

## **Determination of mercury mass concentration in natural water by means of cold-vapor technique**

The is the formal instruction «Method for mercury mass concentration determination in the samples of natural, drinking and refined waste water by means of cold-vapor technique using RA-915 Mercury Analyzer and RP 91 attachment».

The guidelines to this laboratory work is performed according with this instruction.

### 1.0 Scope and application

Method is based on the cold-vapor technique for mercury mass concentration determination in the samples of natural (surface, ground, sea and rain) water, drinking and refined waste water and meets the parameters of ISO/DIS Method 17852.

Samples of natural and waste water must be pre-treated using bromide-bromate mineralization procedure.

### 2.0 Description of the installation

An advanced **mercury analyzer RA-915+** is a unique all-purpose high sensitivity analytical instrument for the environmental monitoring, especially for the real time detection of mercury vapor in air, mercury detection in water, natural and stack gases, oil and condensate, solid and sediments, foodstuff and so on.



**RA-915+ Mercury Analyzer** is a portable multifunctional atomic absorption spectrometer with Zeeman background correction, which eliminates the effect of interfering impurities. It is the only high sensitivity and selectivity instrument that does not require gold amalgam pre-concentration and subsequent regeneration steps. This enables the user to conduct real time monitoring and detection of a mercury vapor. Being combined with an RP-91 Cold Vapor accessory for water testing, the instrument is designed to determine mercury content in natural

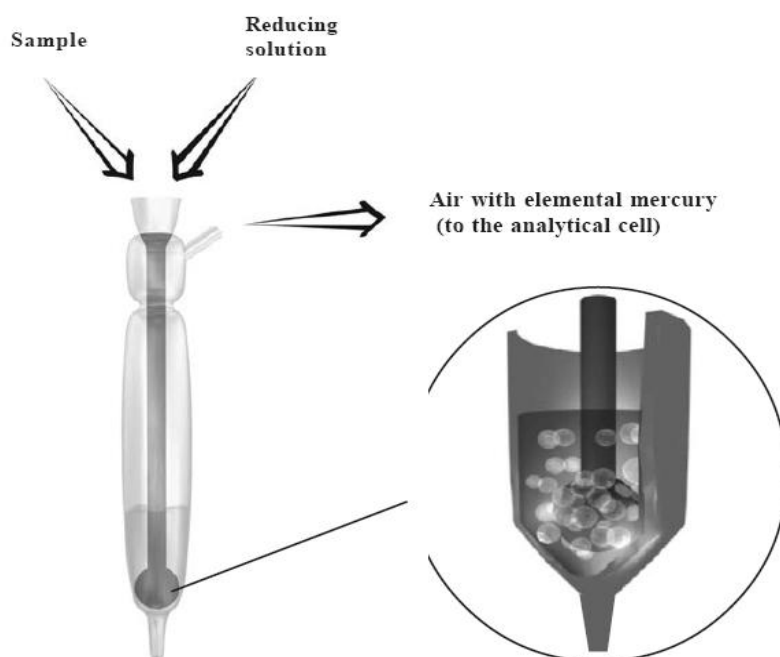
(surface, ground, sea and rain) water, drinking and refined waste water . The mercury detection limits being as low as 0.5 ng/l in water.

#### Method summary

The principle of operation of the RP-91 attachment is based on the reduction of Hg(II) to the atomic state using a reducing solution and then transporting mercury atoms into an analytical cell by an air flow (the "cold vapor" technique).



The mercury concentration is then measured by the RA-915+ atomic absorption mercury analyzer. The operational principle of a system with the RP-91 attachment for analysis of samples by the "cold vapor" technique is shown below. The reducing solution and the sample being analyzed are placed into the bubbler. The elemental mercury, which is formed during continuous air pumping through the bubblers, reach the analytical cell of the RA-915+ analyzer, where the mercury atoms are detected.



The detection limit of cold-vapor technique using RA-915 Mercury Analyzer and RP 91 attachment is 0.5 ng/L (0.5 ppb). The sensitivity of the method depends on the selected operating conditions. Typical working range is 0.01-1.00 mkg/L with bromide-bromate mineralization of the samples.

### 3.0 Apparatus and materials

For the water sample analysis it is strongly recommended to use software (CD with “RA-915P” software is included in standard package).

For installation of “RA-915P” software, PC is needed with minimal system requirements:

Pentium® 200 MHz, 128 Mb RAM, free COM-port, CD-ROM, minimum 30MB free disk space, monitor, mouse, printer

Microsoft Windows® 98/NT/2000/XP/Vista

The analyzer and the PC should be supplied from the same phase. To achieve that, connect the RA-915 to the same line-filter (of “Pilot-Pro” type, for instance) to which the PC is connected. A cable for the instrument connection to PC is included to the delivery set.

