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

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National foreword

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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

$C_{\mathrm{A1,Se}}$	concentration of selenium in prepared sample of the first and second absorber solutions (µg/ml)
$C_{\mathrm{A2,Se}}$	concentration of selenium in prepared sample of the third absorber solution (µg/ml)
$C_{\mathrm{R,Se}}$	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)
$C_{\mathrm{R1,Se}}$	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)
$C_{\mathrm{R2,Se}}$	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)

$c_{\mathrm{S,Se}}$	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)
$q_{\mathrm{m,Se}}$	rate of mass discharge of selenium expressed as elemental selenium (mg/s)
$q_{V,\mathrm{fg},i}$	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)
$V_{G,\mathrm{d}}$	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)
$V_{main,\mathrm{d}}$	volume of dry flue gas sample in main stream, normalized to STP, in side-stream sampling (m^3)
$V_{S,\mathrm{d}}$	volume of dry flue gas sample for particulate selenium analysis normalized to STP (m^3)
$V_{side,\mathrm{d}}$	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.

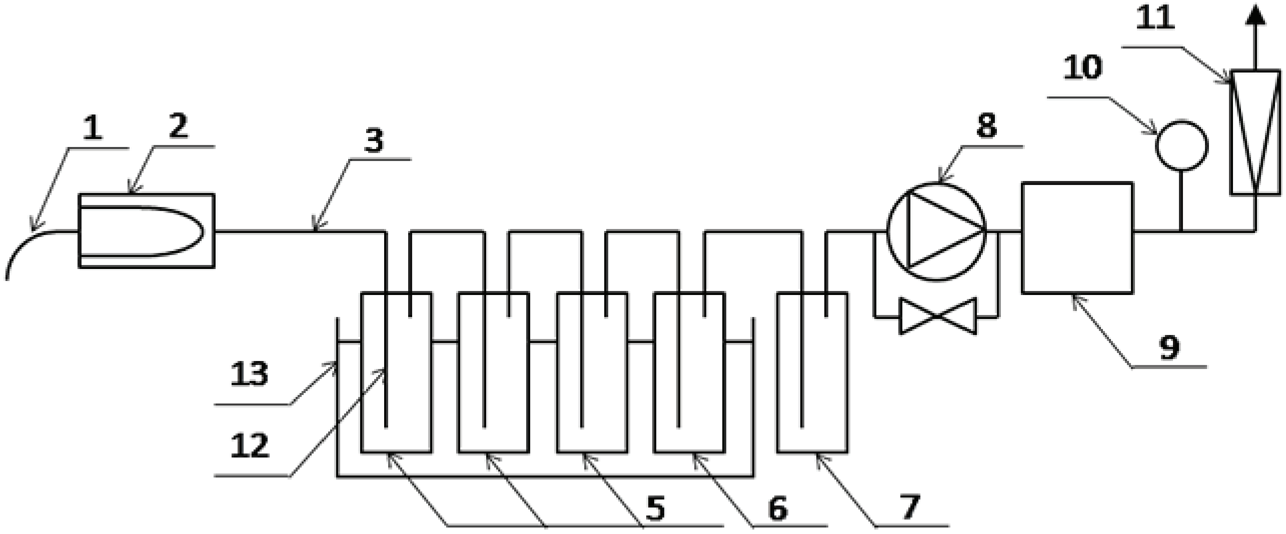
7 Apparatus

7.1 General.

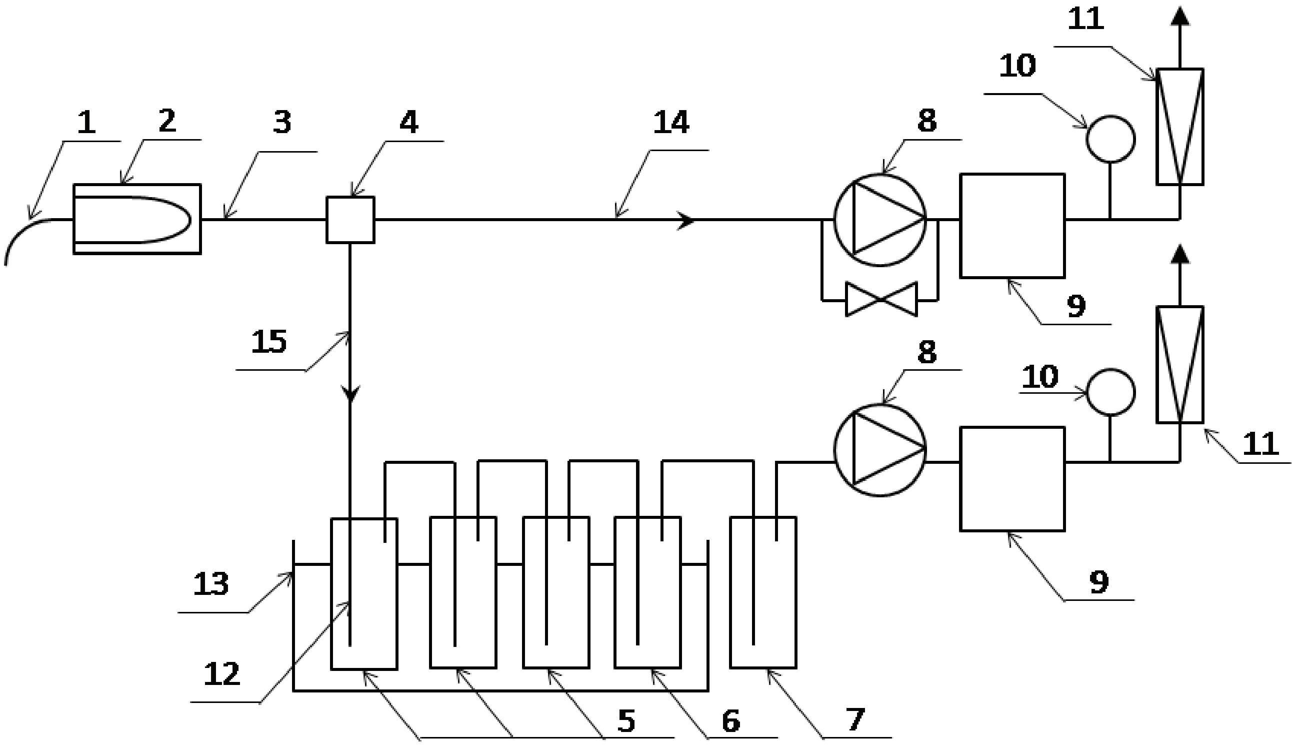
Two types of absorber systems, a main-stream and a side-stream arrangement, can be employed. Schematics of both systems are given in Figure 1. In the main-stream system all the sampled flue gas is passed though the absorber solutions, while in the side-stream arrangement only a part of the sampled flue 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



