Ultra-Trace Level Mercury Analysis

Asia Pacific Mercury Monitoring Network

Center for Environmental Monitoring and Technology
National Central University

Mercury Detection Techniques

Method Source	Method Number	Media Name	Instrumentation	Detection Level
EPA-NERL	245.2	Water	CVAA	0.2 $\mu g\ L^{-1}$
EPA	7470A	Various	CVAA	0.2 $\mu g\ L^{-1}$
USGS	I-2462	Water	CVAA	0.1 $\mu g\ L^{-1}$
USGS	I-7462	Water	CVAA	0.5 $\mu g\ L^{-1}$
NOAA_NST	131	Soil/Sediment	CVAA	0.012 $\mu g\ L^{-1}$
EPA-EAD	1631	Water	CVAFS	0.0002 $\mu g\ L^{-1}$
EPA-OSW	6010 C	Various	ICP-AES	17 $\mu g\ L^{-1}$
EPA-NERL	200.8	Water	ICP-MS	0.2 $\mu g\ L^{-1}$
ASTM	D6502	Water	XRF	1 $\mu g\ L^{-1}$

Detection Level

AA **AF**

Name of concentration unit	*Part per thousand*	*Part per million*	*Part per billion*	*Part per trillion*	*Part per quadrillion*	*Part per quintillion*	*Part per sextillion*
Volume/volume concentration	vpth (ppth v/v)	vpm (ppm v/v)	vpb (ppb v/v)	vpt (ppt v/v)	vpq (ppq v/v)	vpq_{ui} (ppq_{ui} v/v)	vps (pps v/v)
Mass-mass concentration	ppth	ppm	ppb	ppt	ppq	ppq_{ui}	pps
Percentage (%)	10^{-1}	10^{-4}	10^{-7}	10^{-10}	10^{-13}	10^{-16}	10^{-19}
Amount of analyte in 1 g sample	1 milligram (1 mg)	1 microgram (1 µg)	1 nanogram (1 ng)	1 picogram (1 pg)	1 femtogram (1 fg)	1 attogram (1 ag)	1 zeptogram (1 zg)

Concentration of major ions in rainwater.

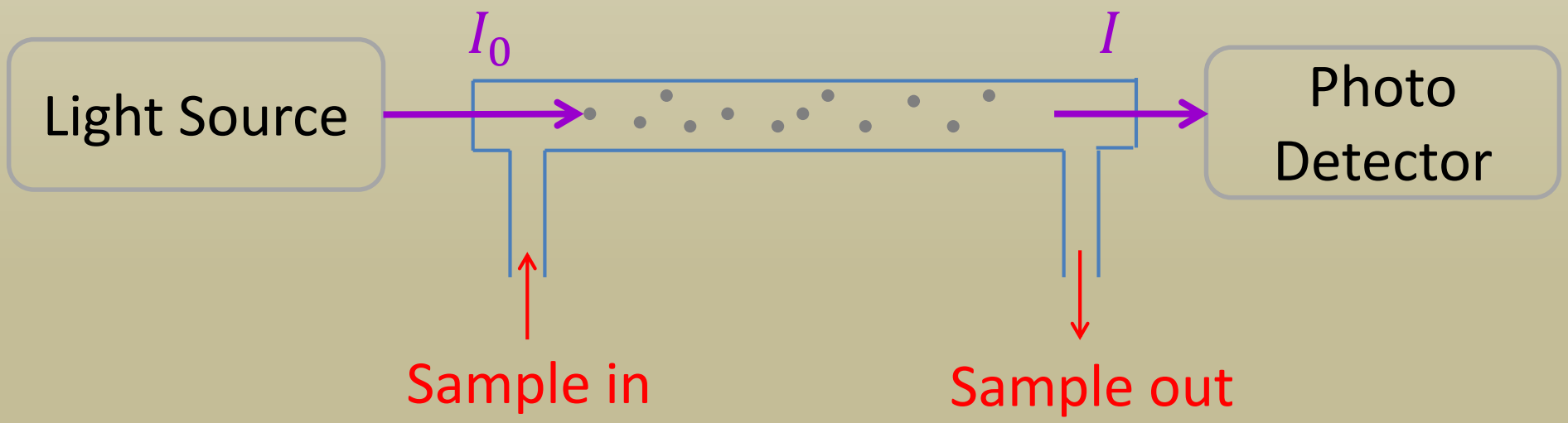
Concentration of Hg and MeHg in rainwater and ambient air.

Schematic Diagram of Atomic Absorption Spectroscopy

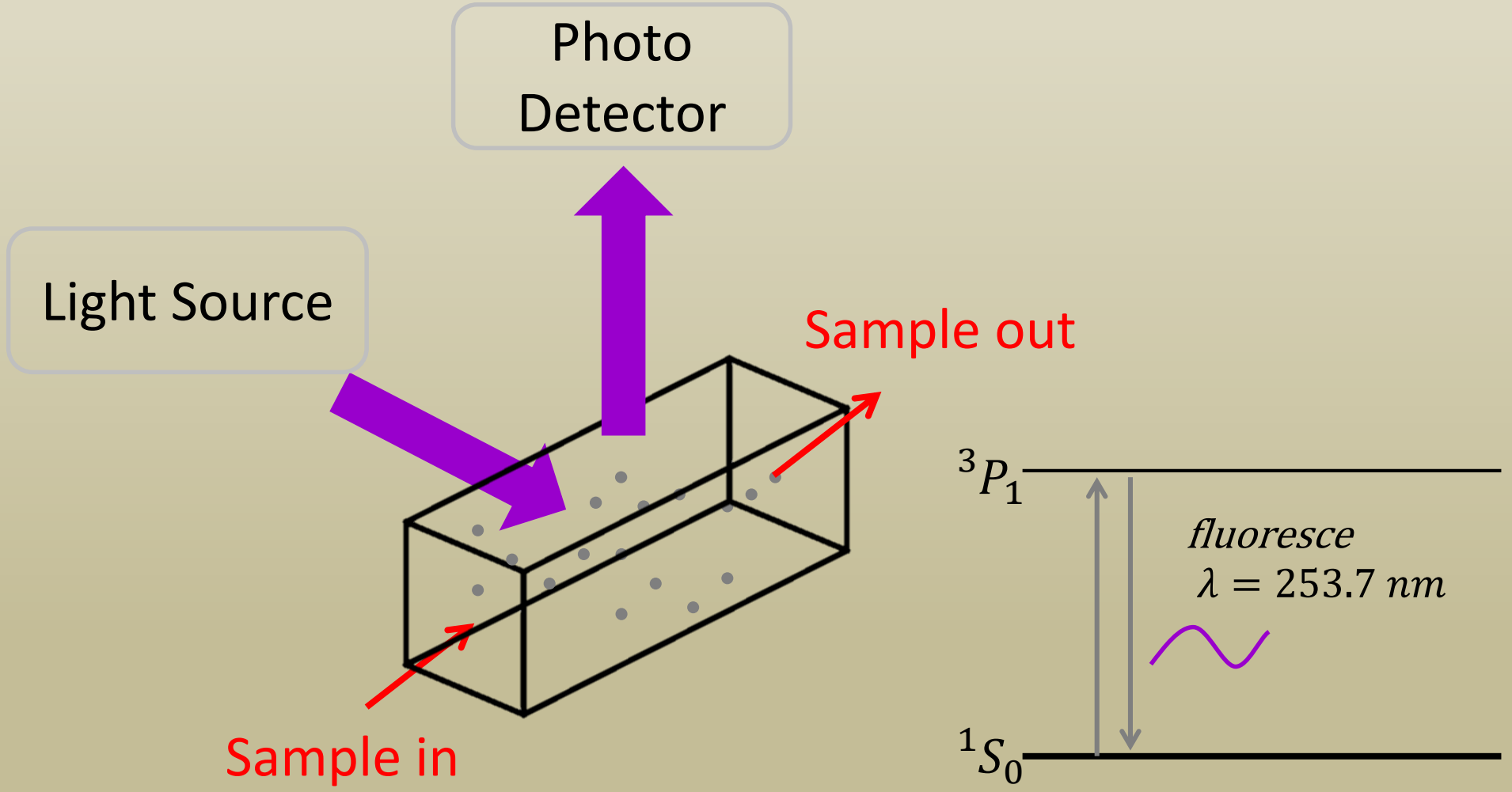
- Mercury atmos in the cell **absorb** light energy
- Photo detector measures **slight decrease** in intensity through cell