The work place for RA-915 Mercury Analyzer and a PC installation is a laboratory bench, equipped with electrical outlet and lighting. It’s desirable to have hood near the table for work with the attachments.

The following is the list of reagents, measuring equipment, materials which are necessary for the total mercury determination in liquid samples using RA-915 with RP-91 attachment.

FLUKA and MERCK catalog numbers are given for reference, to show the needed reagents grade. In “comments” the MINIMUM quantity of glassware and reagents required for installation or occasional (from time to time) analysis is given.

	Comments
Volumetric flasks, 2-100-2, 2-50-2, 2-25-2 accuracy rating	
Laboratory balance 2-accuracy rating	
Volumetric pipettes (graduated), 2-accuracy rating, 1, 2, 5, 10 ml or micropipette systems with an assortment of metal-free, disposable pipette tips	1 ml – 6 pcs, 2 ml – 3 pcs, 5 ml – 4 pcs, 10 ml – 2 pcs
Volumetric pipettes with one mark, 2-accuracy rating, 10 and 20 ml	2 pcs
Volumetric cylinder 100 ml	4 pcs
Distilled water.	ISO 3696 grade 1
Stannum dichloride dihydrate (Fluka 96528)	250 g
Sulfuric acid (d - 1.83 g/cm <sup>3</sup> ) chemically pure (for washing glassware)	0.5 L
Nitric acid (d - 1.37 g/cm <sup>3</sup> ) super pure	0.7 L
Potassium dichromate (K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ) (chemical pure Fluka 60188)	0.05 kg
Caustic soda, pure (tablets) NaOH (Fluka 71690)	1 kg
Hydrochloric Acid super pure «MERCK K33245186 420»	1 L
Hydroxylamine hydrochloride	
Silicone oil	0.01 L
Potassium bromide super pure	0.05 kg
Potassium bromate chemically pure	0.05 kg
Heat-resistant beaker 500 and 1000 ml	
Erlenmeyer flask 200 (250) ml	
Beakers 50 and 100 ml	50ml - 5pcs, 100 ml – 2 pcs
Water bath	
Electric hotplate	
Mercury Ions Stock Standard (1 g/L)	

#### 4.0 Reagents and Standarts

##### 4.1 Chromic mixture

10 g portion of the potassium dichromate ( $K_2Cr_2O_7$ ) should be carefully dissolved in 100 ml of concentrated sulfuric acid ( $d=1,83\text{ g/cm}^3$ ). Some residue of the initial potassium dichromate is allowed. Chromic mixture should be kept in dark glass vessel and can be used for 3 months.

#### 4.2 Potassium dichromate ( $K_2Cr_2O_7$ ) solution (4 %)

Place 4 g portion of the potassium dichromate ( $K_2Cr_2O_7$ ) in 100 ml flask and dissolve it in 96 ml of the distilled water. The resulting solution can be kept in the dark place for 3 months.

#### 4.3 Potassium dichromate ( $K_2Cr_2O_7$ ) solution (0.05 g/L) for sample preserving

In the thermostable beaker place 15 ml of the distilled water and then carefully add with stirring 15 ml of the concentrated nitric acid ( $d=1.37\text{ g/ml}$ ). After cooling transfer the solution to the flask (100 ml capacity), add 1.25 ml of the potassium dichromate solution (4.2) and dilute the mixture up to the mark. The solution can be kept in the dark place for 1 months.

#### 4.4 Dilution solution

In the thermostable beaker place 500-600 ml of the distilled water and then carefully add with stirring 50 ml of the concentrated nitric acid ( $d=1.37\text{ g/ml}$ ). After cooling transfer the solution to the flask (1 L capacity), add 5 ml of the potassium dichromate solution (4.2) and dilute the mixture up to the mark. The solution can be kept in the dark place for 3 months.

#### 4.5 Hydrochloric acid solution (4 Mole/L)

Add 167 ml of concentrated hydrochloric acid to 200 ml of water in a heat-resistant glass beaker (volume 500 ml). After cooling transfer the solution to the 500 ml volumetric flask and dilute the solution to 500 ml.

#### 4.6 Tin(II) chloride solution ( $SnCl_2 \cdot 2H_2O$ , 2 %)

Place 40 ml of distilled water and 20 ml concentrated hydrochloric acid) in a 200-250 ml Erlenmeyer flask and gradually add 4 g of tin(II) chloride while carefully heating the flask (boiling should be avoided) until all the precipitate dissolves. After cooling dilute the resulting solution with distilled water to 200 ml. The solution can be kept in a fridge for 3 days.

#### 4.7 Potassium bromate solution ( $KBrO_3$ , 0.033 Mole/L)

Place 0.556 g of potassium bromate in a 100 ml volumetric flask and dissolve it in 50 ml of distilled water. Then bring the solution up to the mark. The solution can be kept in the dark place for 1 week.