b) Side-stream sampling

Key

1	nozzle	9	gas meter
2	filter and filter housing	10	thermometer and manometer
3	transfer line	11	rotameter
4	T-piece	12	impinger nozzle
5	HNO_3/H_2O_2 impingers	13	cooler bath
6	dry impinger	14	main stream
7	drying tube or silica gel	15	side stream
8	pump		

Figure 1 — Schematic diagram of a sampling train

7.2 Nozzle. The diameter shall be chosen to be compatible with the required gas sampling volume flow rate. The choice of the nozzle shall be in accordance with ISO 9096 or ISO 12141.

The nozzle shall be capable of withstanding the temperature in the duct. It shall be resistant to chemical attack from various pollutants in the duct. Suitable materials for selenium sampling are silica glass, PTFE and titanium.

The nozzle shall be cleaned thoroughly before each sample run by rinsing with distilled water. The rinse shall be repeated until the rinse water shows no evidence of particulate matter.

7.3 Filter and filter housing. The silica fibre filter is placed in the duct between the nozzle and the transfer line (in-stack filtration). Silica fibre filters without binders are recommended. The filter holder shall have an airtight seal against leakage. If the flue gas temperature is below the dew point or the filter housing cannot be inserted in the duct, the filter housing shall be placed outside the duct (out-stack filtration) in accordance with ISO 9096 or ISO 12141.

NOTE If the out-stack filtration is employed, separation between particulate and gaseous selenium is difficult and only total selenium can be determined.