Beer–Lambert law

$$A = -log\frac{I}{I_o} = k \times l \times c$$



Schematic Diagram of Atomic Fluorescence Spectroscopy



AA vs AF

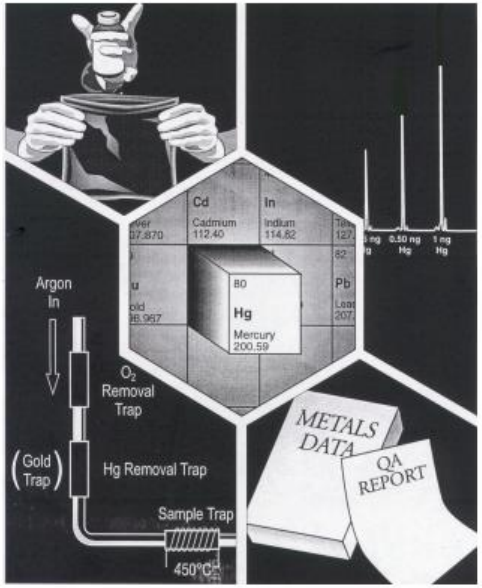
AA	AF
Amount of absorption is set by Beer's law ➢ Limited dynamic range	Inherently linear ➢ Detector linear over > 5 orders of magnitude
Not particularly sensitive ➢ Looking for very small decreases in a bright background lamp signal	Much more sensitive than atomic adsorption ➢ MDL < 0.1 pg absolute
Inherently cross sensitive to any molecular species that absorbs in the UV at 253.7 nm ➢ Organics, SO_2, O_3, … **A LOTS**	Not subject to interferences ➢ Interfering compounds often present in concentrations thousands of times higher than Hg

Reference

EPA
United States
Environmental Protection
Agency

Method 1631, Revision E:
Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

August 2002



Series 2600-IVS

Total Mercury in Water

via US EPA Method 1631

Analytical Guide

Tekran Model 2600-IVS Instrument and Model 2521 Auto-Sampler

Rev: 1.24

Jun 2015

TEKRAN
Instruments Corporation

WHERE MEASUREMENT BEGINS™

Reference

Note: This Method is performance based. The laboratory is permitted to omit steps or modify procedures provided that all performance requirements in this Method are met. The laboratory must not omit or modify any procedure defined by the term "shall" or "must" and must perform all quality control tests.

Scope and Application

1. Method 1631, Revision E (the "Method") is for determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). The Method is based on a contractor developed procedure and on peer-reviewed, published procedures for the determination of mercury in aqueous samples, ranging from sea water to sewage effluent

Scope and Application

2. This Method is for determination of Hg in the range of 0.5 – 100 ng/L. Application may be extended to higher levels by selection of a smaller sample size or by calibration of the analytical system across a higher range. For measurement of blank samples, the Method may be extended to a lower level by calibration to a lower calibration point.

Scope and Application

3. The ease of contaminating ambient water samples with mercury and interfering substances cannot be overemphasized. This Method includes suggestions for improvements in facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable trace metals determinations. Certain sections of this Method contain suggestions and other sections contain requirements to minimize contamination.

Scope and Application

4. The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrument limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be 0.2 ng/L when no interferences are present. The minimum level of quantitation (ML) has been established as 0.5 ng/L. An MDL as low as 0.05 ng/L can be achieved for low Hg samples by using a larger sample volume, a lower BrCl level (0.2%), and extra caution in sample handling.

Scope and Application

5. Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this Method because they lack an exact definition. However, the information provided in this Method is consistent with the summary guidance on clean and ultraclean techniques

Scope and Application

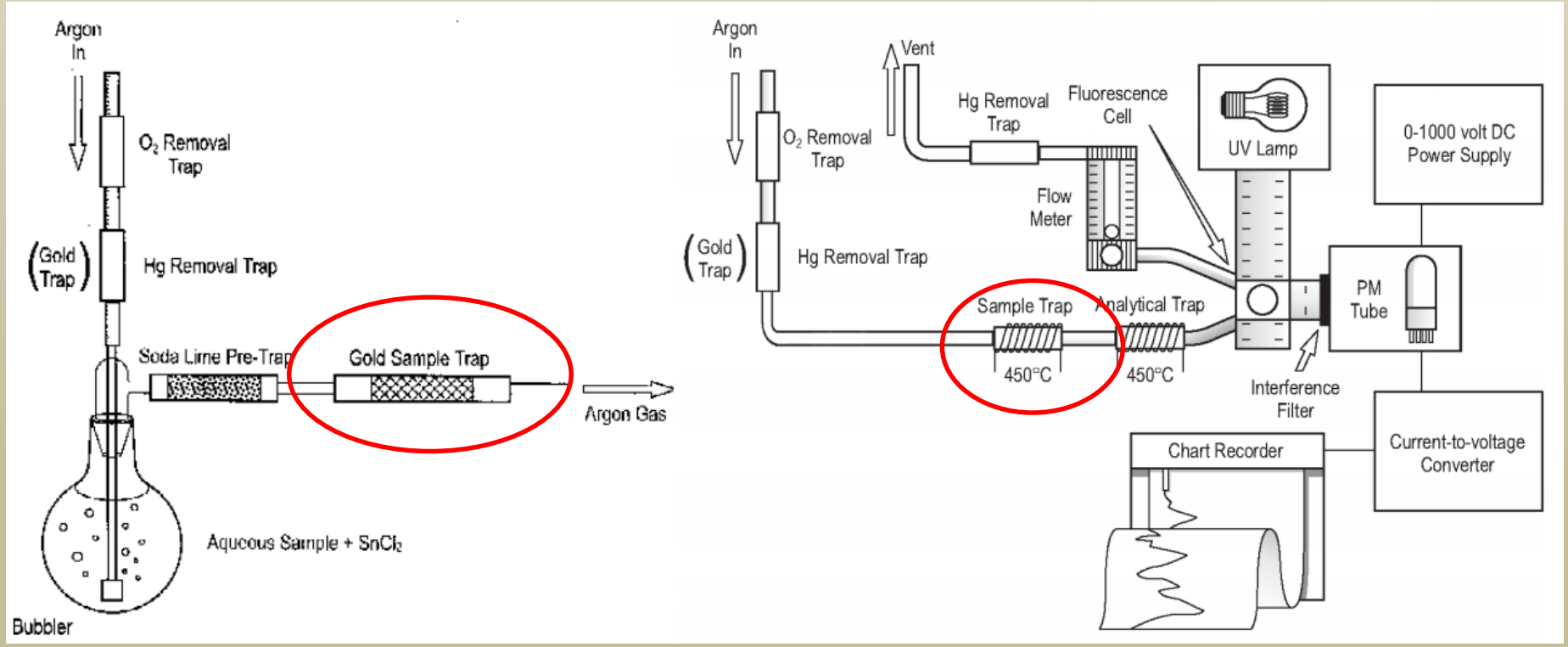
6. This Method is "performance based." The laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurements if all performance criteria are met.