#### 4.8 Potassium bromide solution ( $KBr$ , 0.2 Mole/L)

Place 2.38 g of potassium bromate in a 100 ml volumetric flask and dissolve it in 50 ml of distilled water. Then bring the solution up to the mark. The solution can be kept in the dark place for 1 month.

#### 4.9 Bromide-bromate mixture solution

Mix the solutions 4.7 and 4.8 in the proportion 1:1. Freshly prepared mixture should be used.

#### 4.10 Hydroxyl amine hydrochloride solution (100 g/L)

Place 2.5 g of hydroxyl amine hydrochloride in a 25 ml volumetric flask and dissolve it in 10-15 ml of distilled water, then bring it up to the mark. Freshly prepared solution should be used.

#### 4.11 Sodium hydroxide (NaOH, 30 %)

Place 70 ml of distilled water in a heat-resistant glass beaker and add carefully with stirring 30 g of NaOH. After dissolving and cooling transfer the solution to the polyethylene or PTFE vessel. The solution can be kept for 1 month.

Add this solution to the second bubbler in the multipath operating mode to prevent acid vapor penetration to the multipath cell.

#### 4.12 Mercury standard solutions

Standard sample of mercury ions is used ( $C(\text{Hg})=1.0 \text{ g/L}$ ) for all preparations.

##### 4.12.1 Mercury stock solution $C(\text{Hg})=10.0 \text{ mg/L}$

Place 30 ml of the dilution solution (4.4) in a 200 ml volumetric flask. Then place 2 ml of a standard sample of mercury ions solution ( $C(\text{Hg})=1.0 \text{ g/L}$ ). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. The solution can be kept in a fridge for 6 months.

##### 4.12.2 Mercury stock solution $C(\text{Hg})=100 \text{ mg/L}$

Place 30 ml of the dilution solution (4.4) in a 100 ml volumetric flask. Then place 1 ml of a mercury stock solution  $C(\text{Hg})=10.0 \text{ g/L}$  (4.12.1). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. The solution can be kept in a fridge for 3 months.

##### 4.12.3 Mercury stock solution $C(\text{Hg})=1.0 \text{ mg/L}$

Place 30 ml of the dilution solution (4.4) in a 100 ml volumetric flask. Then place 1 ml of a mercury stock solution  $C(\text{Hg})=100 \text{ mg/L}$  (4.12.2). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. The solution can be kept in a fridge for 1 week.

##### 4.12.4 Mercury stock solution $C(\text{Hg})=0.10 \text{ mg/L}$

Place 30 ml of the dilution solution (4.4) in a 100 ml volumetric flask. Then place 10 ml of a mercury stock solution  $C(\text{Hg})=1.0 \text{ mg/L}$  (4.12.4). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. This solution should be used freshly prepared.

#### 4.12.5 Mercury stock solution $C(\text{Hg})=0.05 \text{ mkg/L}$

Place 30 ml of the dilution solution (4.4) in a 100 ml volumetric flask. Then place 5 ml of a mercury stock solution  $C(\text{Hg})=1.0 \text{ mkg/L}$  (4.12.4). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. This solution should be used freshly prepared.

#### 4.12.6 Mercury stock solution $C(\text{Hg})=0.01 \text{ mkg/L}$

Place 30 ml of the dilution solution (4.4) in a 50 ml volumetric flask. Then place 0.5 ml of a mercury stock solution  $C(\text{Hg})=1.0 \text{ mkg/L}$  (4.12.4). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. This solution should be used freshly prepared.

### 5.0 Sample collection and pre-treatment

For the determination of mercury at very low concentrations, any potential contamination sources (traces of mercury in the laboratory work area, on the glassware and sampling bottles) are extremely important and should be avoided. All re-usable labware in contact with the sample is to be cleaned prior to use. Clean labware must be stored in a clean area until ready for use.

Carry out the sampling using as sampling vessels narrow neck bottles, manufactured of polytetrafluorethene (PTFE), perfluoro(ethene-propylene) (FEP), borosilicate glass or quartz.

All the glassware and sampling vessels should be cleaned using hot water and then with heated nitric acid solution (1:1) or chromic mixture (4.1). Strongly contaminated pieces of glassware are to be soaked in chromic mixture for 12-24 hours. After that glassware should be thoroughly washed with distilled water. Prior to be used for sampling, samples treatment and preparation of the reagents and stock solutions glassware must be checked for presence of mercury residues (traces). "Control" sample is to be prepared as follows. Every 10 pieces of glassware should be subsequently washed by 100 ml portion (aliquot) of the "dilution solution" (4.4).

