Automated Analysis of Heavy Metals (Total and Speciation) in Environmental Samples

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Introduction

There is an increasing demand to automate the testing processes for both environmental and drinking water samples. Monitoring of water for public consumption, specifically metals, is incredibly important for ensuring people's right to safe, potable water. Similarly, automation of environmental sample monitoring can help to enhance accuracy in reporting both man-made environmental contamination and typical environmental levels of total metals and elemental species.

Elemental Scientific has developed the prep*FAST* IC to automate total metals methods (such as EPA 6020B) along with elemental speciation measurements (e.g., bromide, iodide, chloride, and chromium species) into one automated sequence when combined with an ICPMS. The use of ESI's *Xceleri* software allows for seamless ICPMS method switching, QC rule execution, sample flagging for speciation, and automated, customizable calibrations.

Materials and Methods

Water samples were gathered from city (business and residential) and natural (lake, river, and reservoir) sources from around the Omaha, NE, USA area for the experiments described in this work. Samples were analyzed for total metals and speciation using the autodilution and autocalibration functions of the prep*FAST* IC coupled to an ICPMS.

Conclusions

ESI's prep*FAST* IC driven by the *Xceleri* software package has demonstrated the ability to automate total metals analysis followed by elemental speciation of any flagged samples. The system can evaluate environmental water and drinking water samples for contamination of trace elements in accordance with EPA 200.8 or 6020B, followed by quantitation of toxic/non-toxic elemental species. Significant improvements to elemental species LOD's are achieved over traditional HPLC due to the metal free sample flow path of the prep*FAST* IC.

ESI *Xceleri* Automated ICPMS Method Control

Data Report

	Index	Arrived	Time	Description	52Cr-(Helium Gas)	51V-(Helium Gas)
	23		04/15/2021 09:59:51	Lake Zorinsky	0.99	1.09
	24		04/15/2021 10:03:04	Walnut Creek Lake	0.63	0.33
	25		04/15/2021 10:06:16	Standing Bear Lake	0.92	0.78
	26		04/15/2021 10:09:28	Regency Lake	0.88	0.44
	27		04/15/2021 10:12:40	Wehrspann Lake	0.43	0.62
	28		04/15/2021 10:15:54	Missouri River NP Dodge Boat Ramp	1.02	1.67
C	29		04/15/2021 10:19:07	CRM-RS-B	15.59	0.81
	30		04/15/2021 10:22:19	ESI Tap Water 1 Instant	2.69	1.06
	31		04/15/2021 10:25:31	ESI Tap Water 1 Delayed	2.53	0.90
	32		04/15/2021 10:28:44	ESI Tap Water 2	2.95	1.02
	33		04/15/2021 10:31:59	ESI Tap Water 3	2.51	0.78
	34		04/15/2021 10:35:11	ESI Tap Water 4	3.04	0.70
	35		04/15/2021 10:38:23	ESI Tap Water 4 DUP	2.91	0.84
C	36		04/15/2021 10:41:37	ESI Tap Water 4 SPK-1	19.30	0.89
C	37		04/15/2021 10:44:50	ESI Tap Water 4 SPK-2	18.63	0.65
C	38		04/15/2021 10:48:02	ESI Tap Water 4 SPK-3	18.85	0.71

Figure 1.
Sample reports high for Cr in total metals sequence. *Xceleri* adds sample to speciation template.

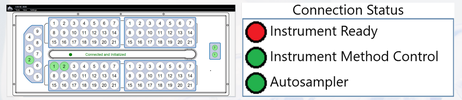

Figure 2.
Xceleri monitors the status of the plasma, method control, and autosampler throughout the analysis. The system will automatically stop when an alarm status is detected.