7. Any modification of this Method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

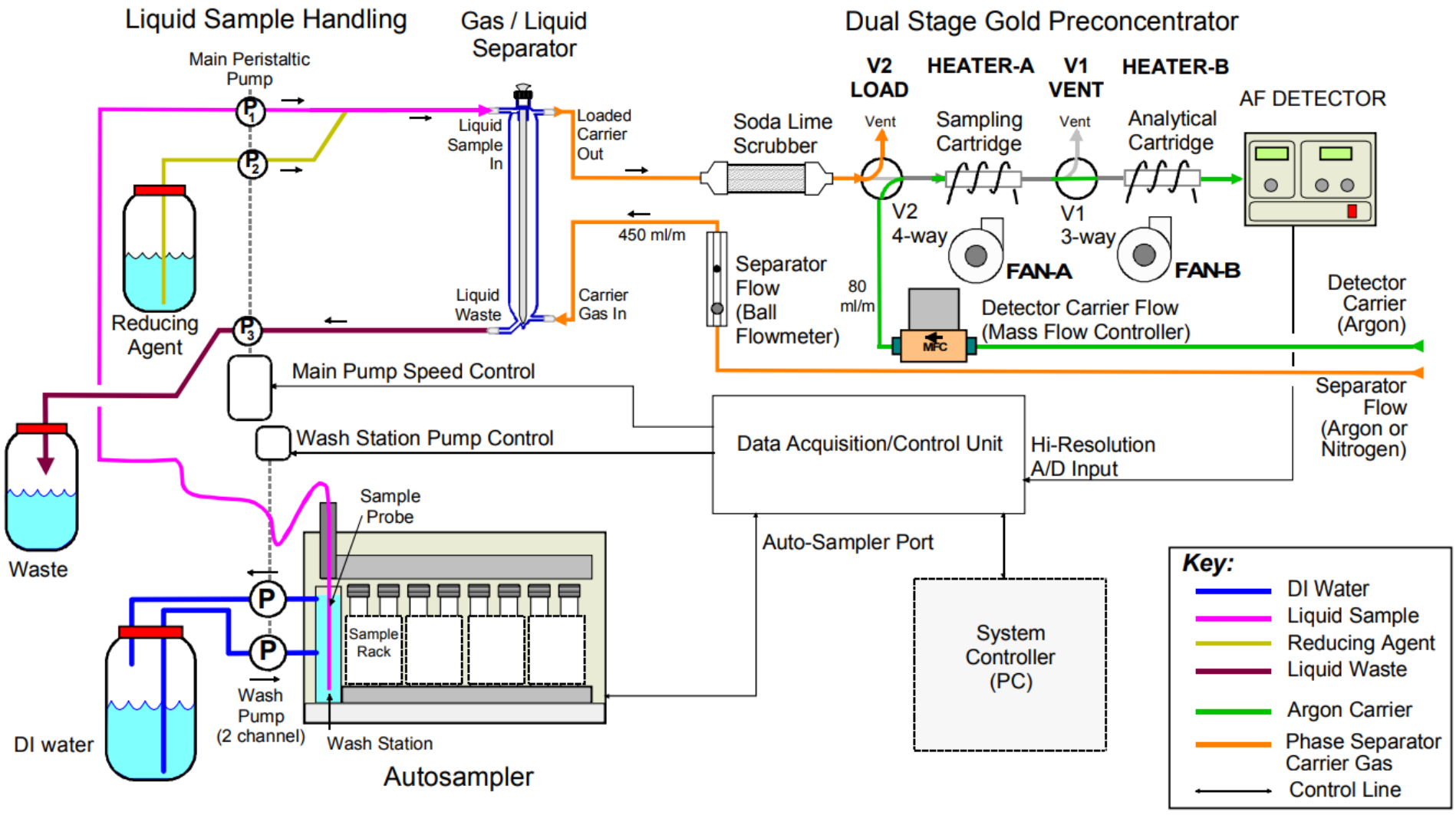
Scope and Application

8. This Method should be used only by analysts experienced in the use of CVAFS techniques and who are trained thoroughly in the sample handling and instrument techniques described in this Method. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedures.

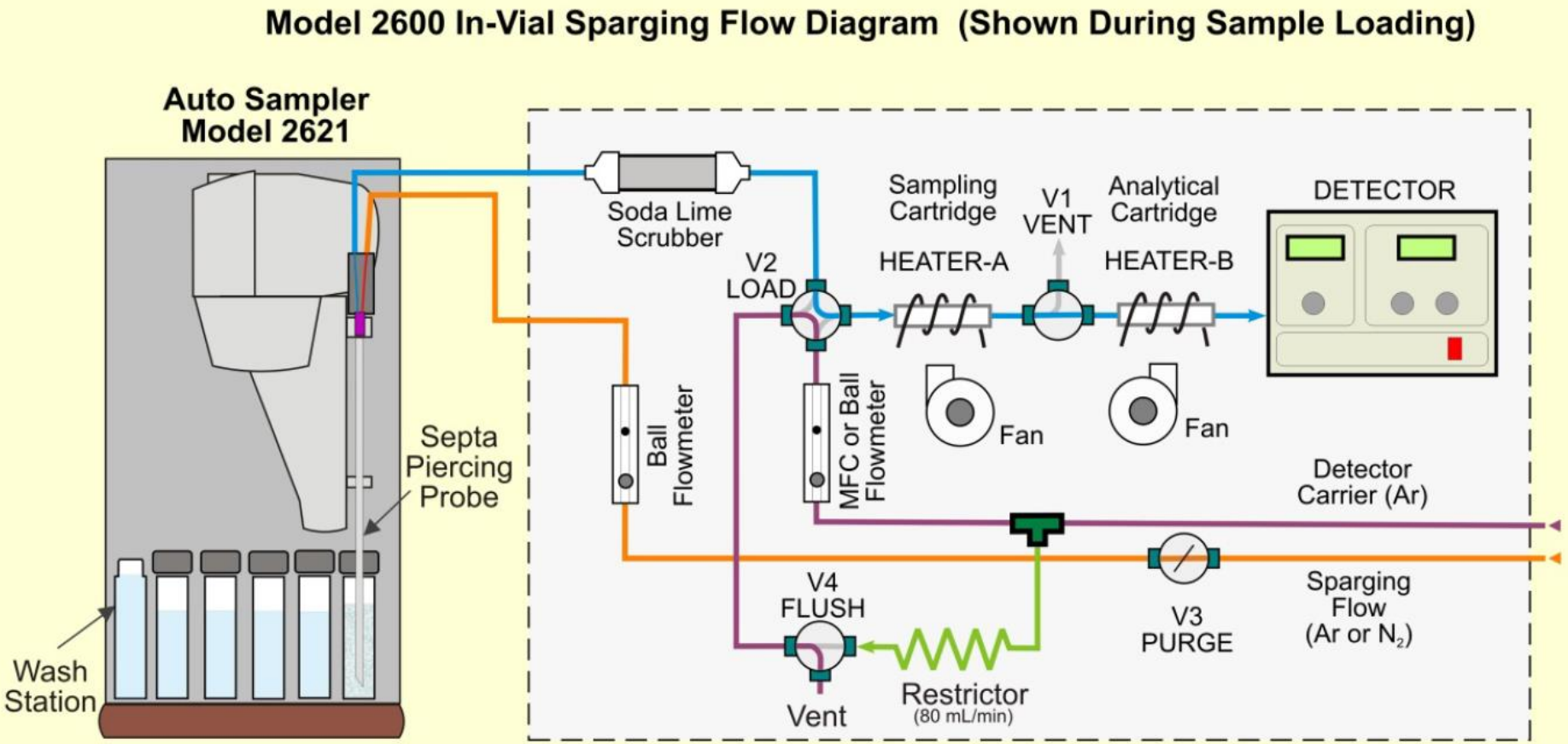
Schematic Diagram of the Bubbler, CVAFS system



Schematic Diagram of the Flow-Injection, CVAFS system



Schematic Diagram of the In-Vial Sparging, CVAFS system



Reagents and Standards

- Reagent water
  - 18 MΩ minimum, ultrapure deionized water
- Hydrochloric acid
  - trace-metal purified reagent-grade HCl containing less than 5 pg/mL Hg. The HCl should be analyzed for Hg before use.

Reagents and Standards

- Nitrogen (Grade 4.5) or Argon (Grade 5.0)
  - the purging gas that has been further purified by the removal of Hg using a gold-coated sand trap.

Reagents and Standards

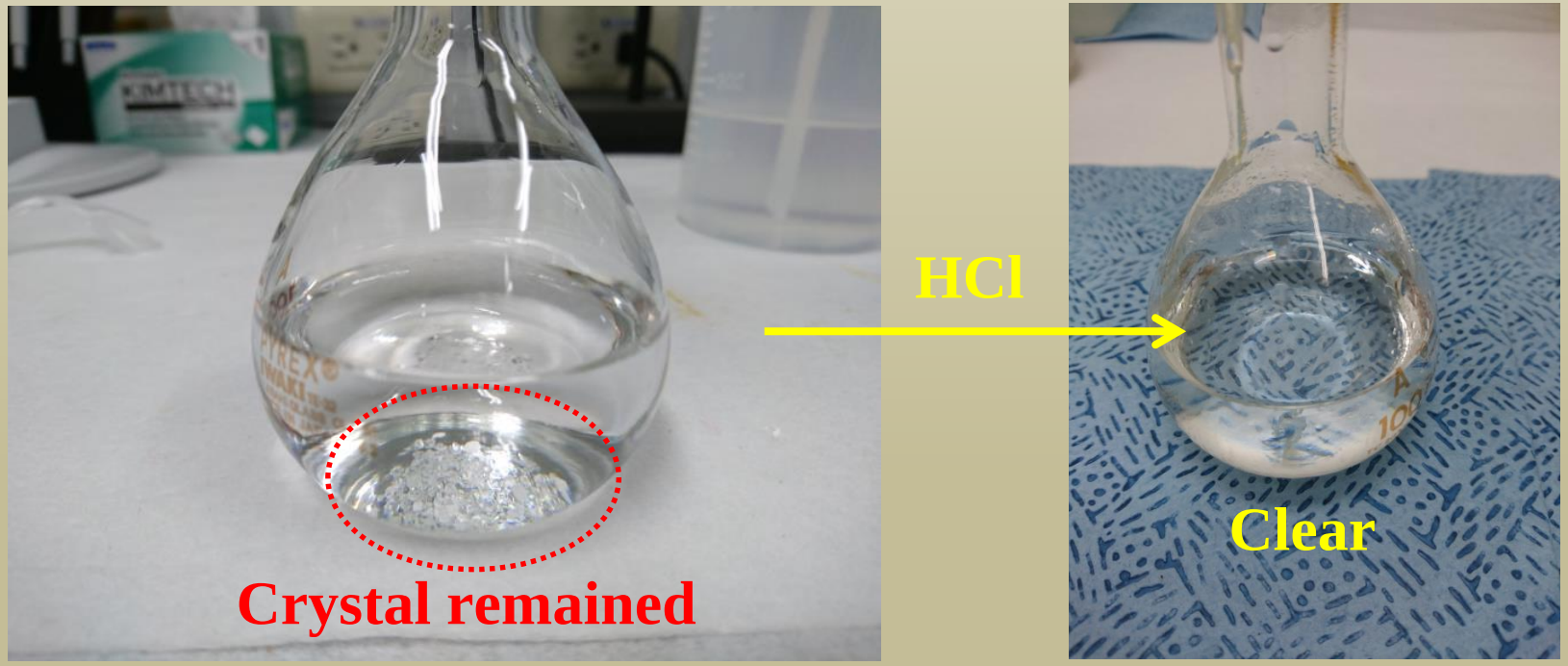
- Equipments
  - Personal protective equipment
  - Microbalance
  - Micropipette
  - Fume hood
  - Volumetric flask
  - Bubbler
  - Flowmeter
  - Perfluoroalkoxy(PFA) bottle

