Regione Toscana
Diritti Valori Innovazione Sostenibilità

3rd MS ENVY Day
Livorno
September 26-28, 2016

"Direct determination of mercury in sea waters by ICP-MS using argon gas dilution (Franco Castellani, Elisa Di Alessandro, Carlo Cini)"

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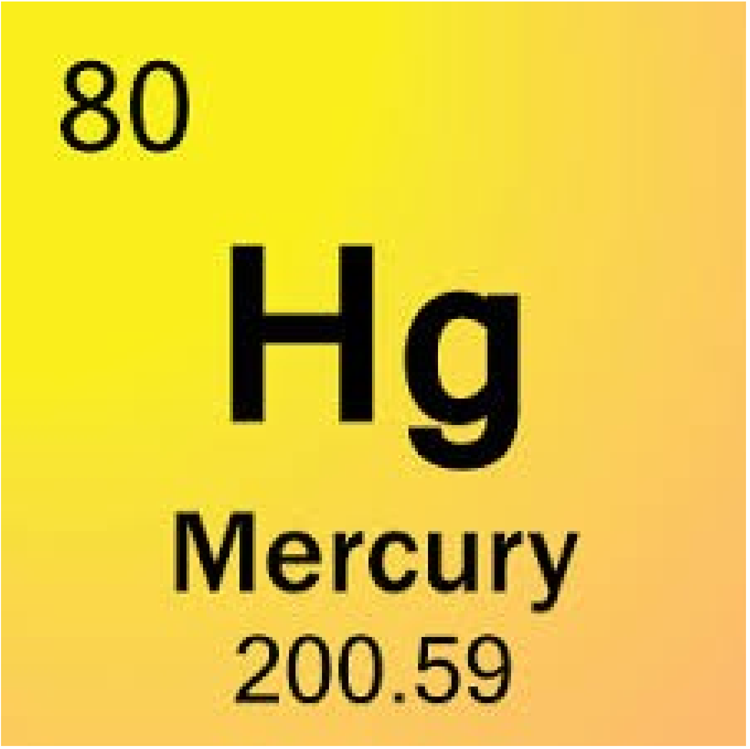
Mercury



Sources of Mercury

"Natural" sources of mercury include:

volcanoes, forest fires, cinnabar (ore) and fossil fuels such as coal and petroleum.

"Anthropogenic" sources of mercury include:

discharge from hydroelectric, mining, and paper industries; incineration of municipal and medical waste and emissions from coal-using power plants; landfills, dental preparations, and laboratory use, manufacture of metals, alkali, and cement.

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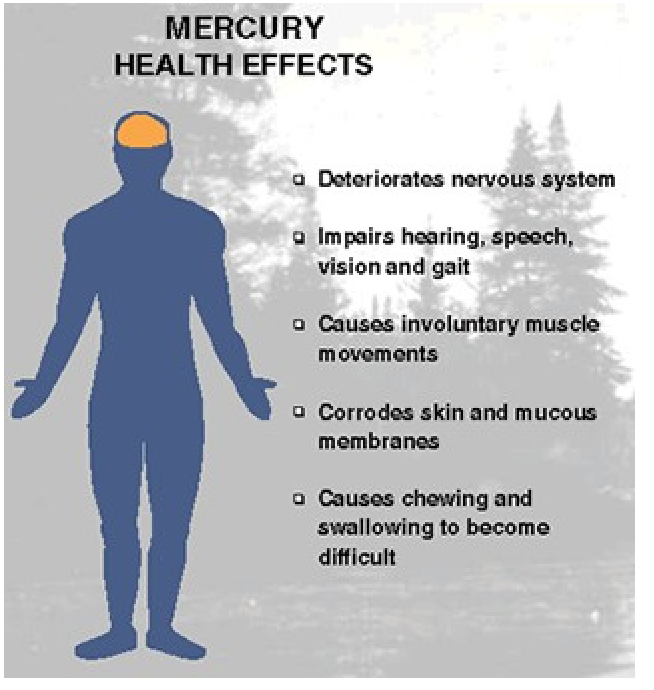
Mercury Forms, toxicity, and health effects

Mercury (Hg) has long been identified as an element that is injurious, even lethal, to living organisms.

Exposure to its inorganic form, Hg (Hg^0) vapor can cause damage to respiratory, neural, and renal systems.

The organic form, methylmercury (Me_2Hg), is substantially more toxic than the inorganic form

Methylmercury attacks the nervous system and exposure can be lethal, as demonstrated by well-known incidents such as those in 1956 in Minimata, Japan.



“Mad as a hatter”

Mercury was used in the manufacturing of felt hats during the 19th century, causing a high rate of mercury poisoning in those working in the hat industry, which led to the phrase "***mad as a hatter***"

Lewis Carrol, the english writer, was familiar with that conditions, and The Hatter character (also called the ***Mad Hatter*** or ***Hatter***) appears in his 1865 novel “Alice's Adventures in Wonderland and its sequel “Through the Looking-Glass”.

Chapter I.

Alice was beginning to get very tired of sitting by her sister on the bank, and of having nothing to do: once or twice she had peeped into the book her sister was reading, but it had no pictures or conversations in it, and where is the use of a book, thought Alice, without pictures or conversations? So she was considering in her own mind, (as well as she could, for the hot day made her feel very sleepy and stupid,) whether the pleasure of making a daisy-chain was worth the trouble of getting up and picking the daisies, when a white rabbit with pink eyes ran close by her.

There was nothing very remarkable in that, nor did Alice think it so very much out of the way to hear the rabbit say to itself "dear, dear! I shall be too late!" (when she thought it over afterwards, it occurred to her that she ought to have wondered at this, but at the time it all seemed quite natural); but when the rabbit actually took a watch out of its waistcoat-pocket, looked at it, and then hurried on, Alice started to her feet, for

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Minamata Convention on Mercury

The Minamata Convention on Mercury is a global treaty to protect human health and the environment from the adverse effects of mercury. It was adopted on **10 October 2013.**

The Convention draws attention to a global and ubiquitous metal that, while naturally occurring, has broad uses in everyday objects and is released to the atmosphere, soil and water from a variety of sources. Controlling the anthropogenic releases of mercury throughout its lifecycle has been a key factor in shaping the obligations under the Convention.

Major highlights of the Minamata Convention include a ban on new mercury mines, the phase-out of existing ones, the phase out and phase down of mercury use in a number of products and processes, control measures on emissions to air and on releases to land and water, and the regulation of the informal sector of artisanal and small-scale gold mining. The Convention also addresses interim storage of mercury and its disposal once it becomes waste, sites contaminated by mercury as well as health issues.