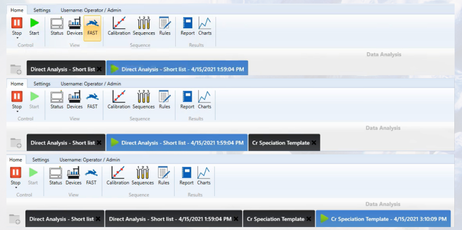

Figure 3.
A) Total metals sequence starts.
B) First total metals sample flags above user-specified limit. *Xceleri* opens speciation template and adds the flagged sample.
C) Total metals sequence finishes. *Xceleri* starts Cr speciation template, calibrates, and runs any flagged samples.

Total Metals

Table 1. Total metals results from city and natural water sources sampled from eastern Nebraska and western Iowa. Method based on EPA 6020B.

	^{9}Be (µg L^{-1})	^{27}Al (µg L^{-1})	^{51}V (µg L^{-1})	^{52}Cr (µg L^{-1})	^{55}Mn (µg L^{-1})	^{56}Fe (µg L^{-1})	^{59}Co (µg L^{-1})	^{60}Ni (µg L^{-1})	^{63}Cu (µg L^{-1})	^{66}Zn (µg L^{-1})	^{75}As (µg L^{-1})	^{78}Se (µg L^{-1})	^{95}Mo (µg L^{-1})	^{107}Ag (µg L^{-1})	^{111}Cd (µg L^{-1})	^{121}Sb (µg L^{-1})	^{137}Ba (µg L^{-1})	^{205}Tl (µg L^{-1})	^{208}Pb (µg L^{-1})	^{232}Th (µg L^{-1})	^{238}U (µg L^{-1})
Iowa Deep Well Water 2	0.000	0.4	6.1	1.6	0.0	0.0	0.032	0.0	1.6	24	0.6	3.2	1.3	0.000	0.00	0.068	57	0.007	0.062	0.68	4.7
Iowa Shallow Well Water 1	0.000	13.5	1.0	0.5	1.1	0.7	0.093	0.9	6.4	58	3.7	0.0	2.2	0.000	0.09	0.239	68	0.017	0.156	0.27	1.0
Fridge Filtered Water	0.021	4.4	2.0	0.9	0.0	0.0	0.012	0.2	1.3	0.9	3.6	1.5	3.3	0.017	0.00	0.172	0	0.003	0.007	0.06	0.8
Tap Unfiltered Water	0.011	1.3	5.2	0.6	0.1	0.0	0.095	0.5	8.3	0.3	3.7	5.7	3.4	0.297	0.05	0.171	0	0.005	0.006	0.07	2.4
Farm Tap Water	0.000	0.5	5.3	3.0	0.2	0.0	0.157	0.2	82	1.2	2.6	1.3	3.3	0.000	0.00	0.153	196	0.002	0.091	0.11	5.5
City Tap Water	0.000	7.9	5.1	0.6	0.4	0.0	0.100	1.0	0.9	0.1	2.9	0.0	3.0	0.097	0.05	0.210	61	0.004	0.033	0.07	2.5
Location A Well Water	0.011	0.0	0.4	1.8	0.5	4.4	0.084	0.6	5.7	24	0.3	6.2	0.6	0.000	0.01	0.085	306	0.004	0.050	0.04	3.0
Location B Well Water	0.031	0.6	0.0	0.8	0.0	1.6	0.000	0.7	503	463	0.0	0.0	0.0	0.000	0.00	0.000	0	0.002	0.666	0.01	0.0
Location B Tap Water	0.000	61.2	1.1	2.0	0.2	1.3	0.081	4.0	5.9	290	0.7	0.0	2.7	0.000	0.07	0.211	44	0.008	0.097	0.03	0.8
Lake Zorinsky	0.011	15.1	1.2	1.0	1.8	9.5	0.134	2.6	0.9	0.1	2.2	0.0	3.5	0.000	0.00	0.382	147	0.015	0.022	0.03	4.0
Walnut Creek Lake	0.000	10.3	0.4	0.6	5.8	6.6	0.114	1.5	0.5	0.1	1.5	1.3	3.4	0.000	0.01	0.138	128	0.006	0.008	0.02	3.2
Standing Bear Lake	0.000	80.4	0.8	0.9	6.8	73	0.123	1.4	0.8	0.8	1.1	0.0	2.1	0.000	0.00	0.185	127	0.009	0.071	0.05	1.2
Regency Lake	0.000	0.6	0.5	0.9	1.8	3.5	0.094	0.3	0.7	0.4	3.2	0.8	0.9	0.000	0.00	0.210	105	0.013	0.014	0.02	0.9
Wehrspann Lake	0.022	7.3	0.7	0.4	8.1	9.5	0.107	1.2	1.0	0.5	1.2	6.7	7.7	0.000	0.02	0.430	163	0.009	0.032	0.04	3.2
Missouri River NP Dodge Boat Ramp	0.011	4.7	1.9	1.0	0.4	5.5	0.102	2.3	1.3	0.6	2.2	4.8	3.5	0.000	0.02	0.457	65	0.019	0.018	0.03	4.4
ESI Tap Water 1 Instant	0.011	79.1	1.2	2.7	0.2	1.2	0.134	2.2	18	132	0.4	6.8	2.6	0.101	0.00	0.315	30	0.011	0.019	0.02	0.6
ESI Tap Water 1 Delayed	0.011	94.3	1.1	2.5	0.4	3.9	0.150	0.7	10	25	0.3	0.0	3.0	0.027	0.00	0.229	27	0.015	0.010	0.02	0.6
ESI Tap Water 2	0.022	87.1	1.2	3.0	0.2	3.4	0.137	0.4	6.8	2.4	0.4	0.0	2.5	0.000	0.00	0.374	28	0.014	0.018	0.02	0.6
ESI Tap Water 3	0.000	32.2	1.0	2.5	0.0	0.6	0.088	3.1	83	53	0.5	7.3	2.8	0.000	0.09	0.245	27	0.009	0.036	0.01	0.5
ESI Tap Water 4	0.045	71.1	0.9	3.0	0.2	2.5	0.113	0.6	5.4	1.6	0.7	0.0	2.8	0.000	0.00	0.274	28	0.015	0.008	0.02	0.6