The filter shall be capable of withstanding prolonged exposures up to 40 K above the sampling temperature to prevent a change in filter quality. The filter efficiency shall be better than 99,5 % on a test aerosol with a mean particle diameter of 0,3 µm at the maximum flow rate anticipated.

The filter housing shall be cleaned thoroughly using the rinse solution (6.9), 0,1 mol/l HNO_3 and distilled water, and dried before sampling.

The filter shall be dried, equilibrated and weighed in accordance with ISO 9096 or ISO 12141.

7.4 Transfer line. It shall be resistant to chemical attack from various pollutants in sample gas. Suitable materials for gaseous selenium sampling are silica glass and PTFE.

The transfer line shall be cleaned thoroughly using rinse solution (6.9), 0,1 mol/l HNO_3 and distilled water, and dried before sampling.

The transfer line shall have a heating system capable of maintaining a gas temperature at its exit of at least 423 K or > 20 K above the dew point temperature, whichever is higher.

7.5 Impinger. The sampling train consists of a series of five impingers. For an efficient absorption of gaseous selenium, three impingers shall be placed in series. The impingers can be made of silica glass, borosilicate glass or PTFE.

The first three impingers shall contain the absorber solution.

The fourth impinger shall be left empty to catch any carryover of the absorber solution.

The fifth impinger shall be used as a drying unit. It shall be filled with silica gel to dry the sample gas prior to the suction unit, gas meter and rotameter. Prior to use, all of the impingers shall be rinsed and cleaned with the rinse solution (6.9), 0,1 mol/l HNO_3 and distilled water in this order and shall be dried thoroughly.

The geometry of the impingers and quantity of absorber solution shall be such that a gaseous selenium absorption efficiency of not less than 90 % is achieved at the chosen sampling flow rate and in the concentration range examined.

If the selenium mass concentration of the third impinger is more than 10 % of the total concentration in the sampled gas then the overall result shall be rejected.

For high absorption efficiency it is advisable to distribute the gas stream in the absorber solution as homogeneously as possible and have reasonably long contact time between gas and solution. The absorber solution should not be carried over to the next impinger by the gas stream. In practice, sufficient free space will also break down any foam which can be formed while the gas is bubbling through the solution.

NOTE If the side-stream sampling is employed or particulate selenium and gaseous selenium are sampled separately, the convenient size for impingers is 250 ml and the optimum volume of absorber solution is 100 ml.

7.6 Suction unit. The pump is used to extract the sample through the sampling train. It shall be an airtight pump capable of maintaining the selected sampling flow rate throughout the sampling period and shall be adjusted using a flow regulator.

7.7 Thermometer. It shall be fitted into the sampling train between the drying unit and the gas meter. The thermometer shall be capable of measuring absolute temperature to within 1 % of the absolute temperature.

7.8 Manometer. It shall be used to measure the difference in pressure between the gas entering the gas meter and atmosphere. It shall be capable of measuring pressure difference to within 1 % of the differential pressure.

7.9 Gas meter. The volume of the dried sample gas shall be measured using a calibrated gas meter. The gas meter shall be accurate within 2 % at the volume determined from the sampling system flow rate.

7.10 Rotameter. It shall be capable of measuring the flow rate to within ± 10 % of the flow.

7.11 Barometer. It shall be used to measure the local atmospheric pressure in kilopascals (kPa) to within 1 % of the absolute pressure.

8 Sampling

8.1 General

Sampling for particulate selenium is performed isokinetically and sampling for gaseous selenium is performed either isokinetically or anisokinetically. If the representative sampling is allowed and the flow rates or the total sampling volumes for the measurement of gaseous and particulate selenium is different, particle selenium and gaseous selenium are sampled separately by using either a side-stream sampling system or two main-stream sampling systems.

A safe working platform shall be provided at the sampling position so that all the sampling points can be reached with safety in accordance with ISO 10396.

8.2 Sampling position and sampling point

Sampling is carried out at a location which meets the requirements of ISO 9096 or ISO 12141. Sampling shall be conducted at a suitable access port through which the sampling probe can be passed into the duct. The port shall be capable of being sealed when not in use. If the representative sampling is allowed, sampling of gaseous selenium shall be performed at a point adjacent to the selenium particulate sampling point.