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Mercury in natural waters

In natural waters there are three main Hg species found in the dissolved phase:

- inorganic Hg (Hg^{2+} and its complexes);

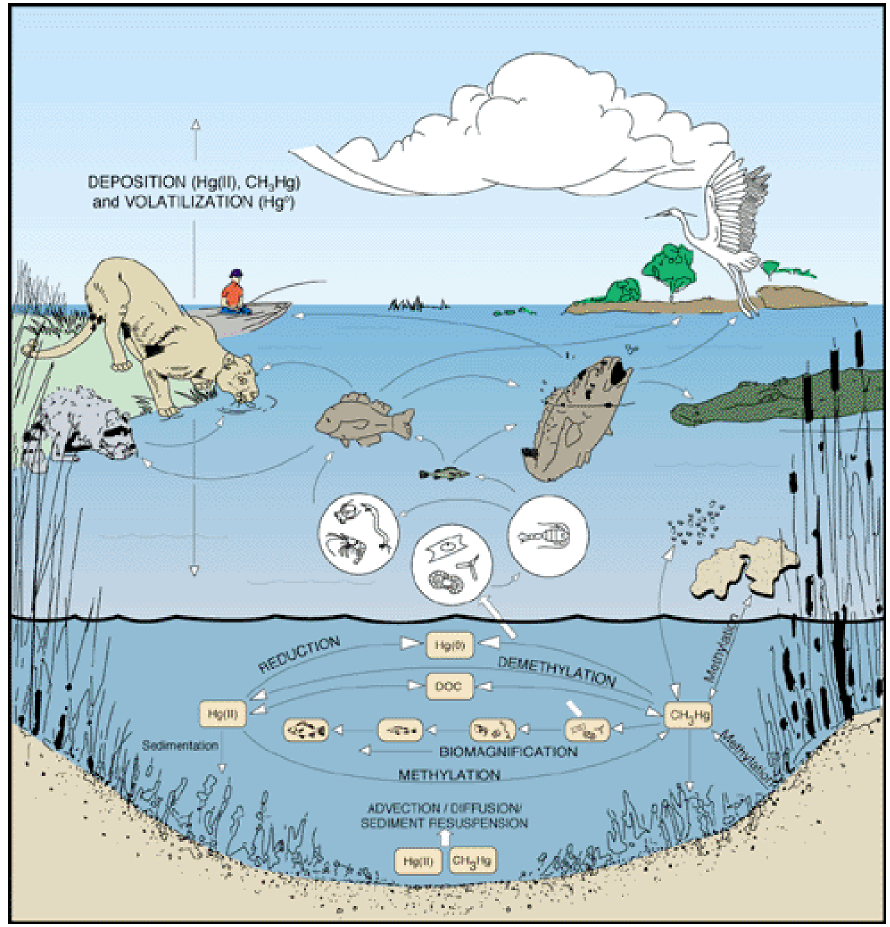
- organic Hg (monomethylmercury

and

dimethylmercury CH_3Hg^+; Me_2Hg)

- elemental Hg (Hg0)

All of these species are highly mobile, as shown by the biogeochemical Hg cycle.



(Image from"Aquatic Cycling of Mercury in the Everglades")

Biogeochemical mercury cycle

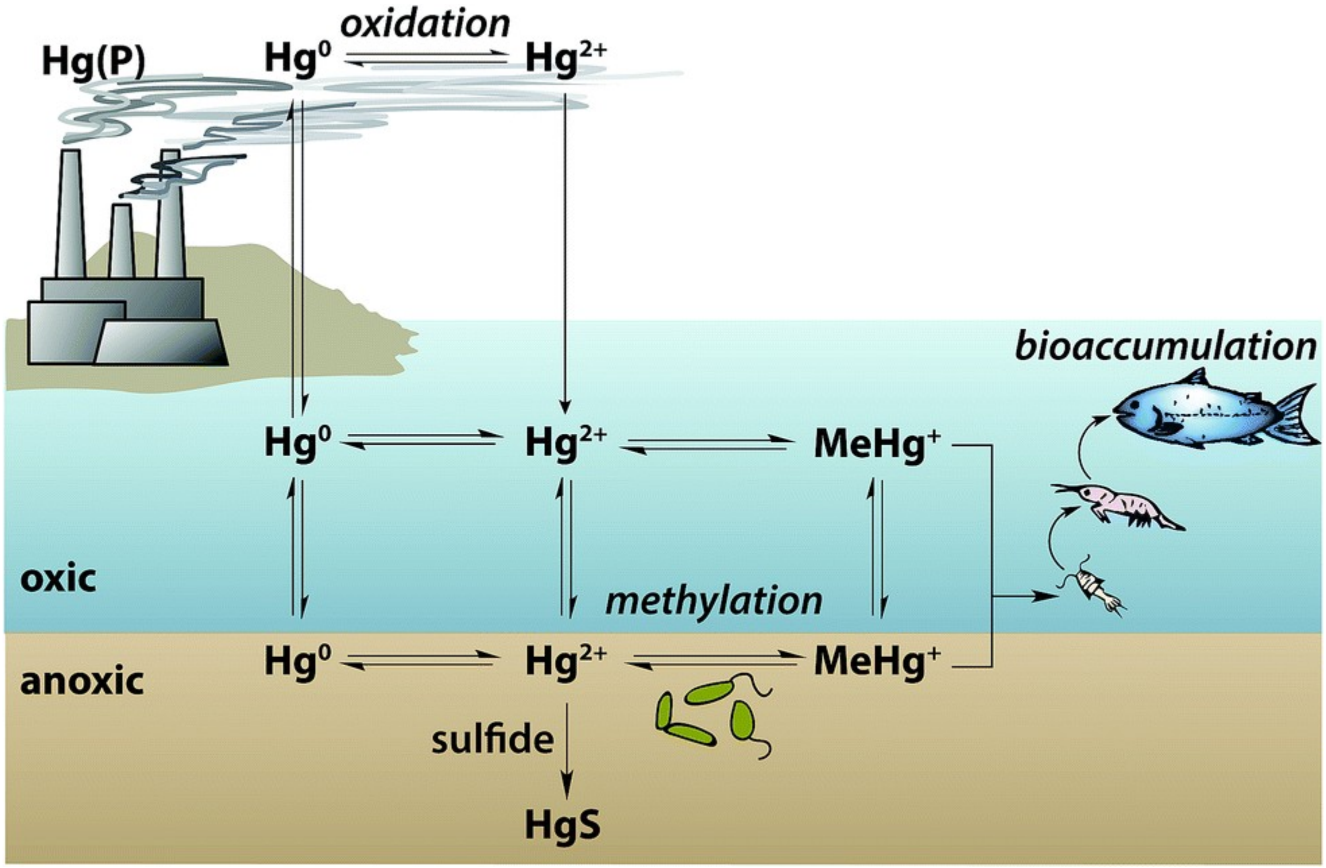


Image from. “Elucidation of biogeochemical factors influencing methylmercury production Paul R. Ericksona and Vivian S. Lin*a Show Affiliations Environ. Sci.: Processes Impacts, 2015,17, 1708-1711”

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Bioaccumulation of mercury in the food chain

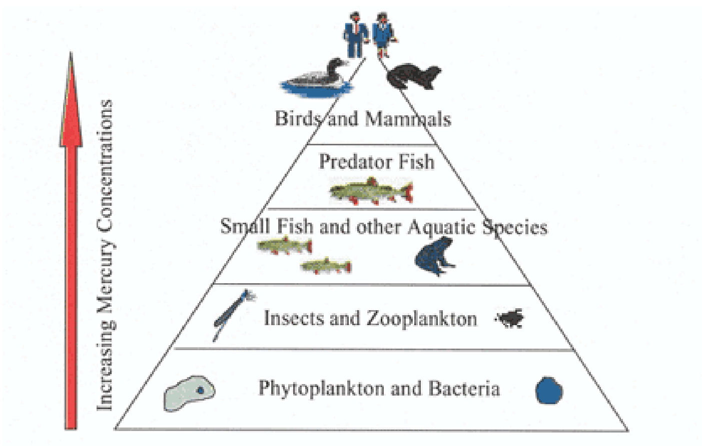

Figure 1. Accumulation of mercury in the food chain.