Reagents

- Stannous chloride ($SnCl_2$)

Reagents

- Stannous chloride ($SnCl_2$)
  - Bring 20 g of $SnCl_2 \cdot 2H_2O$ and 10 mL concentrated HCl to 100 mL with reagent water.

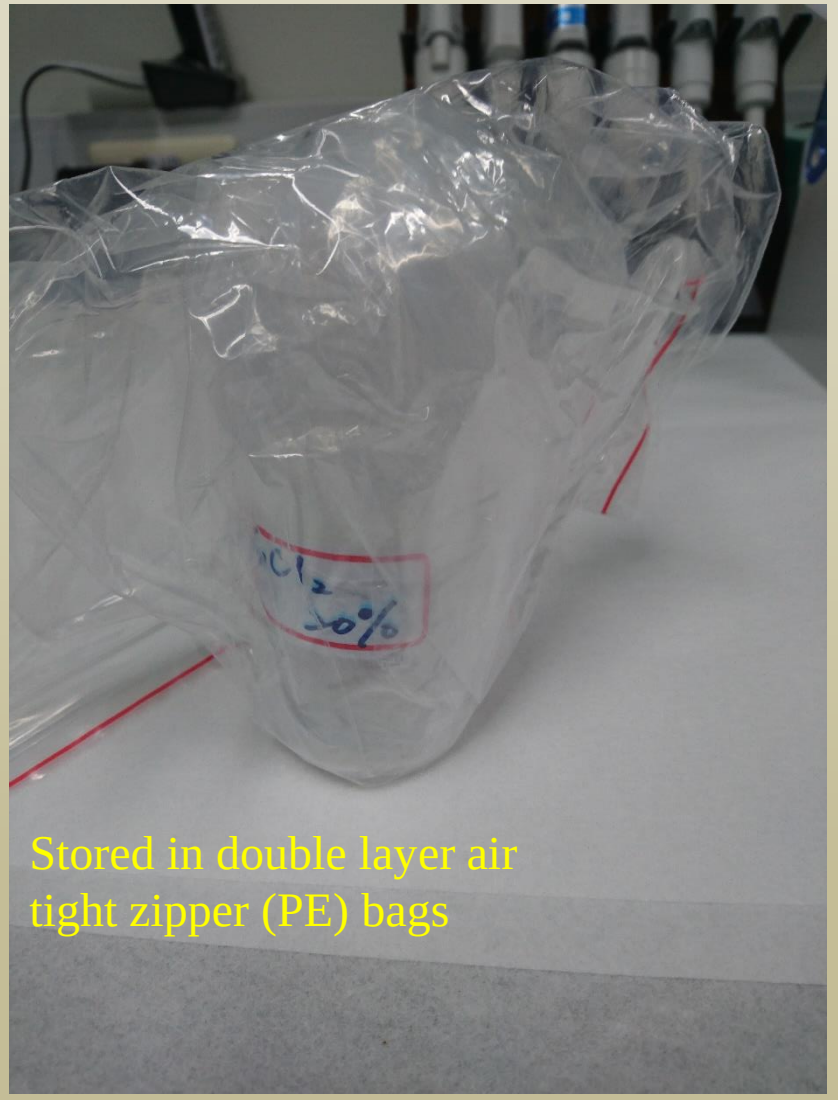


Reagents

- Stannous chloride ($SnCl_2$)
  - Purge overnight with mercury-free N_2 at 500 mL/min to remove all traces of Hg.

Reagents

- Stannous chloride ($SnCl_2$)
  - Store tightly capped.



Reagents

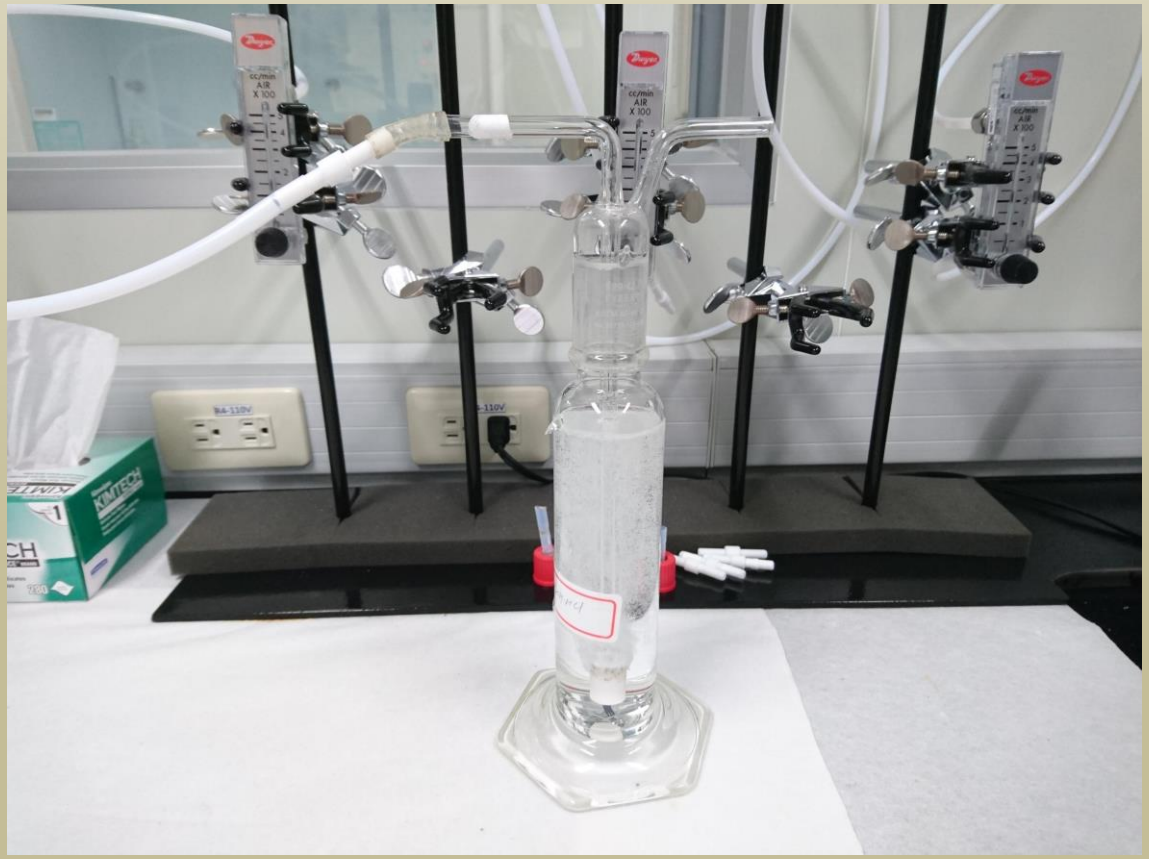
- Hydroxylamine hydrochloride (HH)

Reagents

- Hydroxylamine hydrochloride (HH)
  - Dissolve 30 g of $NH_2OH \cdot HCl$ in reagent water and bring to 100 mL.

