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TECHNICAL STUDY No. 5

Comparison between measurements obtained by ICP/MS and with other methods for Fe, Ti and Hg

This document is delivered for information and is based on the results and the observations from A.G.L.A.E.'s interlaboratory proficiency testing schemes.

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1. OBJECTIVE OF THE STUDY

The aim of this study is to check if there are deviations between results obtained by ICP/MS and those obtained with other methods currently used for the analysis of iron, titanium and mercury in clean waters (clear waters such as tap waters or bottled waters).

2. DATA AND METHOD

Method

For this study, proficiciency tests organised by the Association since 2012 were processed for new data treatments by separating the participants' results according to the method they used. For iron and titanium it represents 7 tests. For mercury, only 4 tests are concerned because before 2013 the number of laboratories which implemented ICP/MS was too low.
For each test, the robust mean for each analysis technique used by the participants was calculated (algorithm A) and then we compared each mean using its confidence interval of 95% to detect if there was a significant deviation.
We then used data from all these rings to test a global tendancy. For this purpose, the relative trueness of each method was calculated in order to avoid concentration effect from test to test. The aim is that deviations between methods are not concealed by the difference of concentration level. Following the new data processing "method by method", we had for each parameter and each test a mean "m" for each single method. The mean "M" of the results obtained with all methods taken together was calculated and then the ratio between the mean m of each method and the mean M was calculated to obtain the relative trueness. We then carried out an ANOVA on the relative trueness m/M to detect if there was a significant deviation between methods.

Data *(unit in µg/L)*

Test	Parameter	Method	IC_{inf}	m	IC_{sup}	M	m/M	Size
15M3A.1	Fe	ICP/MS	96,4	98,8	101,2	97,2	1,016	36
		ICP/AES and ICP/OES	92,9	95,6	98,3		0,984	43
14M3A.2	Fe	ICP/MS	262,7	270,7	278,6	265,25	1,021	35
		ICP/AES and ICP/OES	254,7	259,8	264,9		0,979	38
14M3A.1	Fe	ICP/MS	87,2	90	92,9	89,05	1,011	30
		ICP/AES and ICP/OES	86,1	88,1	90,1		0,989	49
13M3A.3	Fe	ICP/MS	381,8	393,7	405,6	394,8	0,997	26
		ICP/AES and ICP/OES	388,2	395,9	403,5		1,003	46
13M3A.1	Fe	ICP/MS	549,7	562,7	575,7	556,45	1,011	25
		ICP/AES and ICP/OES	538,5	550,2	562		0,989	52
12M3A.3	Fe	ICP/MS	196,5	201,6	206,7	199,3	1,012	25
		ICP/AES and ICP/OES	193,3	197	200,7		0,988	69
12M3A.1	Fe	ICP/MS	445,9	474,8	503,7	477,4	0,995	16
		ICP/AES and ICP/OES	471,8	480	488,2		1,005	59

Test	Parameter	Method	IC inf	m	IC sup	M	m/M	Size
15M3A.1	Ti	ICP/MS	188,7	192,1	195,5	191,6	1,002	35
		ICP/AES and ICP/OES	187,6	191,2	194,7		0,998	19
14M3A.2	Ti	ICP/MS	92,4	94,3	96,2	93,2	1,012	33
		ICP/AES and ICP/OES	90,1	92,1	94,1		0,988	23
14M3A.1	Ti	ICP/MS	48,2	49,1	49,9	48,2	1,019	34
		ICP/AES and ICP/OES	45,9	47,2	48,6		0,981	22
13M3A.3	Ti	ICP/MS	272,9	279,5	286,1	280,2	0,998	28
		ICP/AES and ICP/OES	274,8	280,8	286,9		1,002	24
13M3A.1	Ti	ICP/MS	163,6	167,0	170,4	165,0	1,012	28
		ICP/AES and ICP/OES	157,9	163,0	168,0		0,988	25
12M3A.3	Ti	ICP/MS	24,2	25,1	26,0	24,1	1,043	27
		ICP/AES and ICP/OES	22,5	23,0	23,6		0,957	35
12M3A.1	Ti	ICP/MS	351,8	364,1	376,3	362,6	1,004	21
		ICP/AES and ICP/OES	353,8	361,2	368,5		0,996	33

Test	Parameter	Method	IC inf	m	IC sup	M	m/M	Size
15M3A.1	Hg	ICP/MS	0,708	0,864	1,02	0,909	0,951	8
		AAS	0,899	0,934	0,969		1,028	30
		AFS	0,897	0,929	0,96		1,022	30
14M3A.2	Hg	ICP/MS	2,23	2,633	3,037	2,710	0,972	10
		AAS	2,579	2,77	2,96		1,022	19
		AFS	2,604	2,726	2,847		1,006	34
14M3A.1	Hg	ICP/MS	0,431	0,526	0,621	0,563	0,935	9
		AAS	0,537	0,569	0,601		1,011	28
		AFS	0,563	0,594	0,625		1,055	28
13M3A.3	Hg	ICP/MS	1,612	1,852	2,092	1,802	1,028	9
		AAS	1,678	1,8	1,922		0,999	23
		AFS	1,674	1,753	1,832		0,973	28