8.3 Minimum sampling duration and minimum sample volume

The minimum sampling period and the number of samples taken depend on the nature of the process that is producing the emissions. If emissions from a cyclical process are to be measured, the total sampling period shall cover at least one cycle of the process operation.

The minimum sampling duration also needs to take into account the detection limit of the analytical method. If the process is operated under a steady-state condition, the minimum sampling time and volume can be calculated prior to sampling by using the expected emitted concentration.

8.4 Other measurements to be made prior to sampling

8.4.1 Volumetric gas flow through duct at the sampling plane

The measurement of the volumetric gas flow at the sampling plane is necessary if the results are to be reported in terms of mass of pollutant emitted per unit time. The measurements shall be carried out in accordance with ISO 16911-1.

8.4.2 Moisture content of gas

The moisture content of flue gas is necessary to calculate the selenium concentration on wet basis and the isokinetical flow rate.

8.4.3 Oxygen content of gas

If the results are to be reported after correction to a particular oxygen concentration, measurement of the flue gas oxygen concentration is necessary during the sampling period.

8.5 Assembly of sampling apparatus

Assemble the sampling equipment as illustrated in Figure 1. Allow the sampling system equipment to reach operating temperature then check the system for leaks as described in 8.7.

8.6 Sampling

Carefully insert the probe into the duct with the nozzle facing downstream, avoiding contact with any parts of the duct. Seal the opening of the access port to minimize air ingress.

Record the time and the current gas meter reading. Turn the sampling probe until the entry nozzle is facing upstream within ± 10°, open the shut-off valve, start the suction device and adjust the flow rate in order to obtain isokinetic sampling. When moving points, it is required that the pump remains switched on and that the isokinetic flow rate is immediately checked and adjusted if necessary. The sampling flow rate shall be sufficient to allow vigorous bubbling within the first three impingers of the sampling train but not so vigorous that the solution is carried over into the fourth empty impinger. A constant sampling flow rate shall be maintained within the range described in 8.8. Metered temperature and ambient pressure should be recorded periodically.

At the end of the sampling period, the suction control valve shall be closed and the sampling pump switched off. The gas meter shall be read. A leak test of the equipment should then be carried out.

NOTE If the side-stream sampling is employed or particulate selenium and gaseous selenium are sampled separately, a sampling flow rate for gaseous selenium between 0,5 l/min and 3,0 l/min can be sufficient to allow vigorous bubbling. If the sampling durations of gaseous and particulate selenium are significantly different, the sampling of the shorter duration can be repeated during the longer sampling duration.

8.7 Checking for leaks

A pre-sample leak check should be carried out at the maximum vacuum expected during sampling and the post-sample leak check should be carried out at the maximum vacuum reached during sampling. The leakage flow rate, determine by pressure variation or a calibrated rotameter with appropriate scale after evacuation of the train at the maximum vacuum, shall be below 2 % of the normal flow rate. During sampling, a leak check can be monitored by measuring continuously the concentration of a relevant gas component (CO_2, O_2, etc.) directly in the duct and downstream of the sampling train; any detectable difference between those concentrations indicates a leak in the sampling equipment parts located out of the stack. This leak shall then be investigated and rectified.

8.8 Quality assurance

Prior to sampling, record the time and the current gas meter reading. During sampling, the flow rate of the sample gas shall be recorded periodically, together with the temperature and pressure at the gas meter to allow the calculation of the average temperature and pressure during the sampling period.

During sampling, operators shall periodically check and correct the following:

- the flow rate for gas sampling has not drifted by more than ± 10 % of the chosen flow rate,
- the flow rate for particulate sampling has been within ± 10 % under the condition of ISO 9096 or −5 % to +15 % under the condition of ISO 12141 of the isokinetic sampling rate, and
- the silica gel has not been exhausted.

If the colour of the silica gel indicates that it is nearly exhausted, then the pump shall be switched off and the sampler withdrawn from the duct to be leak tested before a new bottle of silica gel is fitted into the system.

If any of the components are replaced, then the leak test shall be performed again.

The leak rate measured during any leak test shall not be greater than 2 % of the nominal flow rate. Otherwise the result is invalid.

8.9 Sample recovery

8.9.1 Sample recovery for gaseous selenium

The selenium contained in the impingers shall be carefully recovered as soon as possible after sampling.