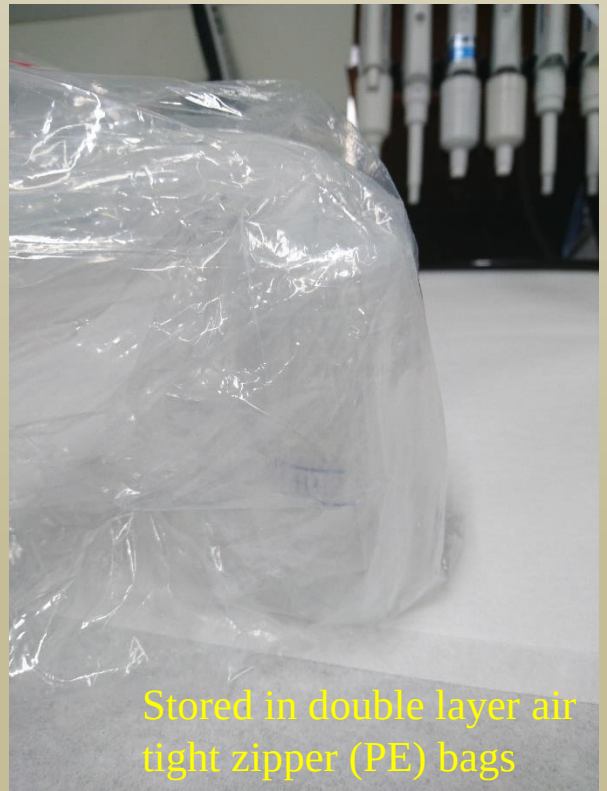
Reagents

- Hydroxylamine hydrochloride (HH)
  - purging overnight at 500 mL/min with Hg-free Ar



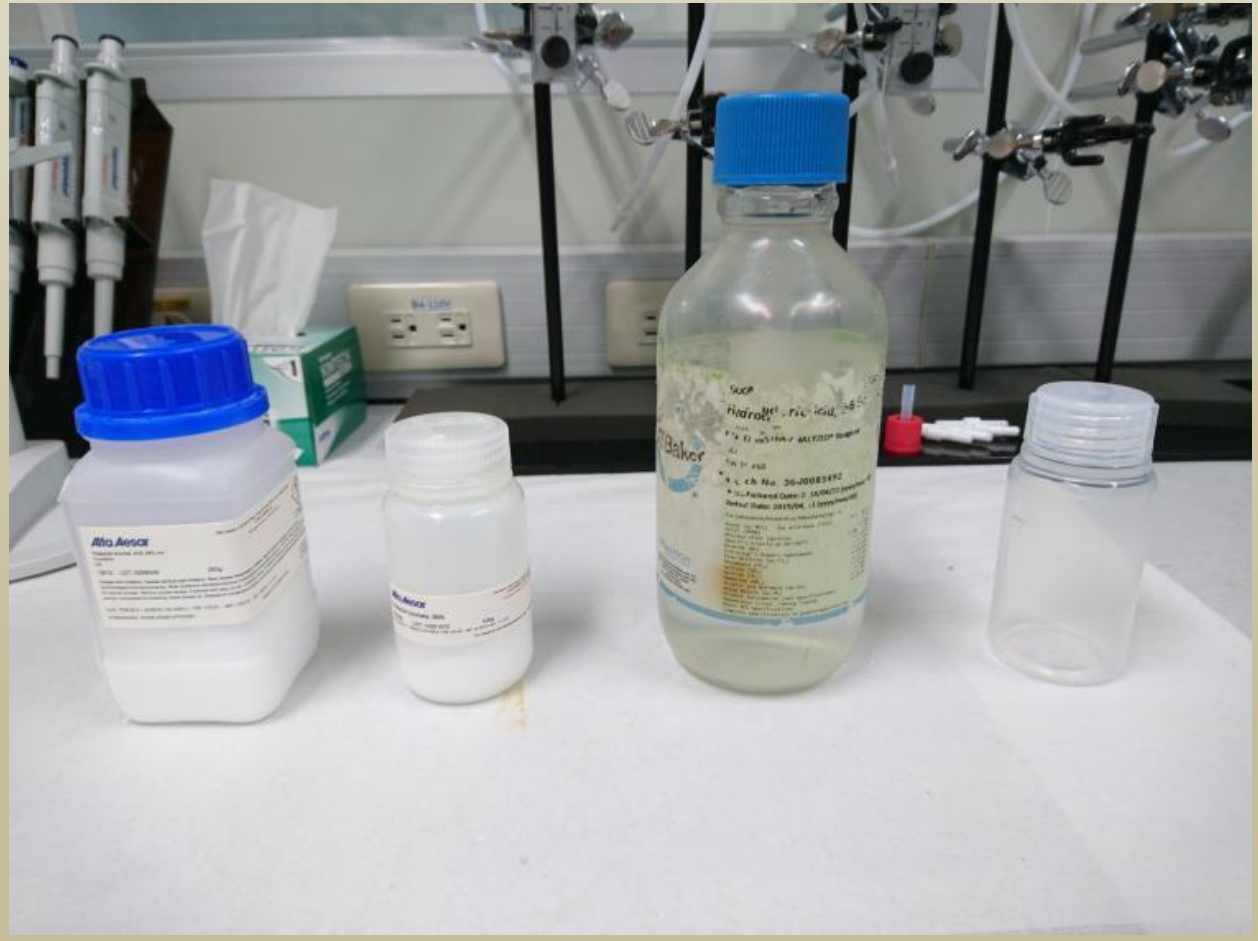
Reagents

- Hydroxylamine hydrochloride (HH)
  - This solution may be purified by the addition of 1.0 mL of $SnCl_2$ solution. (before purge)



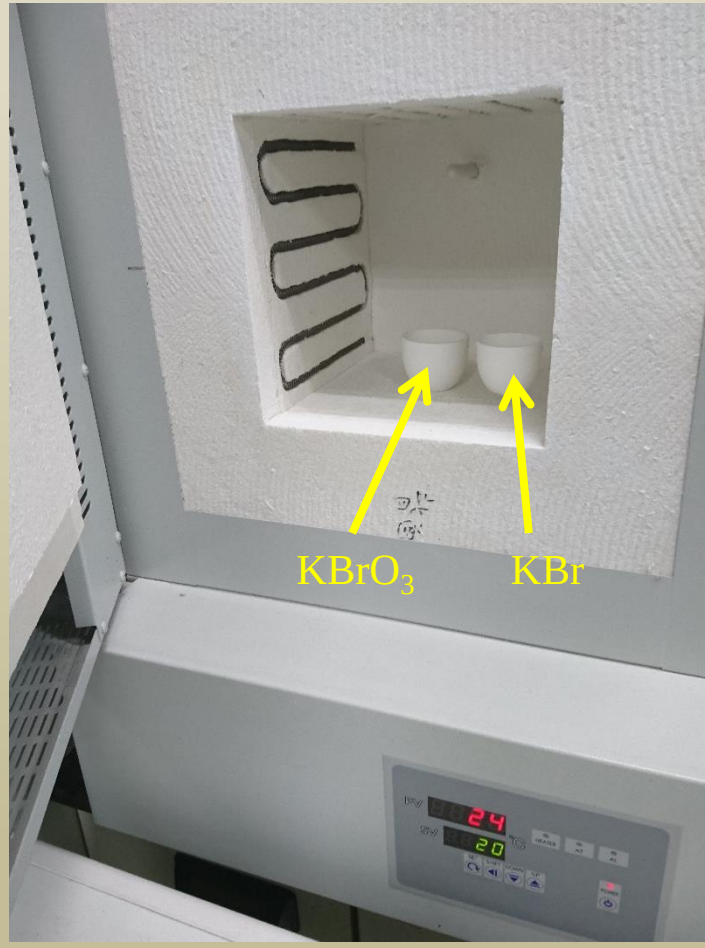
Reagents

- Bromine monochloride (BrCl)