(Reprinted from Clean the Rain, Clean the Lakes: National Wildlife Federation, 2000)

The monitoring of mercury in natural waters is very important due to:

- very high bioaccumulation factor (up to 10^6) in the food chain
- high to toxicity
- third place on the "Priority List of Hazardous Substances" (Comprehensive Environmental Response, Compensation, and Liability Act - CERCLA)
- Eureopean water Framework Directive (2000/60/EC) classifies Hg as one of the "precarious dangerous pollutants" consequently the determination of Hg in water is regulated by law

DIRECTIVE 2013/39/UE

DIRECTIVE 2013/39/UE OF THE EUROPEAN PARLIAMENT has modified DIRECTIVE 2000/60/CE & DIRECTIVE 2008/105/CE establishing a new framework for Community action in the field of mercury water policy

No	Name of substance	CAS number	MAC-EQS inner surface waters	MAC-EQS Other surface waters	SQA Biota
21	Mercury and its compounds	7439-97-6	0,07µg/l	0,07µg/l	20µg/Kg

(MAC-EQS: maximum allowable concentration)

Italian law

In Italy, chemical status has been determineted monitoring the compliance with the environmental quality standards **(EQS)**, including those expressed as maximum allowable concentrations (SQA-CMA) layed down in D.Lgs. 152/06 *s.m.i*, in accordance with the previsions and objectives of Directive 2000/60/EC.

	SQA-MA (acque superficiali interne)	SQA-MA (altre acque di superficie)	SQA-CMA
mercurio	0,03 µg/l	0,01µg/l	0,06 µg/l

Since 2010, in accordance with DIRECTIVE 2000/60/EC, ARPAT has been monitoring surface waters, and, here in Tuscany: mercury, during 2014 (*from: Annuario dei dati ambientali ARPAT 2015*), just as in the previous period, has been the pollutant most responsible for the "***failing to achieve good chemical status***" outcome.

D.Lgs. 172/2015, amending D.Lgs. 152/06 s.m.i, has established for our country, MAC-EQS for Other surface waters & SQA for Biota as layed down in DIRECTIVE 2013/39/UE

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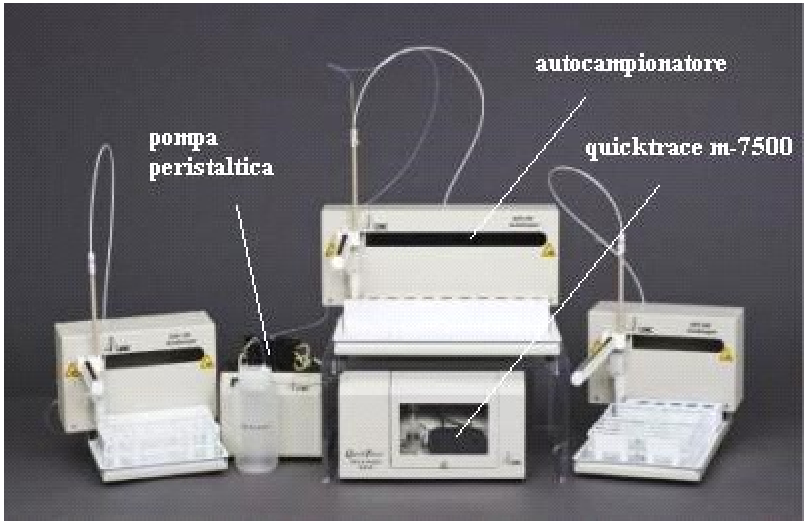
Analysis of Hg in the past

During the past (until september 2015) in the AVL laboratory of Environmental Protection Agency Tuscany Region (ARPAT), we performed analysis of mercury in seawater by a Cold Vapor Atomic Absorbiption analyzer (Cetac QuickTrace ™ M-7500 CVAAS) by a modified method based on EPA 245.7 "***Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry***".

This method requires samples preservations in sample vials with 1:1 hydrocloridiric acid and digestion with 0.1 N potassium bromide/potassium bromate solution, followed by reduction with 12% hydroxylamine; reduction of the inorganic mercury to elemental mercury was carried out by excess online addition of 10% stannous chloride in 7% hydrocloridiric acid.



(Illustration from CETAC Technologies brochure)

Analysis of Hg in seawater now

- Thermo Scientific iCAP Qc ICP-MS
- Argon Gas Diluition Kit
- Argon Gas Humidifier
- Autosampler CETAC ASX520
- platinum cones

