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Stationary source emissions — Sampling and determination of selenium compounds in flue gas

Émission des sources fixes — Échantillonnage et détermination des composés de sélénium dans les effluents gazeux

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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Introduction

Since it is estimated that selenium is exhausted from stationary sources like coal combustion plants, the investigation of the emission amounts of selenium from the stationary source is increasingly important for preventing a potential risk.

This International Standard describes a method for the sampling and determination of selenium compounds in a flue gas passing through ducts or chimneys. Selenium compounds generally exist both in vapour phase and in solid phase in flue gases, this method allows the determination of both gaseous and particulate selenium concentrations in flue gases.

Stationary source emissions — Sampling and determination of selenium compounds in flue gas

1 Scope

This International Standard describes the method for the sampling and determination of selenium compounds in both vapour phase and solid phase that are entrained in flue gases carried in stacks or ducts. The selenium content in flue gas is expressed as a mass concentration of elemental selenium in the stack gas.

Particulate and gaseous selenium compounds are captured by a filter and an absorber solution, respectively. The total concentration of selenium compounds in flue gas is expressed as the sum of both concentrations.

The concentrations of selenium in both samples are determined using inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrometry (GFAAS). Hydride generation (HG) techniques coupled to atomic spectrometry can also be used such as HG-AAS, HG-AFS (atomic fluorescence spectrometry), HG-ICP-OES and HG-ICP-MS.

The detection limit for gaseous selenium compounds is 0,3 μg/m^3 using HG-ICP-MS at a sampling volume of 0,12 m^3. The detection limit for particulate selenium compounds is 0,001 2 μg/m^3 using this technique at a sampling volume of 2,0 m^3.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 9096, *Stationary source emissions — Manual determination of mass concentration of particulate matter*

ISO 10396, *Stationary source emissions — Sampling for the automated determination of gas emission concentrations for permanently-installed monitoring systems*

ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 12141, *Stationary source emissions — Determination of mass concentration of particulate matter (dust) at low concentrations — Manual gravimetric method*

ISO 15586, *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace*

ISO 16911-1, *Stationary source emissions — Manual and automatic determination of velocity and volume flow rate in ducts — Part 1: Manual reference method*

ISO 17294-1, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

ISO 17294-2, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements*

ISO/TS 17379-1, *Water quality — Determination of selenium — Part 1: Method using hydride generation atomic fluorescence spectrometry (HG-AFS)*

ISO/TS 17379-2, *Water quality — Determination of selenium — Part 2: Method using hydride generation atomic absorption spectrometry (HG-AAS)*

ISO 20988, *Air quality — Guidelines for estimating measurement uncertainty*

ISO 23210:2009, *Stationary source emissions — Determination of PM10/PM2,5 mass concentration in flue gas — Measurement at low concentrations by use of impactors*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
gaseous selenium compounds
selenium compounds passing through a filter having at least 99,5 % collection efficiency for 0,3 µm diameter particles

3.2
isokinetic sampling
sampling at a flow rate such that the velocity and direction of the gas entering the sampling nozzle are the same as those of the gas in the duct at the sampling point

3.3
particulate selenium compounds
selenium compounds contained in a solid phase particle collected by a filter having at least 99,5 % collection efficiency for 0,3 µm diameter particles

3.4
sampling point
specific position on the sampling section at which a sample is extracted

3.5
STP
standard conditions for temperature, 273,15 K, and pressure, 101,325 kPa

4 Symbols and abbreviated terms

4.1 Symbols

$C_{A1,Se}$	concentration of selenium in prepared sample of the first and second absorber solutions (µg/ml)
$C_{A2,Se}$	concentration of selenium in prepared sample of the third absorber solution (µg/ml)
$C_{R,Se}$	concentration of selenium in prepared sample of rinse solution that washed transfer line from the filter housing to the first impinger nozzle in main-stream sampling (µg/ml)
$C_{R1,Se}$	concentration of selenium in prepared sample of rinse solution that washed transfer line from the filter housing to the T-piece in side-stream sampling (µg/ml)
$C_{R2,Se}$	concentration of selenium in prepared sample of rinse solution that washed transfer line after the T-piece to the first impinger nozzle in side-stream sampling (µg/ml)