Withdraw the probe from the duct and allow it to cool so that it can be handled.

The contents of the first and second impingers shall be quantitatively transferred into a volumetric flask of an appropriate volume. Each impinger shall be rinsed with approximately 20 ml of 0,7 mol/l HNO_3/3 mol/l H_2O_2, and these washings shall be added to the volumetric flask. Add water to a constant volume and record the volume of the solution in the volumetric flask. For an efficient absorption of gaseous selenium, the third impinger solution is recovered using the same operation and is transferred in another volumetric flask. Add water to a constant volume and record the volume of the solution in the volumetric flask.

After recovery of the particulate matter according to 8.9.2, rinse nozzle, filter housing, transfer line and the first impinger nozzle with approximately 10 ml of the rinse solution (6.9). Repeat this process for three times. Then, transfer all the rinse solutions into a volumetric flask. Add water to a constant volume and record the volume of the solution in the volumetric flask.

The recovered absorber and the rinse solution shall be kept in each sample container. Seal the sample containers and clearly label with the date and a unique identifier to enable the sample to be traced back to the measurement.

If a side-stream sampling is employed, the parts from nozzle to T-piece and the transfer line from T-piece to the first impinger nozzle shall be rinsed with the rinse solution (6.9) separately. Then transfer each rinse solution in different volumetric flasks and add water to a constant volume. Record the volume of the solution in each volumetric flask. The recovered rinse solutions shall be kept in each sample container.

8.9.2 Sample recovery for particulate selenium

Carefully remove the filter from the filter housing and place it in its labelled Petri dish container. To handle the filter, use either acid-washed polypropylene or PTFE coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter, any particulate matter upstream of the filter and filter fibres that adhere to the filter holder gasket to the Petri dish according to ISO 9096 or ISO 12141.

8.10 Field blank

An equipment field blank shall be taken at each site at which measurements are carried out by performing all of the steps of the sampling gas procedure, but without drawing exhaust gas through the sampling equipment. The resulting solution shall be treated, labelled and handled in the same manner as the test solutions. The results for the field blank shall be reported along with the samples from that site.

9 Sample preparation

9.1 General

The methods given for particulate selenium analysis are valid for plane filters of approximately 100 mg per filter, and a maximum of 10 mg of particulate matter collected on the filter. If the actual figures differ significantly from these values, the amounts of HNO_3 and HF solutions described in 9.2.2 and 9.3.2 respectively shall be changed proportionally.

9.2 Sample preparation for analysis with hydride generation

9.2.1 Sample preparation for gaseous selenium analysis

Transfer 25 ml of the recovered samples described in 8.9.1 into a 100 ml beaker. Add 1 ml of concentrated H_2SO_4 and 2 ml of concentrated HNO_3. Heat the solution on a hot plate until white fumes of H_2SO_4 are evolved and cool the solution.

Add 20 ml of 6 mol/l HCl and heat the solution at about 363 K for 1 h. Transfer the solution into a 25 ml volumetric flask and add water to make a volume of 25 ml.

9.2.2 Sample preparation for particulate selenium analysis

Desiccate the filter and filter catch without heating (do not heat the filters to speed the drying), and then weigh the desiccated sample.

Place the desiccated sample in a closed pressurized fluoroplastic vessel made of PTFE, PFA or FEP. Add 2 ml of concentrated HNO_3 and 3 ml of concentrated HF to the vessel. Heat the closed pressurized vessel at 383 K for 1 h.

Transfer the digested solution into a fluoroplastic beaker and heat the solution to dryness on a hot plate to evaporate hydrofluoric acid. Then, add 20 ml of 6 mol/l HCl and heat the solution at about 363 K for 1 h.

Filter the solution using an acid-resistant filter paper (0,45 µm). Dilute to 25 ml (or the appropriate volume for the expected selenium concentration) with water. Measure and record the volume of the sample.

NOTE 9.2.1 and 9.2.2 are important procedure for hydride generation (HG) technique (reference to ISO/TS 17379-1 and ISO/TS 17379-2).

9.3 Sample preparation for analysis without hydride generation

9.3.1 Sample preparation for gaseous selenium analysis

Recovered samples described in 8.9.1 are used as the analytical sample.