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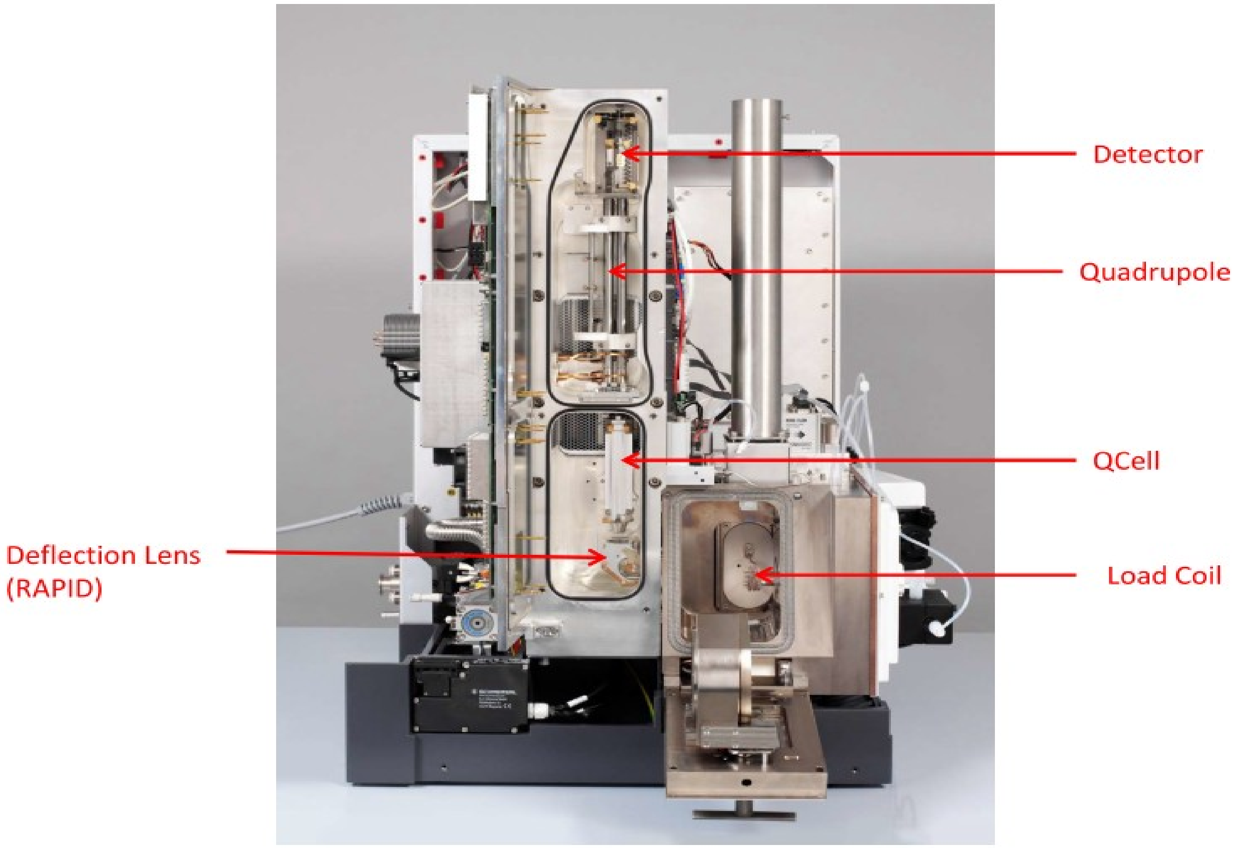
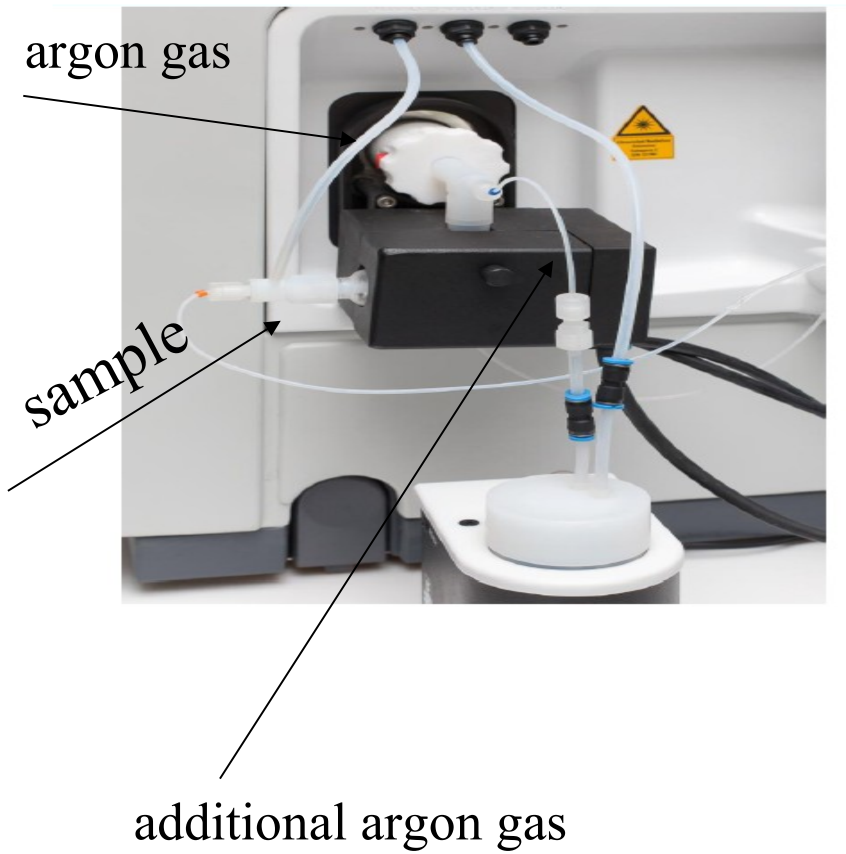
ICP-MS i CAP Q Front view



(Illustration from Thermo Fisher Scientific brochure)

AGD - Argon Gas Dilution



- In AGD-ICP-MS analyses, an additional argon gas is introduced at spray chamber elbow to the plasma

- the argon gas flow trhough the nebulizer is reduced while the total gas flow to the plasma is maintained by the addition of a "make up" argon gas flow to the aereosol leaving the chamber.

- Since the absolute amount of sample entering the plasma is limited the dissociaton of heavy matrix samples is improved, reducting matrix deposition on the ICP-MS interface

AGD - Argon Gas Dilution

- Minimal spread of signal between low and high masses
- Minimal drift over a period of 7.5 hrs
- NOT internal standard corrected
- Achieved plasma robustness avoids internal standard suppression, so that calibration can be carried out in dilute nitric acid.

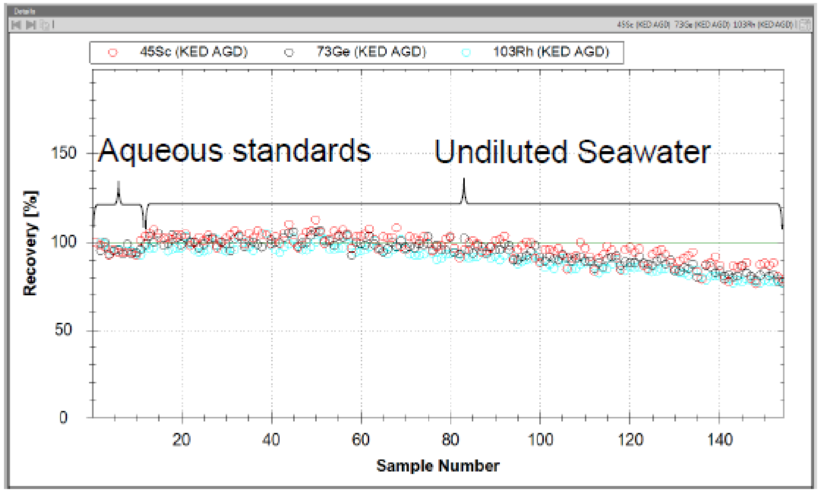


Illustration from Thermo Fisher Scientific brochure

AGD + Argon Gas Humidifier system

Argon Gas Humidifier system is used to re-wet the plasma in order to improve the recovery of signal for elements (eg. Hg) with higher Ionization Potential (IP) and meet the lower recovery limits (75% - *APHA standard methods for examination of water and waste water 22st ed 2012 3125*)

When carbon is introduced to the plasma via addition of isopropanolo (10%v/v) to the I.S. solution, AGD-ICP-MS recoveries meet 80 %

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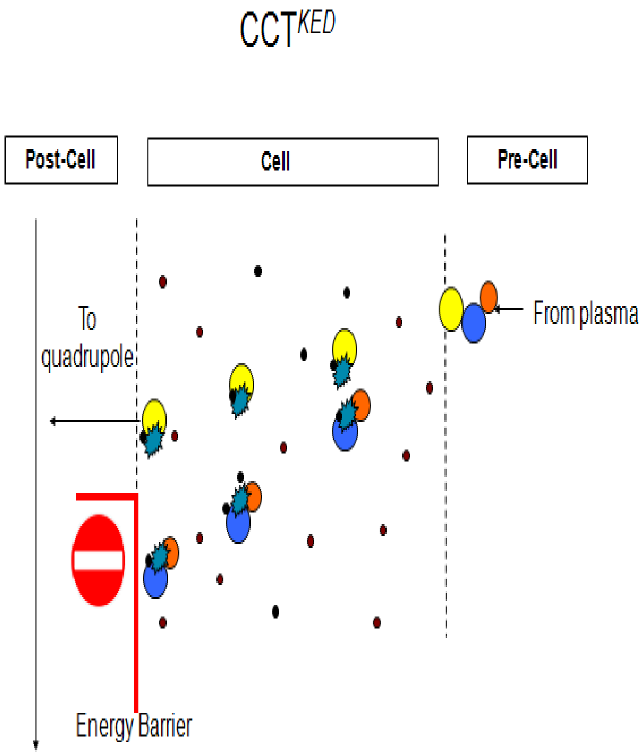
Instrument setting and performances

	Neb.-Flow	Add. Gas 1	Extraction lens 2	CCT Focus lens
STD	**1.15**		- 106 V	- 5.16 V
STD AGD	**0.25**	**0.95**	- 172 V	0.60 V

Analyte	STD	STD AGD with Ar-Humidifier	KED AGD with Ar-Humidifier
Li	69918	3062	<100
Co	115528	5448	1800
In	270492	16103	3200
U	336109	29235	25200
Oxides	1,95 %	0,86%	0,25%
Double charged	2,22 %	1,03%	1,8%

KED (Kinetic Energy Discrimination)



In the cell pressurized with Helium gas, extraction lens ensures that analyte and polyatomic ions enter the cell from plasma with uniform kinetic energies.