$c_{S,Se}$	concentration of selenium in prepared sample solution for particulate selenium analysis (µg/ml)
d	density of reagent solution (g/ml)
p_{atm}	atmospheric pressure (kPa)
p_{av}	average pressure difference between the sample gas before the gas meter and the atmosphere (kPa)
$q_{m,Se}$	rate of mass discharge of selenium expressed as elemental selenium (mg/s)
$q_{V,fg,i}$	volume flow rate of flue gas through the sampling plane at conditions *i* of temperature, pressure, moisture and oxygen content (m^3/s)
T_{av}	average temperature of the sample gas before the gas meter (K)
$u(y)$	standard uncertainty (µg/m^3)
V_d	volume of dry flue gas sample normalized to STP (m^3)
V_f	final gas meter reading at the end of sampling (m^3)
$V_{G,d}$	volume of dry flue gas sample for gaseous selenium analysis normalized to STP (m^3)
V_i	initial gas meter reading at the beginning of sampling (m^3)
V_l	volume of air drawn through the gas meter during any intermediate leak tests (m^3)
V_m	volume of dry flue gas sample (m^3)
$V_{main,d}$	volume of dry flue gas sample in main stream, normalized to STP, in side-stream sampling (m^3)
$V_{S,d}$	volume of dry flue gas sample for particulate selenium analysis normalized to STP (m^3)
$V_{side,d}$	volume of dry flue gas sampled in side stream, normalized to STP, in side-stream sampling (m^3)
v_{A1}	volume of recovered sample of the first and second absorber solutions (ml)
v_{A2}	volume of recovered sample of the third absorber solution (ml)
v_R	volume of recovered sample of rinse solution that washed transfer line from the filter housing to the first impinger nozzle in main-stream sampling (ml)
v_{R1}	volume of recovered sample of rinse solution that washed transfer line from the filter housing to the T-piece in side-stream sampling (ml)
v_{R2}	volume of recovered sample of rinse solution that washed transfer line after the T-piece to the first impinger nozzle in side-stream sampling (ml)
v_S	volume of prepared sample solution for particulate selenium analysis (ml)
w_W	average moisture content of the flue gas at the sampling plane during the sampling period (%)
$y_{1,j}$	*j* th concentration value of the first measuring system (µg/m^3)
$y_{2,j}$	*j* th concentration value of the second measuring system (µg/m^3)

$\rho_{G,Se,dry}$	mass concentration of gaseous selenium expressed as elemental selenium in the flue gas on a dry basis at STP (µg/m^3)
$\rho_{S,Se,dry}$	mass concentration of particulate selenium expressed as elemental selenium in the flue gas on a dry basis at STP (µg/m^3)
$\rho_{Se,dry}$	mass concentration of total selenium expressed as elemental selenium in the flue gas on a dry basis at STP (µg/m^3)
$\rho_{Se,dry,O}$	mass concentration of selenium expressed as elemental selenium in the flue gas on a dry basis at STP and reference oxygen concentration (µg/m^3)
$\rho_{Se,i}$	mass concentration of selenium expressed as elemental selenium at conditions *i* of temperature, pressure, oxygen and moisture conditions (µg/m^3)
$\rho_{Se,wet}$	mass concentration of selenium expressed as elemental selenium in the flue gas on a wet basis at STP (µg/m^3)
$\rho_{Se,wet,O}$	mass concentration of selenium expressed as elemental selenium in the flue gas on a wet basis at STP and reference oxygen concentration (µg/m^3)
$\varphi_{O,d}$	volume fraction of the oxygen on a dry basis measured during the sampling (%)
$\varphi_{O,ref}$	volume fraction of the reference oxygen for the process (%)