3. RESULTS & INTERPRETATIONS

Iron

Test	Parameter	Method	Significant deviation ?	Absolute deviation with ICP/MS (in µg/L)	Relative deviation (in %)	Method which gives higher results
15M3A.1	Fe	ICP/MS ICP/AES and ICP/OES	no	-3,2	-3%	ICP/MS ↗
14M3A.2	Fe	ICP/MS ICP/AES and ICP/OES	no	-10,8	-4%	ICP/MS ↗
14M3A.1	Fe	ICP/MS ICP/AES and ICP/OES	no	-1,9	-2%	ICP/MS ↗
13M3A.3	Fe	ICP/MS ICP/AES and ICP/OES	no	+2,1	+1%	ICP/AES and ICP/OES ↗
13M3A.1	Fe	ICP/MS ICP/AES and ICP/OES	no	-12,5	-2%	ICP/MS ↗
12M3A.3	Fe	ICP/MS ICP/AES and ICP/OES	no	-4,6	-2%	ICP/MS ↗
12M3A.1	Fe	ICP/MS ICP/AES and ICP/OES	no	+5,2	+1%	ICP/AES and ICP/OES ↗

Conclusion: the deviation for each test did not appear as significant with an error risk of 5%. This deviation between ICP/AES (or ICP/OES) and ICP/MS is on average 1,8%. However, it should be noted that results obtained by ICP/MS are higher for 5 tests out of 7. The ANOVA shows that this tendancy is statistically significant with an error risk of 5%.

Titanium

Test	Parameter	Method	Significant deviation?	Absolute deviation with ICP/MS (in µg/L)	Relative deviation (in %)	Method which gives higher results
15M3A.1	Ti	ICP/MS ICP/AES and ICP/OES	no	-0,9	-0,5%	ICP/MS ↗
14M3A.2	Ti	ICP/MS ICP/AES and ICP/OES	no	-2,2	-2,3%	ICP/MS ↗
14M3A.1	Ti	ICP/MS ICP/AES and ICP/OES	no	-1,8	-3,9%	ICP/MS ↗
13M3A.3	Ti	ICP/MS ICP/AES et ICP/OES	no	+1,3	+0,5%	ICP/AES and ICP/OES ↗
13M3A.1	Ti	ICP/MS ICP/AES and ICP/OES	no	-4,0	-2,5%	ICP/MS ↗
12M3A.3	Ti	ICP/MS ICP/AES and ICP/OES	no	-2,1	-9,0%	ICP/MS ↗
12M3A.1	Ti	ICP/MS ICP/AES and ICP/OES	no	-2,9	-0,8%	ICP/MS ↗

Conclusion: the deviation for each test did not appear as significant with an error risk of 5%. This deviation between ICP/AES (or ICP/OES) and ICP/MS is on average 2,6%. However, it should be noted that results obtained by ICP/MS are higher for 6 tests out of 7. The ANOVA shows that this tendancy is statistically significant with an error risk of 1%.

Mercury

Test	Parameter	Method	Significant deviation?	Absolute deviation with ICP/MS (in µg/L)	Relative deviation (in %)	Method which gives higher results
15M3A.1	Hg	ICP/MS AAS AFS	no	 0,07 0,06	 8,1% 7,4%	AAS ↗
14M3A.2	Hg	ICP/MS AAS AFS	no	 0,14 0,09	 5,2% 3,5%	AAS ↗
14M3A.1	Hg	ICP/MS AAS AFS	no	 0,04 0,07	 8,1% 12,9%	AFS ↗
13M3A.3	Hg	ICP/MS AAS AFS	no	 -0,05 -0,10	 -2,8% -5,3%	ICP/MS ↗

Conclusion: the deviation for each test did not appear as significant with an error risk of 5%. This deviation between ICP/MS and other methods is on average 4,6%. Results obtained by ICP/MS are lower than others in 3 cases out of 4. However, this global deviation did not appear as statistically significant. This tendancy should be confirmed over a higher number of tests.

4. SYNTHESIS

No deviations were observed during tests organised since 2012 between results obtained by ICP/MS and those obtained with other methods for the analysis of Fe, Ti and Hg in clean waters. However, for Fe and Ti we could observe a statistically significant tendancy, results obtained by ICP/MS are higher than those obtained by ICP/AES (or ICP/OES). ICP/MS results are on average 1% higher for Fe and 2,6% higher for Ti.