Polyatomic intefering species have larger cross section areas then analyte ions of similar mass; since these species are much larger then the target ions and enter the cell with similar energies they will undergo more collisions, reaching the cell exit with much lower kinetic energy then the corresponding analyte ions.

An appropiate energy barrier will block the polyatomic ions from passing into the analyzer, while allowing the target ions to continue.

(*illustration from "ICP-MS Operators Training Course iCAP Q Training Manual" by Unity Lab Services part of Thermo Fisher Scientific*)

Calibration Curve

Calibration

9/14/2016 1:27:15 PM

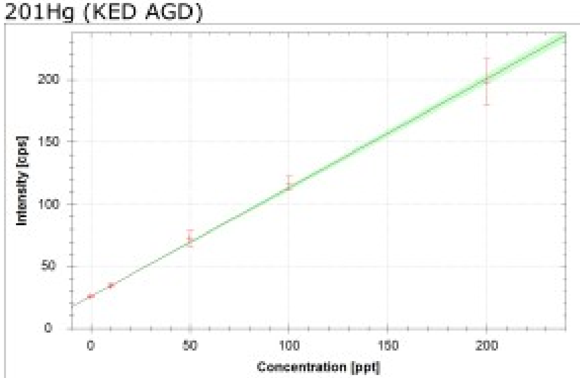
QTEGRA

Calibration Curves:

Instrument Name:	Serial Number:
iCAP Q	Undefined

Labbook:	Labbook Path:
14-06-16 Hg salt.imexp	_Application Data\Workspace\LabBooks\AGD

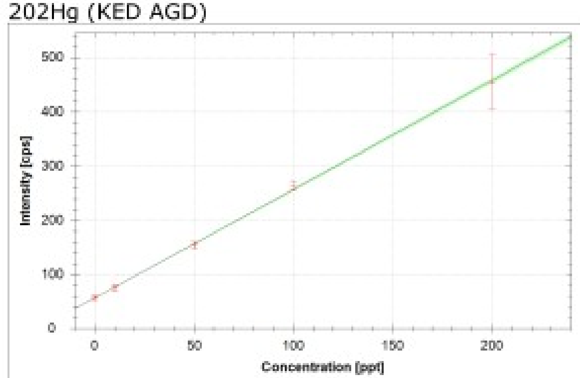
201Hg (KED AGD)



f(x) = 0.8740*x + 25.8785
$R^2 = 0.9983$

LoD = 0.7952 ppt

202Hg (KED AGD)



f(x) = 2.0045*x + 56.7337
$R^2 = 0.9995$

LoD = 6.2085 ppt

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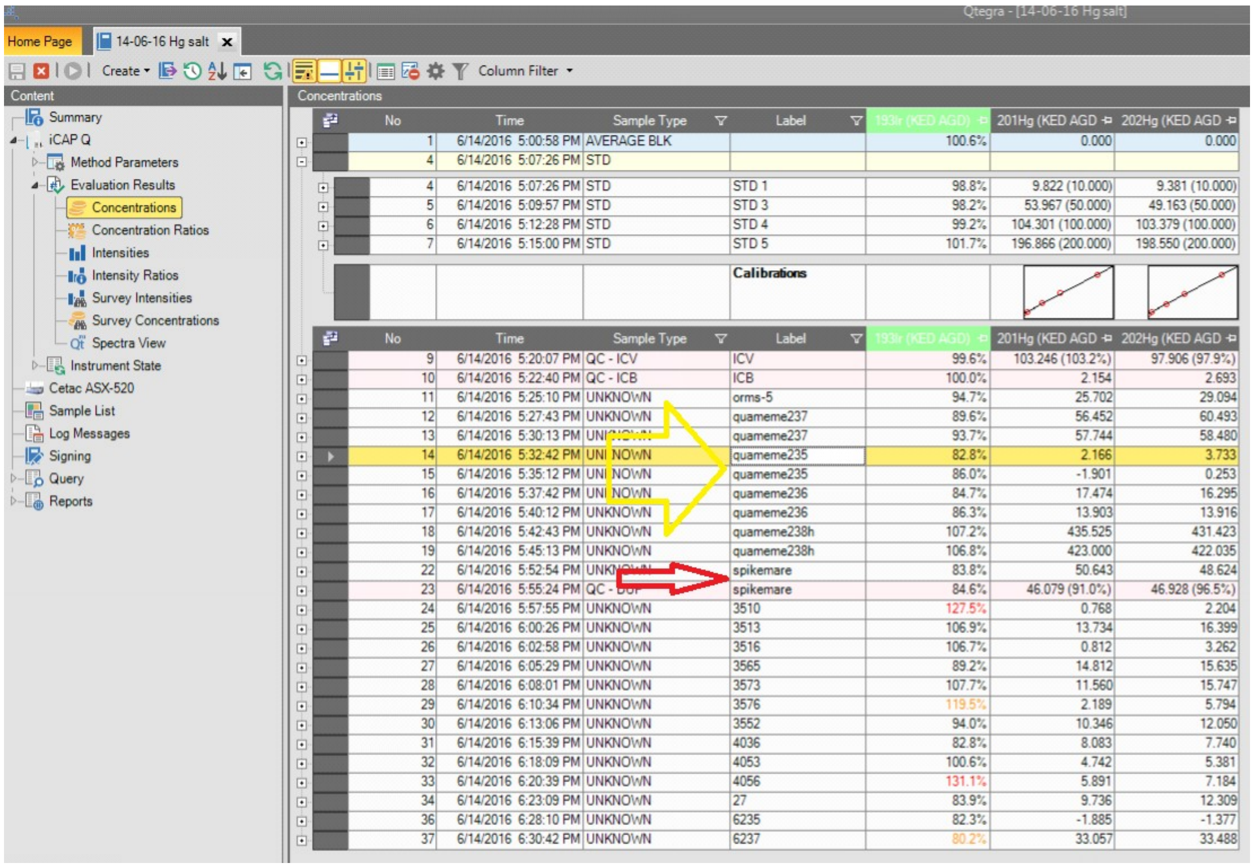
Results



No	Time	Sample Type	Label	193Ir (KED AGD)	201Hg (KED AGD	202Hg (KED AGD
1	6/14/2016 5:00:58 PM	AVERAGE BLK		100.6%	0.000	0.000
4	6/14/2016 5:07:26 PM	STD				
4	6/14/2016 5:07:26 PM	STD	STD 1	98.8%	9.822 (10.000)	9.381 (10.000)
5	6/14/2016 5:09:57 PM	STD	STD 3	98.2%	53.967 (50.000)	49.163 (50.000)
6	6/14/2016 5:12:28 PM	STD	STD 4	99.2%	104.301 (100.000)	103.379 (100.000)
7	6/14/2016 5:15:00 PM	STD	STD 5	101.7%	196.866 (200.000)	198.550 (200.000)