4.2 Abbreviated terms

AAS	atomic absorption spectrometry
AFS	atomic fluorescence spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
HG	hydride generation
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
FEP	hexafluoroethene propene, perfluoro(ethane-propene)
PFA	perfluoroalkoxy
PTFE	polytetrafluoroethylene

5 Principle

Selenium compounds generally exist both in vapour phase and in solid phase in a flue gas. Particulate and gaseous selenium compounds are captured by a filter and an absorber solution, respectively. The concentration of selenium in a flue gas is expressed as the sum of both concentrations.

To determine particulate selenium contents in a flue gas, a stack sample gas is taken isokinetically and particles are collected on a filter in accordance with ISO 9096 or ISO 12141.

To determine gaseous selenium content in a flue gas, a stack sample gas is taken through a filter. Gaseous selenium compounds that pass through the filter are collected in an absorber solution. Since some of gaseous selenium compounds, mostly SeO_2, are adsorbed and in some cases reduced to elemental selenium on the inner surface of a sampling system in the presence of steam and SO_2, the sampling

system components such as the filter housing, heated transfer line and impinger nozzle is rinsed by an oxidation solution to recover the stuck selenium.

If the flow rates and the total sampling volumes for the measurements of particulate and gaseous selenium are the same, particulate and gaseous sampling shall be performed simultaneously with an isokinetic sampling procedure.

Each sample is prepared to be analysed by either ICP-OES, ICP-MS or GFAAS. HG-AAS, HG-AFS, HG-ICP-OES or HG-ICP-MS may be used if greater analytical sensitivity is required to determine the selenium concentration.

6 Reagents

6.1 General. To carry out the method, the following reagents are required to be of a recognized analytical grade.

6.2 Water, complying with grade 1 s specified in ISO 3696 for all sample preparation and dilutions.

6.3 Nitric acid, $d(HNO_3)$ = 1,4 g/ml.

NOTE Nitric acid is available both as $d(HNO_3)$ = 1,40 g/ml [$w(HNO_3)$ = 650 g/kg] and $d(HNO_3)$ = 1,42 g/ml [$w(HNO_3)$ = 690 g/kg].

6.4 Hydrogen peroxide, $w(H_2O_2)$ = 30 %.

6.5 Sulfuric acid, $d(H_2SO_4)$ = 1,84 g/ml.

6.6 Potassium permanganate, $KMnO_4$.

6.7 Selenium stock solution, complying with selenium standard solutions as specified in ISO/TS 17379-1 and ISO/TS 17379-2.

6.8 Absorber solution, mixture of 0,7 mol/l HNO_3 solution and 3 mol/l H_2O_2 solution.

Add carefully 50 ml of concentrated HNO_3 (6.3) to a 1 000 ml volumetric flask containing approximately 500 ml of water, and then add 333 ml of 30 % H_2O_2 (6.4) carefully. Add water with stirring to make a volume of 1 000 ml.

6.9 Rinse solution, mixture of 0,06 mol/l $KMnO_4$ solution and 1,8 mol/l H_2SO_4 solution.

Add carefully with stirring 100 ml of concentrated H_2SO_4 (6.5) to a 1 000 ml volumetric flask containing approximately 500 ml of water, and then add 10 g of $KMnO_4$ (6.6) carefully with stirring. Add water with stirring to make a volume of 1 000 ml.

6.10 Sample gas drying agent, self-indicating coarse grade silica gel.

6.11 Hydrofluoric acid, $w(HF)$ = 40 %.

6.12 Hydrochloric acid solution, $c(HCl)$ = 6 mol/l.

Add carefully with stirring 250 ml of concentrated HCl [$d(HCl)$ = 1,19 g/ml] to a 500 ml volumetric flask containing approximately 150 ml of water. Add water with stirring to make a volume of 500 ml.