If measured mercury concentration in the control sample was found to be more than  $0.02 \text{ mkg/L}$  (20 ppb) the glassware ought to be cleaned and checked once more.

#### Sample preservation

The capacity of the selected sample shouldn't be less than 200 ml. Sample preservation is performed by 1 ml of potassium dichromate solution (4.3) addition to each 100 ml of the sample. Preserved sample should be analysed in 3 days.

Prepare a reagent blank containing the same amounts of reagents and analyse along with the corresponding sample.

## 6.0 Instrumental set up

Please, refer to the RA-915 User's Manual (Section "Pre-Operational Procedures", p. 18) and RP-91 attachment User's Manual (Section "Pre-Operational Procedures", p. 8) for assembling the attachment and getting system ready.

### Multi-path cell operating mode

Please, refer to the RP-91 attachment User's Manual (Section "Main Operation Stages", p. 10-13) for details of using RA-915P software.

Use multi-path cell when the mercury content ratio of <math>0.2-1000\text{ ng/L}</math> is expected

Set the rotameter for the air consumption at  $0.2 - 10\text{ L/min}$

Keep the air intake at a level of  $4\text{ L/min}$

Set optical bridge to the position "III"

Set the cell to "multipath" in the Graph window

### Calibration

Start the program. In the main menu select "Liquid" mode. Start Graph in the Graph Window by pressing "Run" button. Inject 4 ml of reducing solution (4.6) into the bubbler and wait for 15-20 sec. Press button "Statistics" (it will be active after 30 sec) and pay attention to the RSD value (standard deviation). This value must be less than 5.0 %. Start integration by pressing "Run" button in the Integration window. Inject 5 ml of Mercury stock solution  $C(\text{Hg})=0.1\text{ mkg/L}$ . Wait for the analysis being completed (or after 60 sec) and press "End" button. Empty the bubbler and rinse it with 20 ml of distilled water.

Repeat the measurement several times injecting the same amount of stock solution.

Repeat the procedure with the dilution solution (as blank) and mercury stock solutions  $C(\text{Hg})=0.05\text{ mkg/L}$  and  $0.01\text{ mkg/L}$  instead of stock solution.

After the solutions measurements are completed perform the device calibration using RA-915P software.

## 7.0 Procedure

Samples of natural and waste water must be pre-treated using bromide-bromate mineralization procedure.

### 7.1 Sample mineralization procedure

Two 40 ml sample aliquots are to be put into the 50 ml volumetric flask; then 7.5 ml of hydrochloric acid (4.5) and 1 ml of the bromide-bromate mixture solution (4.9) are to be added. Mix thoroughly the resulting solution. If the yellow colour of the solution is blanking add an extra 1 ml of the bromide-bromate mixture solution. Bring the solution up to the mark with distilled water and mix thoroughly.



Blank sample is to be prepared using distilled water instead of sample aliquot (reagent blank if the sample was preserved). Samples with added reagents are to be kept not less than 0.5 hour at room temperature for completing the reaction. Before the analysis 0.5 ml of the hydroxyl amine hydrochloride solution (4.10) is to be added to each sample.

NB: If there is a sediment in the sample, the aliquot portion must be taken after intense stirring, without filtration.

## 7.2 Sample analysis

### Multi-path cell operating mode

Please, make sure that system is ready (see section 6.0).

Start the program. In the main menu select “Liquid” mode. Start Graph in the Graph Window by pressing “Run” button. Inject 4 ml of reducing solution (4.5) into the bubbler and wait for 15-20 sec. Press button “Statistics” (it will be active after 30 sec) and pay attention to the RSD value (standard deviation). This value must be less than 5.0 %. Start integration by pressing “Run” button in the Integration window. Inject 5 ml of preserved or mineralized sample. Wait for the analysis being completed (or after 60 sec) and press “End” button. Empty the bubbler and rinse it with 20 ml of distilled water. Repeat the analysis of the sample.

Repeat the procedure with blank sample.

Obtain the mercury mass concentration in the sample using RA-915P software (Table window). Calculate the mercury mass concentration in the sample aliquot (see section 8.0).

## 8.0 Data analysis and calculations

For the calculation of the final result use the formula

$$X = (C_{\text{sample}} - C_{\text{blank}}) \times Q \times Q_{\text{min}}$$

X - mercury mass concentration in the sample, mkg/L

C<sub>sample</sub> - mass concentration in sample, calculated in the RA-915P software,  
ng/L

C<sub>blank</sub> - mass concentration in blank, calculated in the RA-915P software,  
ng/L

- coefficient of dilution of the initial sample Q=1 without

Q mineralization or  $Q = V(\text{mineralized sample}) [=50 \text{ ml}] / V(\text{aliquot}) [=40 \text{ ml}]$   
= 1.25

Q - coefficient for matching of dimensions = 0.001

min