No	Time	Sample Type	Label	193Ir (KED AGD)	201Hg (KED AGD	202Hg (KED AGD
9	6/14/2016 5:20:07 PM	QC - ICV	ICV	99.6%	103.246 (103.2%)	97.906 (97.9%)
10	6/14/2016 5:22:40 PM	QC - ICB	ICB	100.0%	2.154	2.693
11	6/14/2016 5:25:10 PM	UNKNOWN	orms-5	94.7%	25.702	29.094
12	6/14/2016 5:27:43 PM	UNKNOWN	quameme237	89.6%	56.452	60.493
13	6/14/2016 5:30:13 PM	UNKNOWN	quameme237	93.7%	57.744	58.480
14	6/14/2016 5:32:42 PM	UNKNOWN	quameme235	82.8%	2.166	3.733
15	6/14/2016 5:35:12 PM	UNKNOWN	quameme235	86.0%	-1.901	0.253
16	6/14/2016 5:37:42 PM	UNKNOWN	quameme236	84.7%	17.474	16.295
17	6/14/2016 5:40:12 PM	UNKNOWN	quameme236	86.3%	13.903	13.916
18	6/14/2016 5:42:43 PM	UNKNOWN	quameme238h	107.2%	435.525	431.423
19	6/14/2016 5:45:13 PM	UNKNOWN	quameme238h	106.8%	423.000	422.035
22	6/14/2016 5:52:54 PM	UNKNOWN	spikemare	83.8%	50.643	48.624
23	6/14/2016 5:55:24 PM	QC - DUP	spikemare	84.6%	46.079 (91.0%)	46.928 (96.5%)
24	6/14/2016 5:57:55 PM	UNKNOWN	3510	127.5%	0.768	2.204
25	6/14/2016 6:00:26 PM	UNKNOWN	3513	106.9%	13.734	16.399
26	6/14/2016 6:02:58 PM	UNKNOWN	3516	106.7%	0.812	3.262
27	6/14/2016 6:05:29 PM	UNKNOWN	3565	89.2%	14.812	15.635
28	6/14/2016 6:08:01 PM	UNKNOWN	3573	107.7%	11.560	15.747
29	6/14/2016 6:10:34 PM	UNKNOWN	3576	119.5%	2.189	5.794
30	6/14/2016 6:13:06 PM	UNKNOWN	3552	94.0%	10.346	12.050
31	6/14/2016 6:15:39 PM	UNKNOWN	4036	82.8%	8.083	7.740
32	6/14/2016 6:18:09 PM	UNKNOWN	4053	100.6%	4.742	5.381
33	6/14/2016 6:20:39 PM	UNKNOWN	4056	131.1%	5.891	7.184
34	6/14/2016 6:23:09 PM	UNKNOWN	27	83.9%	9.736	12.309
36	6/14/2016 6:28:10 PM	UNKNOWN	6235	82.3%	-1.885	-1.377
37	6/14/2016 6:30:42 PM	UNKNOWN	6237	80.2%	33.057	33.488

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Results

Sample List Label	193Ir (KED AGD) %	201Hg (KED AGD) ppt	202Hg (KED AGD) ppt
ICV	86.5	97.6	101.2
orms-5	87.5	24.4	23.9
spike	82.3	31.7	31.2
spike	87.0	31.0	32.3
4219	90.0	-2.7	0.1
4220	86.1	-3.3	-1.3
4259	87.1	8.8	10.3
4260	89.6	3.8	8.6
4293	88.5	4.9	6.8
4294	90.4	4.5	3.7
4327	91.0	-3.7	0.3
4405	93.3	-2.0	0.9
4427	93.8	42.5	46.2
4428	91.5	36.6	35.6
4429	95.8	-9.2	-5.5
4527	97.5	8.1	8.9
4529	99.1	33.5	33.4
4531	96.1	4.9	5.8
4403	98.9	-2.1	-0.9
4329	96.9	10.7	12.8
4427	96.8	43.5	42.1
orms-5	96.7	23.0	21.2
4328	85.5	26.4	29.3

Sample List Label	193Ir (KED AGD) Value	201Hg (KED AGD) Value	202Hg (KED AGD) Value
ICV	90.0	118.9	121.2
ICB	93.6	1.7	3.1
quameme	65.9	13.7	13.7
quameme	78.5	13.3	14.3
quameme	82.5	12.0	13.3
2247	87.1	21.0	23.2
2255	82.5	20.8	23.6
2259	77.8	16.7	17.5
2518	102.7	-1.5	-2.2
2522	101.9	119.4	118.2
quameme	72.5	10.1	10.5
quameme	69.7	9.9	9.4
spike	68.7	22.0	22.4
spike	66.6	20.6	21.5

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Accuracy determination

In order to address the accuracy of the method, the recovery of matrix spiked duplicates was determinated several times at different concentrations

Hg level investigated (ppt)	Average	RPD %	Recovery %
20	21,3	6	106,5
30	31,4	5,7	104,5
50	48,4	9,3	96,7

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Quasimeme Results

AQ4 2016.1 - Metals

Sample	QTM235SW	QTM236SW	QTM237SW	QTM238SW	MIC
Mercury (ng/l)					
L420	65.30 **	97.1 **	120.7 **	538	
Q104	2.00	12.4 *	42.9 *	286 **	
Q110	30.00 <	30.0 <	61.0	454	
Q113	15.00 <	15.0 <	54.0	419	
Q114	2.00 <	13.3 *	41.1 **	332 *	
Q121	2.79	19.1	70.2	491	
Q126	5.70 **	20.8	70.8	529	
Q134	2.07	16.6	64.9	511	
Q136	3.02	20.1	-	-	
Q157A	10.00 <	21.4	91.9 *	630 *	
Q158	6.41 **	22.5	85.4 *	518	
Q239	10.00 <	16.5	69.5	483	
Q3372	3.00 <	15.0	58.0	420	
[illegible]	1.81	16.8	66.3	497	
Q3757	2.36	18.1	64.2	464	
Q3779	9.84 **	21.9	78.0	503	
Q409	24.60 **	41.0 **	99.5 **	457	
Q555	100.00 <	100.0 <	-	515	
===== Statistical Results =====					
NDA mean	2.557	18.06	66.89	489.3	
NDA st dev	1.700	3.87	15.16	46.8	
N	11	15	16	17	
Median	3.020	19.10	67.90	491.0	
MAD	1.210	2.60	10.01	34.0	
Total Error	0.420	2.36	8.46	61.3	

Contamination

Contaminations, interferences and samples preparation are the major obstacle that can arise when monitoring mercury at ppt level

According to EPA Method 245.7, samples may become contaminated by numerous routes.

Potential sources of trace metals contamination include:

- metallic or metal-containing labware,

- containers

- sampling equipment

- reagents, and reagent water

- improperly cleaned or stored equipment

- plastic labware

- atmospheric inputs such as dirt and dust.

Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples directly exposed to exhalation.