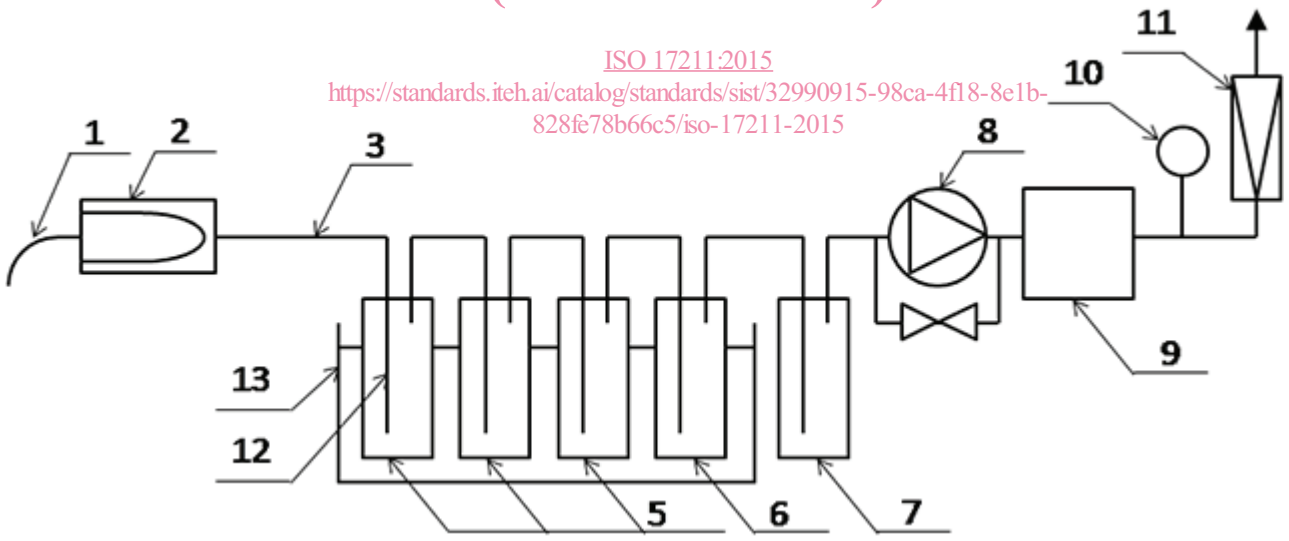
7 Apparatus

7.1 General.

Two types of absorber systems, a main-stream and a side-stream arrangement, can be employed. Schematics of both systems are given in Figure 1. In the main-stream system all the sampled flue gas is passed though the absorber solutions, while in the side-stream arrangement only a part of the sampled flue gas is passed through the absorber solutions. The main-stream sampling is used if the flow rate and total sampling volume for the measurements of gaseous and particulate selenium are the same. The side-stream sampling is used if the flow rate or total sampling volume for the measurements of gaseous and particulate selenium is different.

If the representative sampling is allowed, particulate selenium and gaseous selenium are sampled separately using two main stream sampling. Determine a representative sampling point in accordance with ISO 23210:2009, Annex G. Two sampling nozzles, for particulate selenium and gaseous selenium respectively, are placed at neighbouring points in which the physicochemical parameters such as selenium concentration and gas flow rate are considered to be equivalent. Particulate selenium sample is collected by the filter isokinetically. Gaseous selenium sample is captured in an absorber solution either isokinetically or anisokinetically after particles are removed.

The apparatus consists of a sampling probe including a nozzle and filter assembly that may be heated if required, an impinger train containing absorber solution to capture gaseous selenium, a manometer, a suction pump, a gas meter, and a sample gas volume flow rate measurement system. A thermometer and manometer shall be included in the sampling train to measure the temperature and pressure of the metered gas. A barometer shall be used to measure atmospheric pressure during the test in order that the volume of the gas sampled can be normalized to the standard condition of 273,15 K and 101,325 kPa.



a) Main-stream sampling