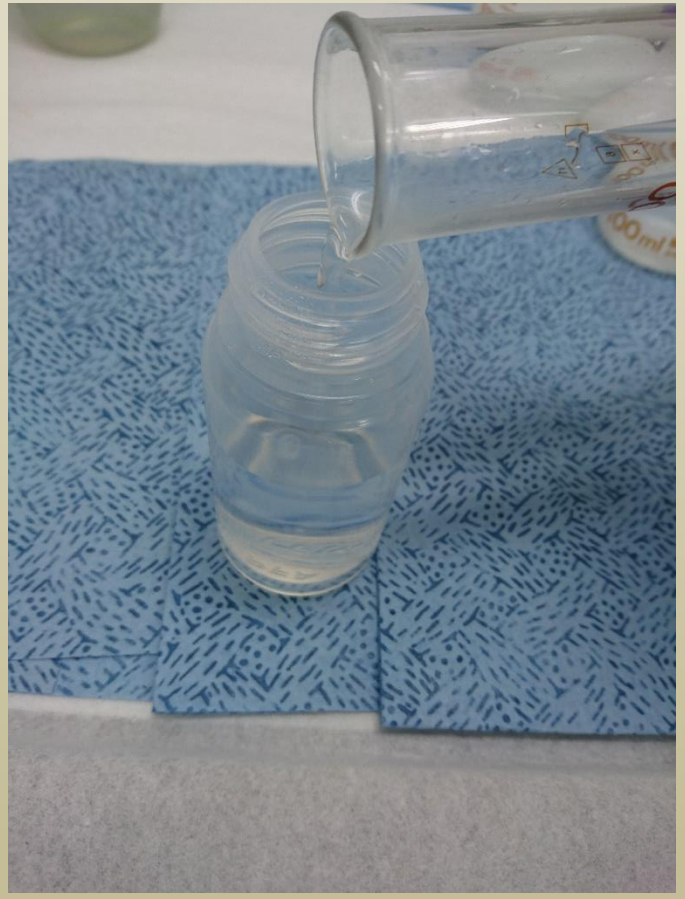
Reagents

- Bromine monochloride (BrCl)
  - Place approximately 2 g of $KBrO_3$ and KBr (reagnt grade) into two saparate weighting bottles. Heat in a mercury free oven at 200℃ for at least 8 hours.
  - This will reduce the amount of mercury in the raw materials



Reagents

- Bromine monochloride (BrCl)
  - In a fume hood, dissolve 1.1 g of reagent grade KBr in 100 mL of low-Hg HCl. Place a clean magnetic stir bar in the bottle and stir for approximately 1 h in the fume hood.



Reagents

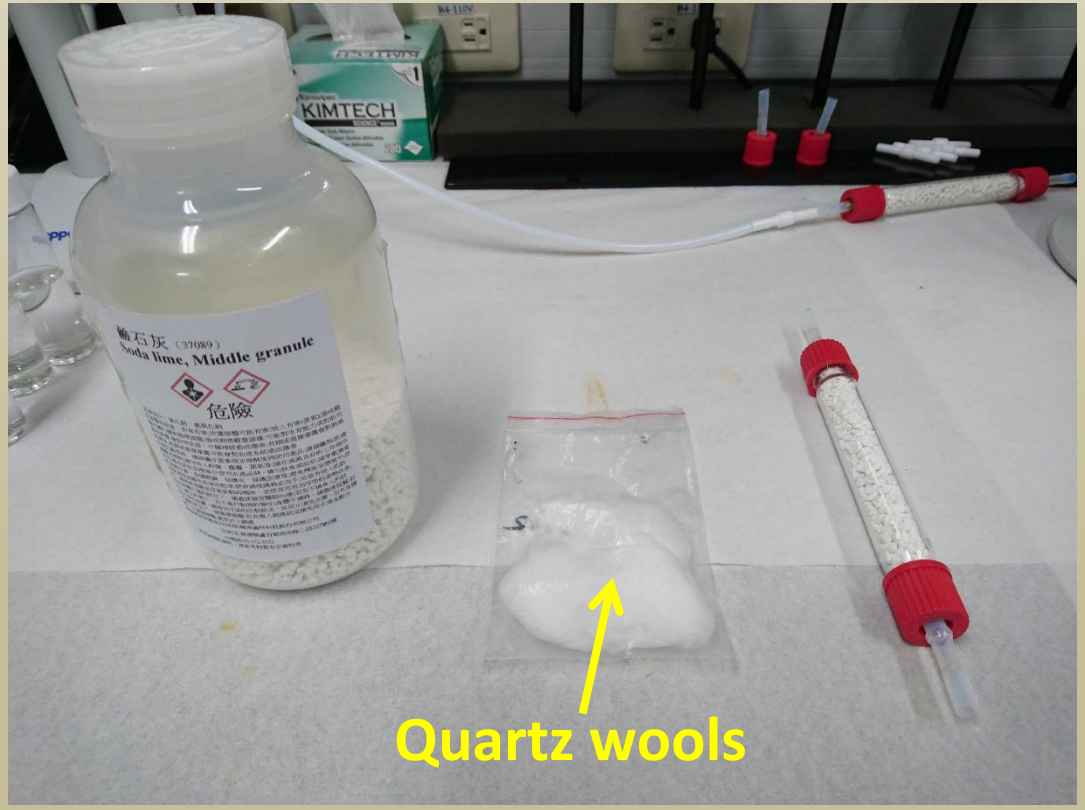
- Bromine monochloride (BrCl)
  - Slowly add 1.5 g reagent grade $KBrO_3$ to the acid while stirring. When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange.

Reagents

- Bromine monochloride (BrCl)
  - Loosely cap the bottle, and allow to stir another hour before tightening the lid.

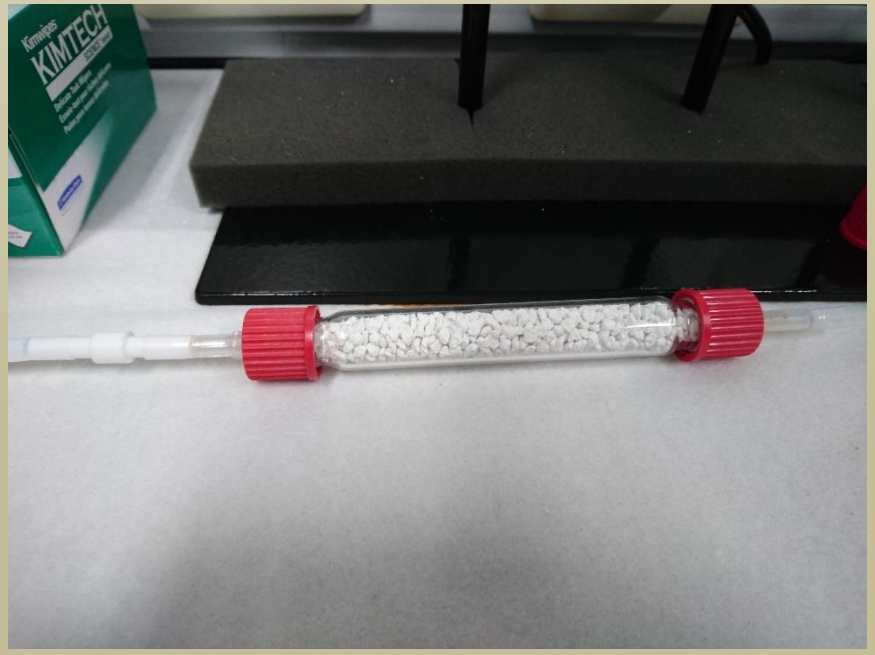
Reagents

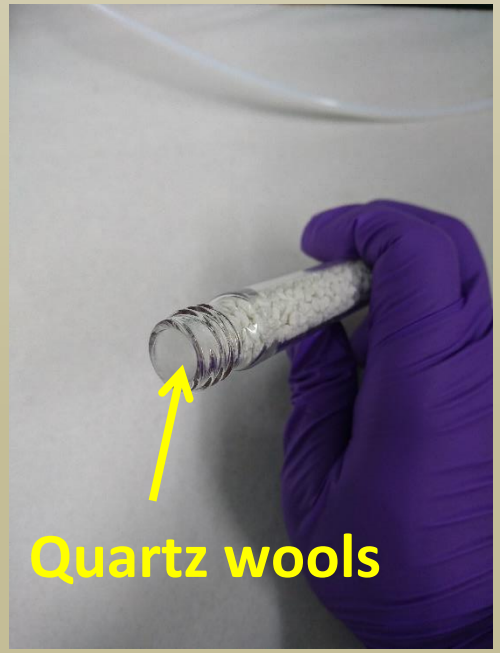
- Sodalime
  - As a drying agent
  - Acid gas scrubber
  - Changed daily



Reagents

- Sodalime
  - Empty and flush thoroughly the trap with DIW
  - Dry and refill the new sodalime
  - Purge the trap overnight





Standards

- Stock mercury standard
  - NIST-certified 10,000 ppm aqueous Hg solution (NIST-3133)
  - Certified 1,000 ppm standard (Certified reference material)

Standards

TraceCERT®
Traceable Certified Reference Materials

Fluka Analytical

Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO Guide 34

This certificate is designed in accordance with ISO Guide 31[1].