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Results of enviromental monitoring of Hg up to 2015 in water column

Stato chimico delle acque marino-costiere - esiti monitoraggio al 2015 - Colonna d'acqua

COLONNA D'ACQUA (µg/L)							
Anno	**Hg**	**Cr**	**Ni**	**As**	**Cd**	**Pb**	**TBT**
Corpo idrico: Costa Versilia							
Stazione: Marina di Carrara							
2011	0,06	1	1	2	<0,1	<1	0,0034
2012	0,05	1	8	1	0,0	1,2	<0,005*
2013	0,10	1	5	2	0,1	0,7	0,3352
2014	0,03	9	3	2	0,1	1,4	0,0005
2015	0,01	1	1	2	0,1	0,6	0,0006
Corpo idrico: Costa del Serchio							
Stazione: Nettuno							
2011	0,02	1	2	2	<0,1	1,2	0,0068
2012	0,06	1	1	1	0,1	0,5	<0,005*
2013	0,02	<1	5	2	0,1	1,3	<0,005*
2014	0,04	2	2	2	0,1	1	0,0014
2015	0,01	1	2	2	0,1	<1	0,0015
Corpo idrico: Costa Pisana							
Stazione: Fiume Morto							
2011	0,02	1	1	3	0,1	<1	0,0088
2012	0,05	1	1	1	0,0	0,9	0,0148
2013	0,05	2	2	2	0,1	<1	<0,005*
2014	0,05	1	1	2	0,1	0,7	0,0004
2015	0,01	1	1	2	0,1	1	0,0016
Corpo idrico: Costa Livornese							
Stazione: Livorno							
2011	0,01						0,0029
2012	0,03	1	5	1	0,1	0,9	<0,005*
2013	0,17	<1	2	2	0,1	<1	0,0035
2014	0,05	1	2	2	0,2	0,9	0,0007
2015							
Stazione: Antignano							
2011	0,02						
2012	0,03	1	3	2	0,1	0,7	0,0128
2013	0,15	<1	1	2	0,1	<1	0,0026
2014	0,09	1	1	2	0,1	<1	0,0006
2015	0,01	1	3	2	0,1	<1	0,0015
Corpo idrico: Costa di Rosignano**							
Stazione: Rosignano Lillatro							
2011	0,01						
2012	0,03	1	3	1	0,0	0,5	0,0075
2013	0,29	<1	3	2	0,1	1,1	0,0013
2014	0,02	2	2	2	0,1	0,8	0,0007
2015	0,01	1	1	2	0,0	<1	0,0006
Corpo idrico: Costa del Cecina**							
Stazione: Marina di Castagneto							
2011	0,02						
2012	0,04	1	2	1	0,1	0,7	0,0270
2013	0,05	1	4	2	0,1	0,6	0,0024
2014	0,03	2	1	2	0,2	1,2	<0,0006*
2015	0,02	1	1	2	0,1	<1	0,0011
Corpo idrico: Costa Piombino							
Stazione: Marina di Salivoli							
2011	<0,01	<0,1	4	2	0,1	0,5	0,0090
2012							
2013	0,05	<1	1	2	0,1	0,5	0,0028
2014	0,07	<1	1	2	0,1	<1	<0,0006*
2015	0,01	1	1	2	0,1	0,6	0,0011
Corpo idrico: Costa Follonica							
Stazione: Carbonifera							
2011	0,02	1	1	3	0,1	0,6	<0,005*
2012	0,03	1	3	<1	0,0	0,5	0,0103
2013	0,06	<1	5	2	0,1	<1	<0,005*
2014	0,10	2	1	2	0,1	<1	0,0007
2015	0,02	2	1	2	0,0	0,8	0,0020
Corpo idrico: Costa Punt'Ala							
Stazione: Foce Bruna							
2011							
2012	0,09	1	1	<1	0,0	0,6	0,0167
2013	0,13	<1	2	2	0,2	<1	0,0167
2014	0,03	5	2	2	0,6	<1	0,0048
2015	<0,01	1	1	2	0,2	<1	0,0008

*, **: vedi note a fine tabella

Limiti di legge (µg/L)

Mercurio – Hg	Cromo – Cr	Nichel – Ni	Arsenico – As	Cadmio – Cd	Piombo – Pb	Tributilstagno composti – TBT
0,01	**4**	**20**	**5**	**0,2**	**7,2**	**0,0002**

(From: Annuario Dati ARPAT 2016; www.arpat.toscana.it)

Stato chimico delle acque marino-costiere - esiti monitoraggio al 2015 - Colonna d'acqua

COLONNA D'ACQUA (µg/L)							
Anno	**Hg**	**Cr**	**Ni**	**As**	**Cd**	**Pb**	**TBT**
Corpo idrico: Costa Ombrone							
Stazione: Foce Ombrone							
2011	0,02						
2012	0,08	1	2	<1	0,0	0,6	<0,005*
2013	0,03	<1	3	2	0,1	0,6	0,0013
2014	0,03	1	1	2	0,2	<1	0,0010
2015	0,03	1	1	7	0,1	0,6	0,0017
Corpo idrico: Costa Uccellina							
Stazione: Cala di Forno							
2011	0,01						
2012	0,03	1	1	<1	0,0	0,6	<0,005*
2013	0,07	<1	3	2	0,1	<1	<0,005*
2014	0,04	2	1	2	0,2	<1	0,0020
2015	0,1	1	1	2	0,1	0,6	0,0021
Corpo idrico: Costa Albegna							
Stazione: Foce Albegna							
2011							
2012	0,07	1	2	1	0,1	0,7	<0,005*
2013	0,05	<1	10	3	0,1	<1	<0,0019
2014	0,05	1	2	2	0,3	0,7	0,0078
2015	0,02	2	1	2	0,1	<1	0,0010
Corpo idrico: Costa dell'Argentario							
Stazione: Porto S. Stefano							
2011	0,02	<0,1	2	2	0,1	<1	<0,005*
2012	0,01						
2013	0,09	<1	3	3	0,1	0,8	<0,005*
2014	0,03	1	3	2	0,1	1,6	0,0006
2015	0,01	1	<1	2	0,2	<1	0,0010
Corpo idrico: Costa Burano							
Stazione: Ansedonia							
2011							
2012	0,08	1	1	1	0,1	1,1	<0,005*
2013	0,05	<1	7	3	0,1	<1	<0,005*
2014	0,04	1	1	2	0,3	1,2	<0,0006*
2015	0,01	1	2	2	0,1	<1	0,0018
Corpo idrico: Costa Arcipelago - Isola d'Elba**							
Stazione: Elba Nord							
2011	0,06	<0,1	1	3	0,1	<1	<0,005*
2012							
2013							
2014	0,03	5	2	2	0,1	0,8	0,0018
2015	0,01	1	1	2	0,1	0,6	0,0009
Stazione: Mola (Elba Sud)							
2011	0,02	<0,1	13	3	0,1	<1	<0,005*
2012	0,03						
2013							
2014	0,03	1	1	2	0,2	<1	<0,0006*
2015	0,01	1	<1	2	0,0	<1	0,0018
Corpo idrico: Costa Arcipelago - Isole minori**							
Stazione: Giglio							
2012	0,08	1	2	1	0,1	<1	<0,005*
2013	0,07	<1	4	3	0,1	<1	0,0015
2014	0,04	1	1	3	0,1	<1	0,0008
2015	0,01	1	<1	3	0,1	<1	0,0016
Stazione: Montecristo							
2012	0,06	1	<1	<1	<0,05	<1	<0,005*
2013							
2014	0,02	2	<1	1	0,1	<1	0,0013
2015	<0,01	1	<1	2	0,1	<1	<0,0006*
Stazione: Capraia							
2012	0,04	<1	<1	1	0,1	<1	<0,005*
2013							
2014	0,01	2	1	2	0,2	<1	<0,0006*
2015	<0,01	1	1	2	0,1	<1	<0,0006*