Halogen and Cr Speciation

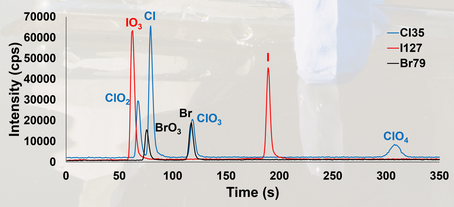

Figure 4. Typical chromatogram for ESI's halogen speciation method.

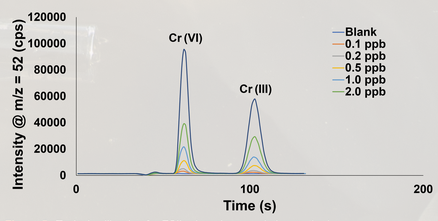

Figure 5. Typical calibration for ESI's chromium speciation method.

Table 2. Halogen and Cr species limits of detection.

Halogen Species	Response Function	Correlation (R^2)	LODs
Br^-	y = 18148 x - 984.1	0.9994	55 ng L^{-1}
BrO_3^-	y = 12864 x - 454.5	0.9992	62 ng L^{-1}
I^-	y = 201926 x - 8371.4	0.9997	33 ng L^{-1}
IO_3^-	y = 292391 x - 2778.3	0.9995	23 ng L^{-1}
Cl^-	y = 567.1 x + 33.8	0.9998	2.5 µg L^{-1}
ClO_2^-	y = 261.8 x - 359.7	0.9998	7.2 µg L^{-1}
ClO_3^-	y = 204.3 x - 220.4	0.9996	6.8 µg L^{-1}
ClO_4^-	y = 149.9 x - 643.6	0.9996	37 µg L^{-1}
Cr (VI)	y = 86132 x - 5317	0.9998	7 ng L^{-1}

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