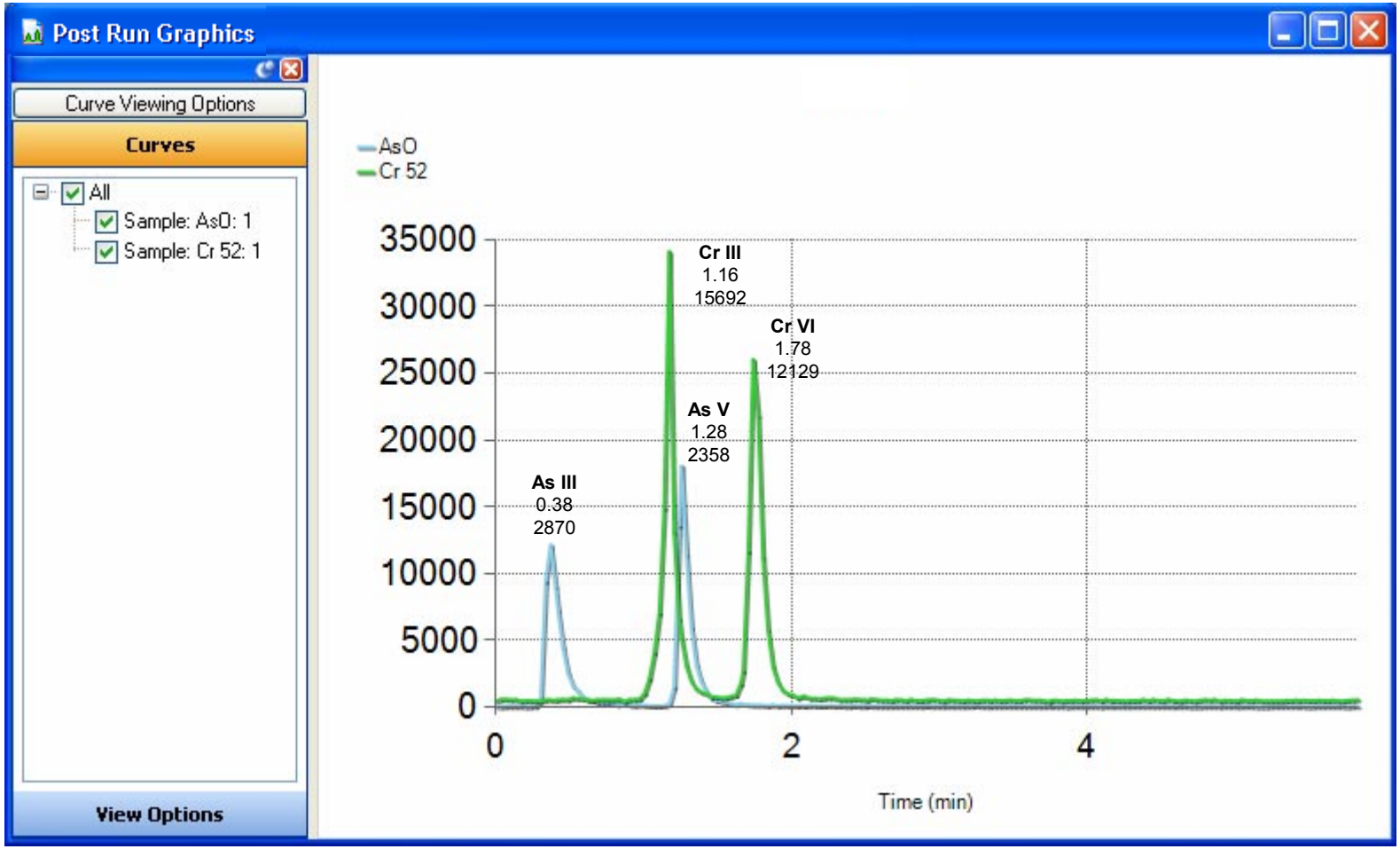
Automation – Sequence setup



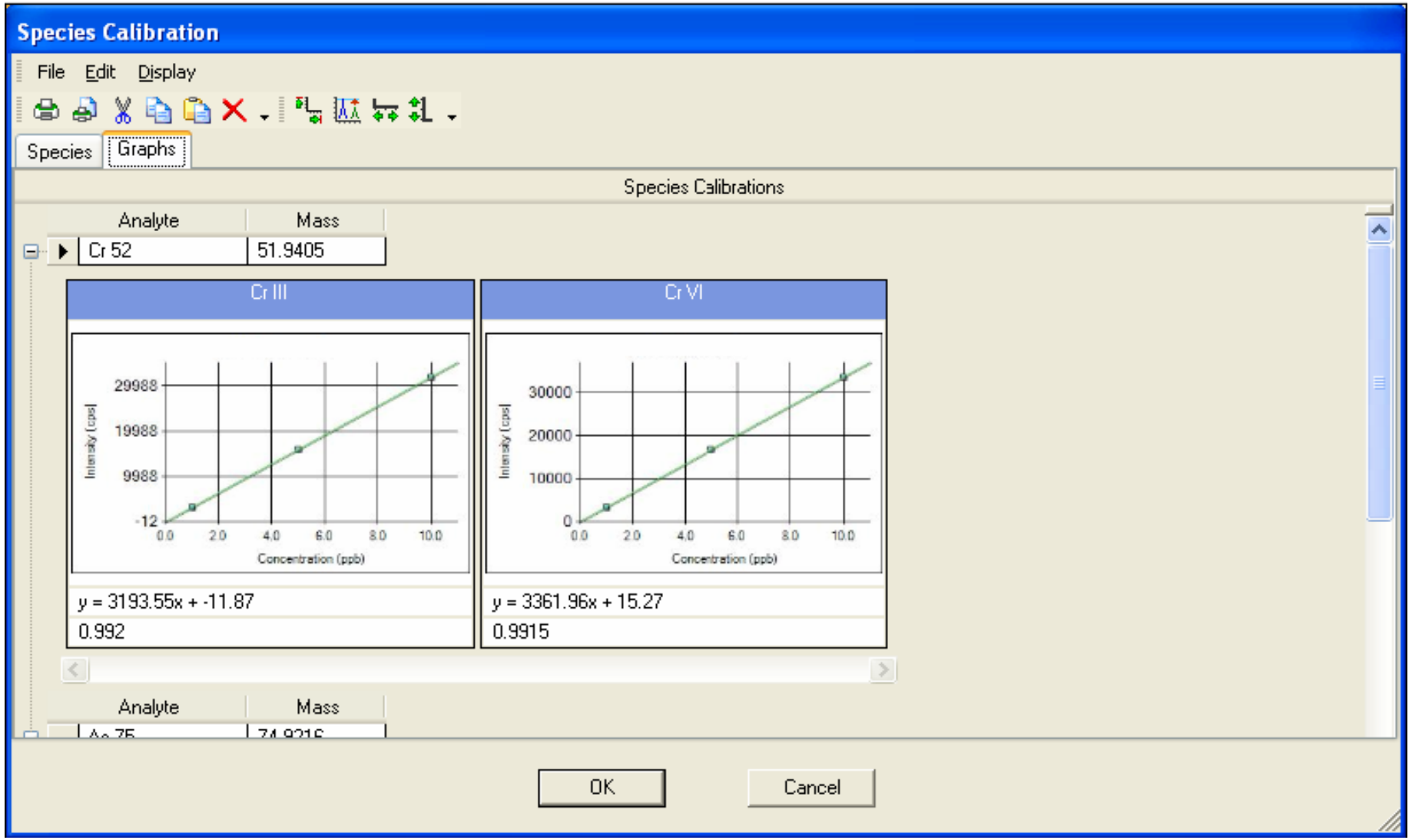
Automation – Real time data viewing



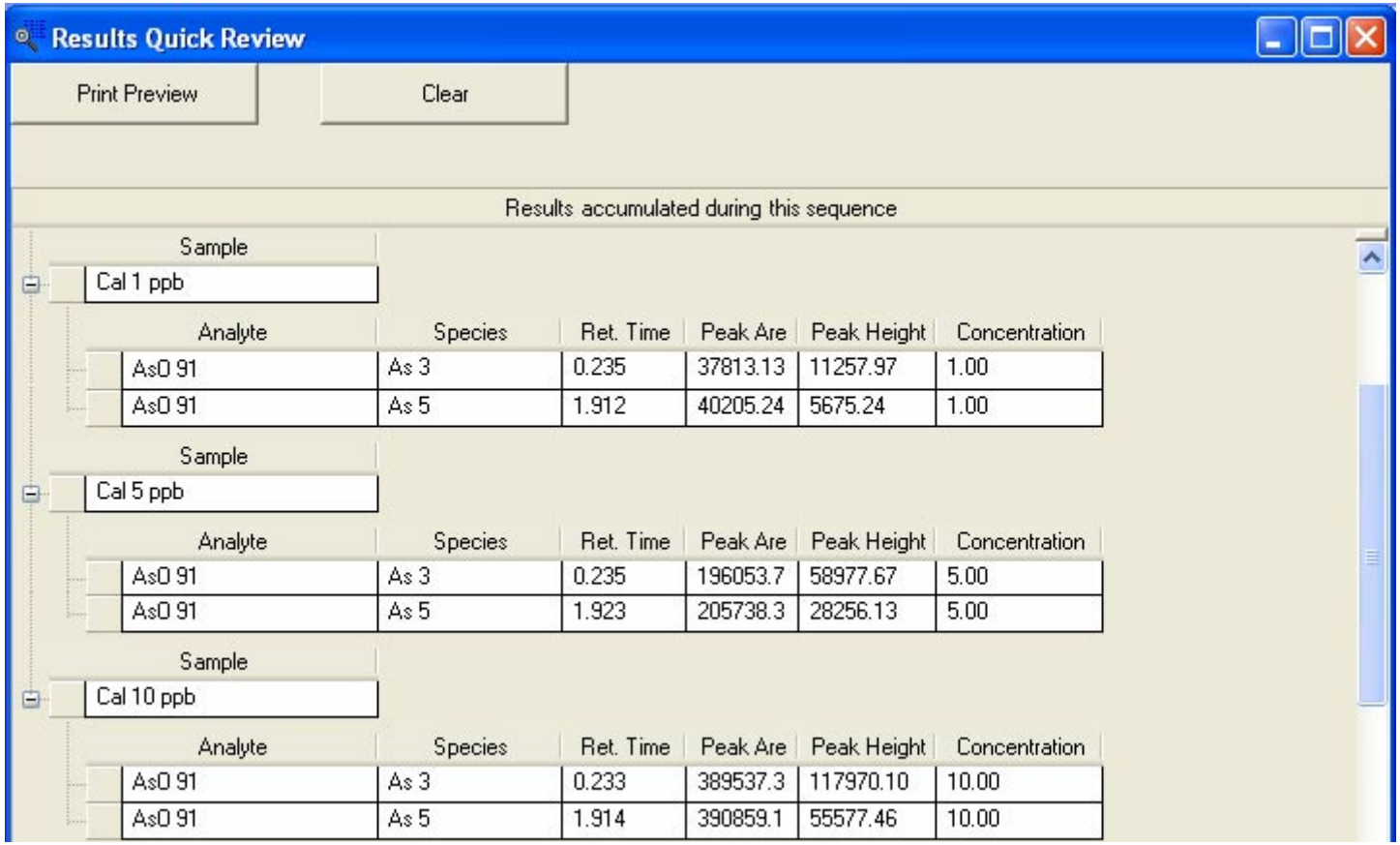
Automation – Post run data processing



Automation – Calibration



Automation – Customisable data reporting



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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

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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

Summary

It was possible to rapidly separate and detect Cr^{3+}, Cr^{6+}, As^{3+} and As^{5+} 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.