Object of certification:	**Mercury standard for AAS**
Product No.:	16482
Lot:	BCBN7650V
Composition:	Mercury metal (pure material) in 12% HNO_3 (prepared from HNO_3 *Trace*SELECT® and water *Trace*SELECT® Ultra, 18.2 MΩ cm, 0.22 µm filtered)
Density at 20°C:	ρ = 1068 kg m^{-3} $u_c(\rho)$ = 0.5 kg m^{-3}
Intended use:	Calibration of AAS, ICP, spectrophotometry or any other analytical technique.
Storing and handling:	This reference material shall be stored between 5 °C and 30 °C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.
Expiry date:	AUG 2017
Bottle opening date:	2015.12.16

Certified value traceable to SI unit kg and uncertainty according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]		
Constituent	Certified value at 20°C and expanded uncertainty [$U = k u_c$, k = 2]	
Mercury	**937 mg kg^{-1} ± 4 mg kg^{-1}**	**1'001 mg L^{-1} ± 4 mg L^{-1}**

1. Concept of Certification and Traceability Statement

To guarantee top reliability of the values for this *Trace*CERT® certified reference material three independent procedures were followed. The values have to agree in the range of their uncertainties, but the impurity corrected value from the gravimetric preparation has been chosen as certified value [4].

1. Gravimetric preparation using pure materials is a practical realization of concentration units, through conversion of masses and mole fraction to mass fraction [4]. If the purity of the materials is demonstrated and if contamination and loss of material is strictly prevented this approach allows highest accuracy and small uncertainties. The certified value of *Trace*CERT® reference materials is based on this approach and directly traceable to the SI unit kilogram.

   Therefore comprehensively characterized materials of highest purity are used (see paragraph 2). All balances are certified by DKD and calibrated with OIML Class E2 (up to 12 kg) and F2 (up to 64 kg) weights. The bulk solution was homogenized by overhead tumbling in a PVDF container for at least 6 hours. A peristaltic pump with perfluorinated polymer tubings was used for bottling.

2. The starting material is measured against a certified reference material (i.e. NIST, BAM or EMPA) followed by gravimetric preparation using balances calibrated with SI-traceable weights. Consequently the value calculated by this unbroken chain of comparisons is traceable to the reference to which the starting material is compared.

3. Whenever applicable the bottled *Trace*CERT® calibration solution is compared to a second reference (e.g. from NIST, BAM or EMPA) which is independent from the first reference.

Sigma-Aldrich Production GmbH, Industriestrasse 25, 9471 Buchs/Switzerland, Tel +41-81-755-2511, Fax +41-81-756-5449, e-mail: fluka@sial.com

SIGMA-ALDRICH®

order : 2015/11/5
open : 2015/12/17

Certificate of Analysis

Certipur® Certified Reference Material

Producer:	**Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany.**
Accreditation:	Merck KGaA is accredited as calibration Laboratory according to **DIN EN ISO/IEC 17025.**
Description of CRM:	**Mercury standard solution 1000 mg/l Hg**
Ord. No.:	1.70226.0100
Lot No.:	HC55470426
Composition:	$Hg(NO_3)_2$ in HNO_3 Suprapur® 2 mol/l
Certified value and uncertainty:	**947 mg/kg Hg ± 7 mg/kg Hg**
	Mass fraction (w/w) ± expanded measurement uncertainty
	The expanded measurement uncertainty U is calculated as $U = k \cdot u_{characterisation}$, where k = 2 is the coverage factor for a 95% coverage probability and $u_{characterisation}$ is the combined measurement uncertainty in accordance to DIN EN ISO/IEC 17025.
Density:	The density of the standard solution is 1.0559 g/cm^3 at 20°C.
Calculated mass concentration:	**1000 mg/l Hg**
Method of Analysis:	Inductively coupled plasma optical emission spectrometry (ICP-OES).
Traceability:	This reference material has been measured applying high precision ICP-OES and is directly traceable to the corresponding **NIST SRM® 3133, lot 061204.** *NIST: National Institute of Standards and Technology, Gaithersburg, USA.*
Storage:	Store at +15°C to +25°C tightly closed in the original container.
Application and correct use:	This reference material is intended for use as calibration standard for atomic absorption spectrometry, spectrophotometry and other analytical techniques. Shake well before use and never pipet directly from the original container.
Date of release:	2015/06/15
Minimum shelf life:	2018/05/31

A. Yildirim

Dipl.-Ing. Ayfer Yildirim
(Laboratory Manager)

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EMD Millipore Corp. · 290 Concord Road, Billerica, MA 01821, USA: +1-781-533-6000

Standards

- Certified Reference Material (CRM)
  - Certificate of Analysis (CoA)
  - Product/Lot No.
  - Certified value and uncertainty
  - Traceability
  - Storage
  - Expiry date