Valori nei limiti di legge — Valori superiori ai limiti di legge — Campioni non programmati

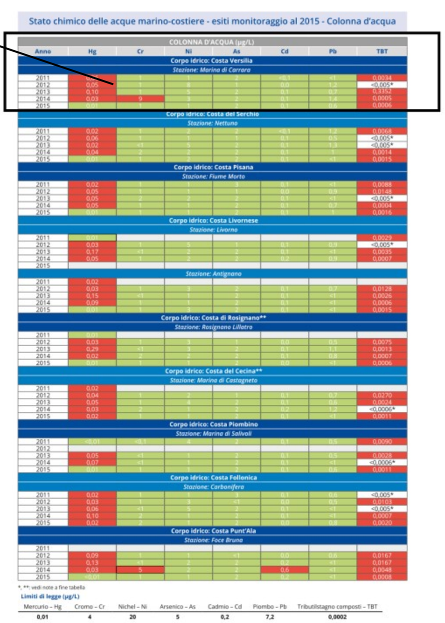
Limiti di legge (µg/L)

Mercurio – Hg	Cromo – Cr	Nichel – Ni	Arsenico – As	Cadmio – Cd	Piombo – Pb	Tributilstagno composti – TBT
0,01	**4**	**20**	**5**	**0,2**	**7,2**	**0,0002**

Results of enviromental monitoring of Hg up to 2015 in water column

Stato chimico delle acque marino-costiere - esiti monitoraggio al 2015 - Colonna d'acqua

COLONNA D'ACQUA (µg/L)							
Anno	**Hg**	**Cr**	**Ni**	**As**	**Cd**	**Pb**	**TBT**
Corpo idrico: Costa Versilia							
Stazione: Marina di Carrara							
2011	0,06	1	1	2	<0,1	<1	0,0034
2012	0,05	1	8	1	0,0	1,2	<0,005*
2013	0,10	1	5	2	0,1	0,7	0,3352
2014	0,03	9	3	2	0,1	1,4	0,0005
2015	0,01	1	1	2	0,1	0,6	0,0006
Corpo idrico: Costa del Serchio							



[Hg] > SQA-CMA

(From: Annuario Dati ARPAT 2016; www.arpat.toscana.it)

3rd MS ENVY Day
Livorno
September 26-28, 2016

Results of enviromental monitoring of Hg up to June 2016 in water column

Marina di Castagneto	0.021	0.018	0.042	<0.010	
Antignano	<0.010	<0.010	0.018	0.021	<0.01
Nettuno	<0.010	0.042	0.033	0.020	<0.010
Marina di Carrara	0.016	<0.010	<0.010	0.020	<0.010
Fiume Morto	<0.010	<0.010	<0.010	0.016	0.011
Elba Nord	<0.010	0.012	<0.010	<0.010	
Elba Sud	<0.010	0.010	<0.010	<0.010	
Salivoli	0.022	0.018	<0.010	0.028	
Montecristo	<0.010				

Porto S.Stefano	0.025	<0.010	<0.010	
Giglio	<0.010	<0.010	<0.010	
Carbonifera	<0.010	0.019	<0.010	0.042
Ansedonia	0.048	<0.010	<0.010	
Albegna	<0.010	0.014	<0.010	<0.010
Cala di Forno	<0.010	0.010	<0.010	<0.010
Foce Ombrone	<0.010	<0.010	<0.010	<0.010
Foce Bruna	0.011	0.052	<0.010	<0.010
Rosignano Lillatro	<0.010	<0.010	<0.010	<0.010

(From: www.sira.arpat.toscana.it; www.arpat.toscana.it)

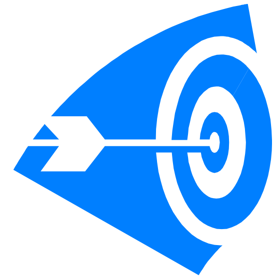
Conclusion

Direct analysis of Mercury in seawater samples, using an ICP-MS and Argon Gas Dilution (AGD), don't require samples preparation and dilution and minimize the sources of contamination.

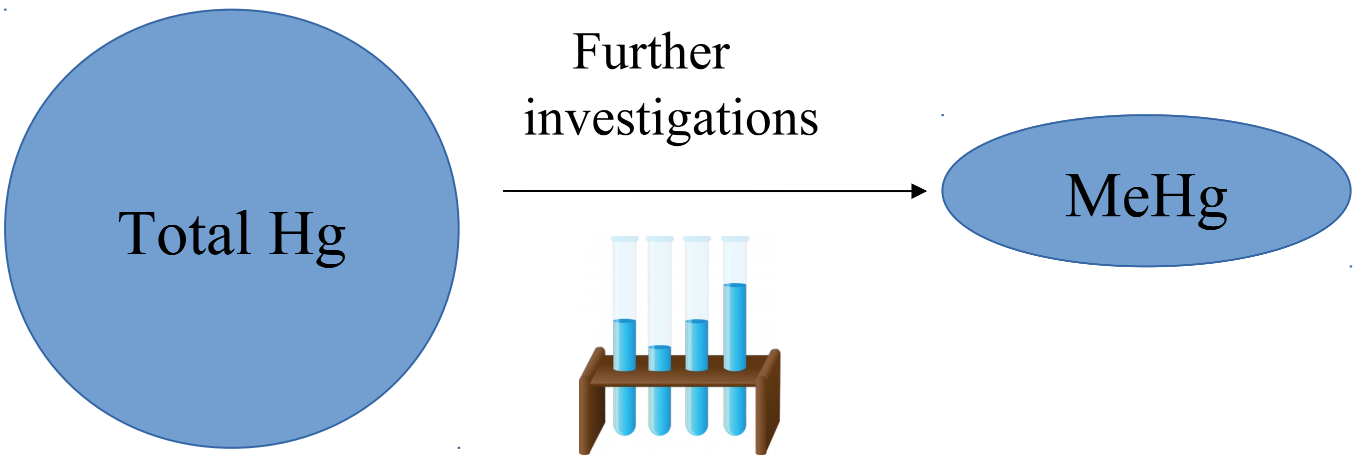
In order to establish the ability to generate acceptable precision and recovery of the system, the laboratory performed analysis of matrix spikes, matrix spike duplicates and participated at the 2016 QUASIMEME Laboratory Performance studies for the determination of mercury in the seawater test materials.

Due to the robustness of the ICP-MS and Argon Gas Dilution (AGD) system, we obtained that the response of the internal standard is almost uneffected by the sample matrix, an excellent accuracy was demonstrated through the determination of the spikes recovery and the performances for the laboratory in 2016 QUASIMEME was satisfactory with $|Z|$score < 2.

Next goal



Our approch with mercury is now aiming to determine its injurious & toxic organic forms, monomethyl and dimethylmercury (MeHg)



Thanks!

Thanks to the staff of “Metals” section of “Chimica I” AVL Laboratory of Livorno, especially Giacomo Sarti, for cooperation, and to Dr. Carlo Cini, Chimica I Chief, for his supervising