order : 2015/11/5
open : 2015/12/19

Certificate of Analysis

Certipur® Certified Reference Material

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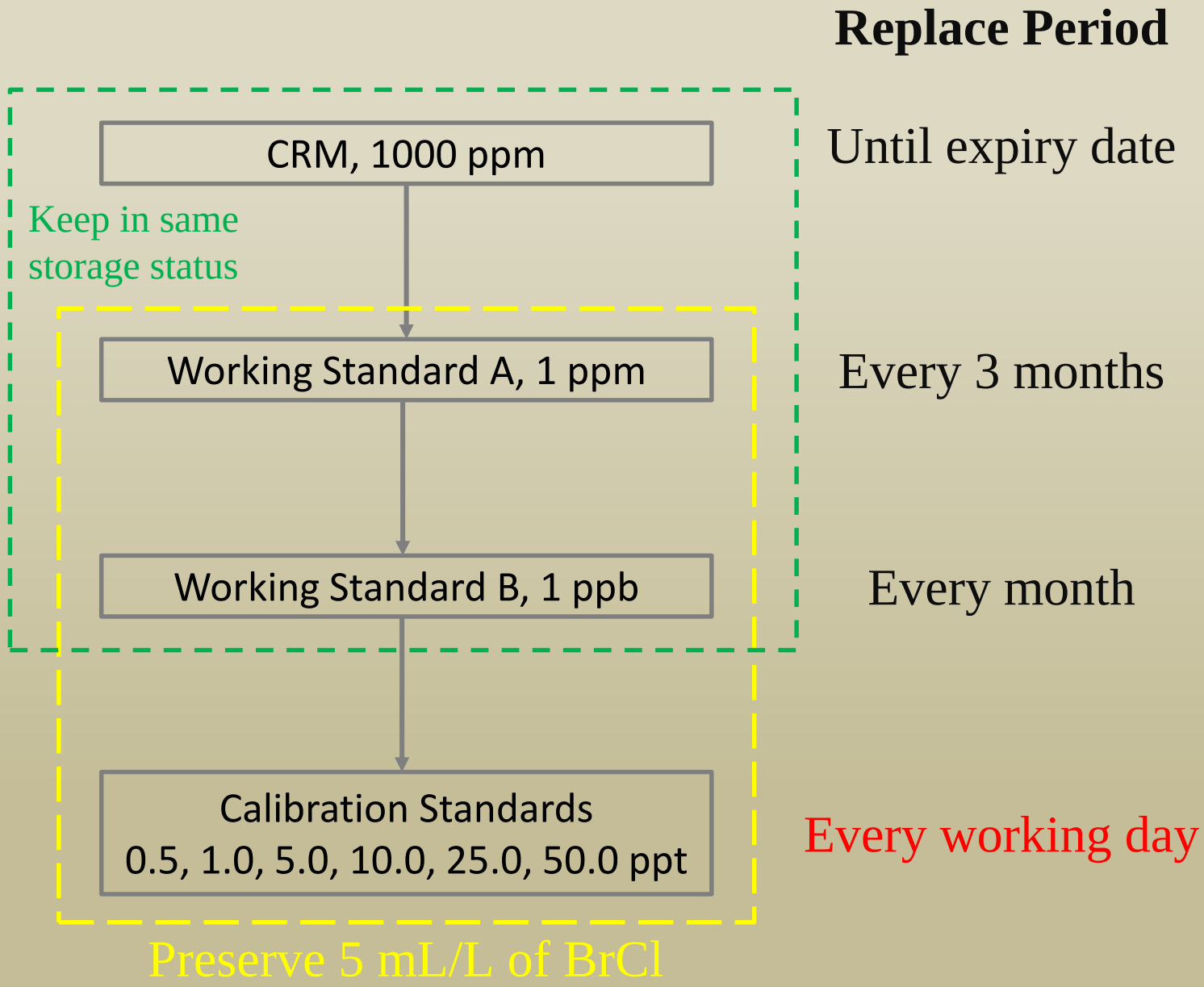
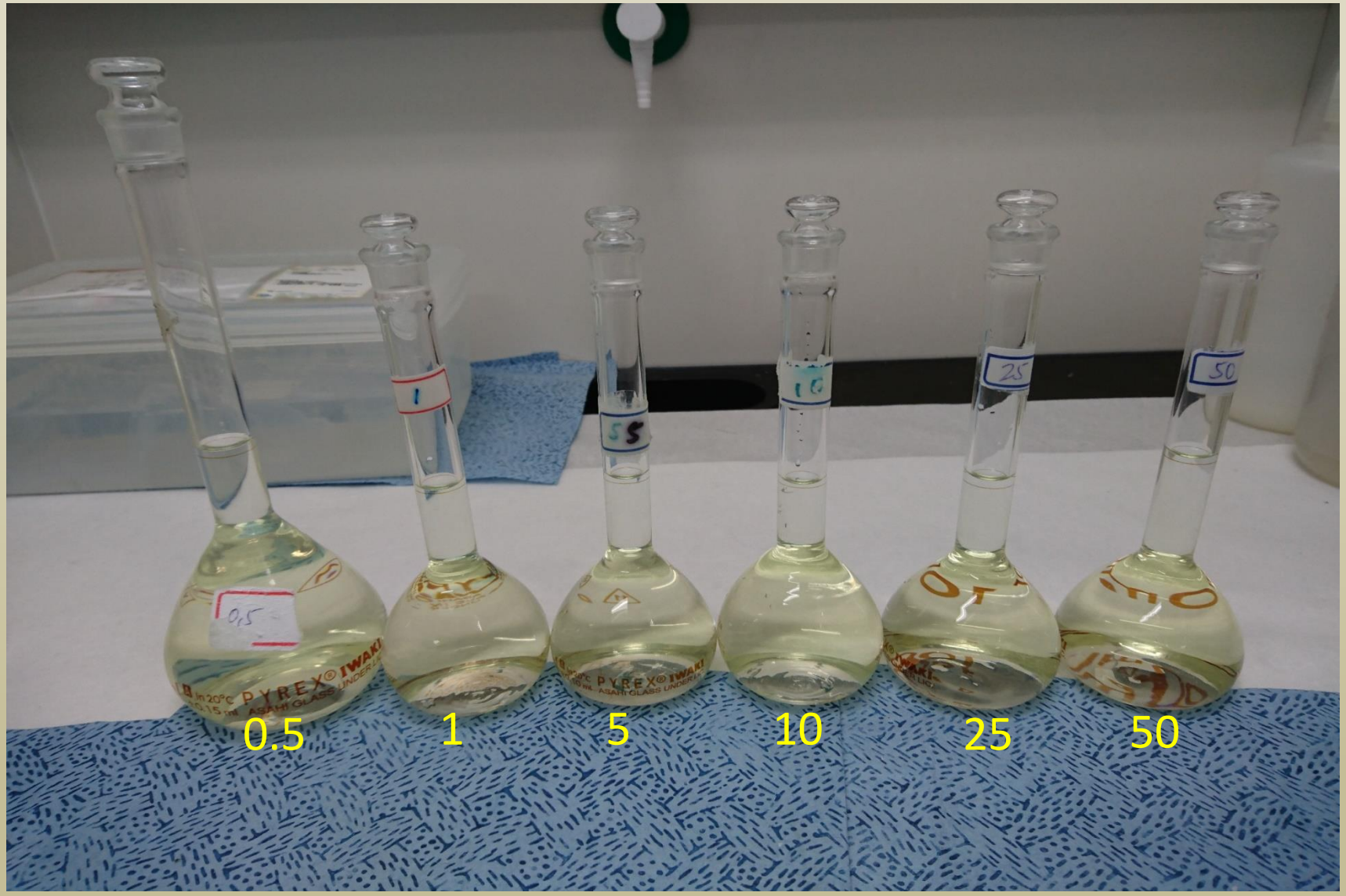
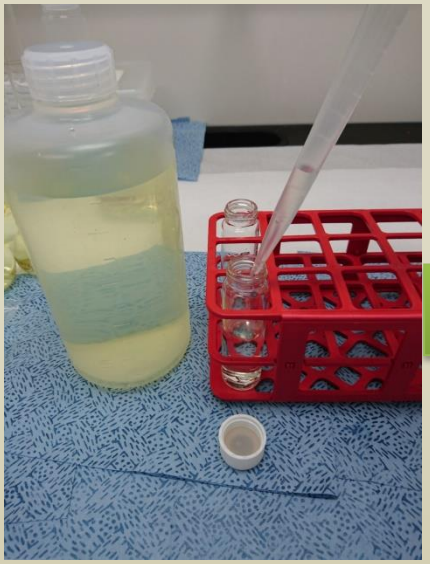
Standards


Replace Period
CRM, 1000 ppm
Until expiry date
Keep in same storage status
Working Standard A, 1 ppm
Every 3 months
Working Standard B, 1 ppb
Every month
Calibration Standards
0.5, 1.0, 5.0, 10.0, 25.0, 50.0 ppt
Every working day
Preserve 5 mL/L of BrCl

Calibration curve

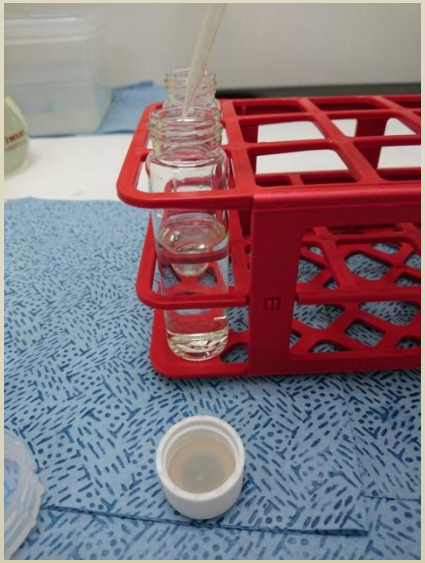


Sample analysis

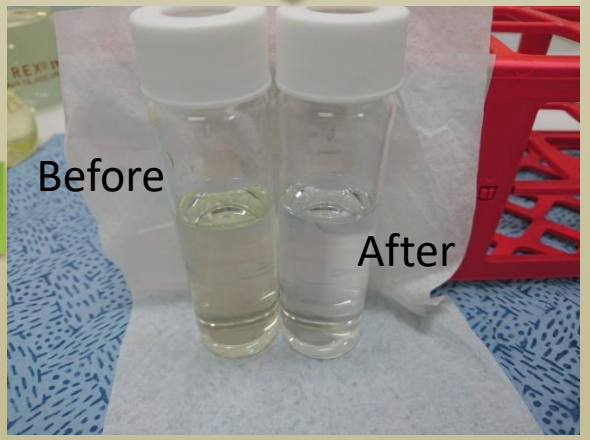


Take 25 mL of sample or standards

Add 0.03 mL HH

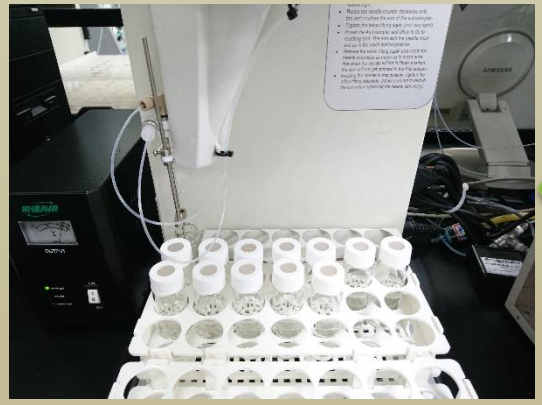


Loose the cap, wait 20 min



The solution should be colorless

Add 0.06 mL SnCl2 and shake



Put the vial on the auto sampler and run

Waste Management

Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste

Samples after analysis must be stored in the hazardous waste tank

Vials Cleaning

Open-top white polypropylene cap

- Clean by DIW

PTFE lined silicone septum

- Use only once

Vials

- Follow the same acid clean procedures
- Heated 30 mins at 180℃. Saparated oven
- 2% BrCl solution might needed ?
- Filled with DIW as blank (check in each cleaning batch, randomly)

Da-Wei Lin
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Https://apmmn.org

Asia Pacific Mercury Monitoring Network

Center for Environmental
Monitoring and Technology
National Central University