9.3.2 Sample preparation for particulate selenium analysis

Desiccate the filter and filter catch without heating (do not heat the filters to speed the drying) and then weigh the desiccated sample.

Place the desiccated sample in a closed pressurized fluoroplastic vessel made of PTFE, PFA or FEP. Add 2 ml of concentrated HNO_3 and 3 ml of concentrated HF to the vessel. Heat the closed pressurized vessel at 383 K for 1 h.

Filter the solution using an acid-resistant filter paper (0,45 µm). Dilute to 25 ml (or the appropriate volume for the expected selenium concentration) with water. Record the volume of the sample.

When preparing and analysing samples containing hydrofluoric acid, glassware shall not be used for filtering apparatus, volumetric flask and ICP torch. An alumina torch should be used.

10 Analytical procedure

The standard method for the determination of selenium in the sample is 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. The details of HG technique and measurement setup are given in ISO/TS 17379-1 or ISO/TS 17379-2. The method appropriate to the level of detection desired in reference to Clause 12 shall be selected.

— Inductively coupled plasma optical emission spectrometry

Analyse the selenium concentration in the samples in accordance with ISO 11885.

— Inductively coupled plasma mass spectrometry

Analyse the selenium concentration in the samples in accordance with ISO 17294 (all parts).

— Graphite furnace atomic absorption spectrometry

Analyse the selenium concentration in the samples in accordance with ISO 15586.

— Hydride generation atomic absorption spectrometry

Analyse the selenium concentration in the samples in accordance with ISO/TS 17379-2.

— Hydride generation atomic fluoresce spectrometry

Analyse the selenium concentration in the samples in accordance with ISO/TS 17379-1.

11 Expression of results

11.1 Calculation of the volume of dry flue gas sampled at sampling conditions, V_m

The volume of dry flue gas sample (V_m) is calculated by subtracting the initial gas meter reading (V_i) from the final gas meter reading (V_f) correcting for any air drawn through the gas meter during leak checks (V_l) when equipment is replaced, or if carried out between sampling. The gas volume measured is on a dry basis.

$$V_\mathrm{m} = V_\mathrm{f} - V_\mathrm{i} - V_\mathrm{l} \tag{1}$$

where

V_m is the volume of dry flue gas sample (m^3);

V_f is the final gas meter reading at the end of sampling (m^3);

V_i is the initial gas meter reading at the beginning of sampling (m^3);

V_l is the volume of air drawn through the gas meter during any intermediate leak tests (m^3).

11.2 Calculation of the volume of dry flue gas sample normalized to standard temperature and pressure, V_d

Calculate the volume of dry flue gas sample normalized to standard temperature and pressure, V_d, using Formula (2).

$$V_\mathrm{d} = V_\mathrm{m} \times \frac{\left(p_\mathrm{atm} + p_\mathrm{av}\right) \times 273{,}15}{T_\mathrm{av} \times 101{,}325} \tag{2}$$

where

V_d is the volume of dry flue gas sample normalized to STP (m^3);

V_m is the volume of dry flue gas sample (m^3);

p_{atm} is the atmospheric pressure (kPa);

p_{av} is the average pressure difference between the sample gas before the gas meter and the atmosphere (kPa);

T_{av} is the average temperature of the sample gas before the gas meter (K).

11.3 Mass concentration of selenium expressed as elemental selenium in the flue gas on a dry basis at STP, $\rho_{Se,dry}$

The mass concentration of total selenium is calculated as the sum of gaseous and particulate selenium concentrations.

$$\rho_\mathrm{Se,dry} = \rho_\mathrm{G,Se,dry} + \rho_\mathrm{S,Se,dry} \tag{3}$$

For the main-stream arrangement,

$$\rho_\mathrm{G,Se,dry} = \frac{\boldsymbol{C}_\mathrm{A1,Se} \times v_\mathrm{A1} + \boldsymbol{C}_\mathrm{A2,Se} \times v_\mathrm{A2} + C_\mathrm{R,Se} \times v_\mathrm{R}}{\boldsymbol{V}_{G,\mathrm{d}}} \tag{4}$$

$$\rho_{\mathrm{S,Se,dry}} = \frac{C_{\mathrm{S,Se}} \times v_{\mathrm{S}}}{V_{S,\mathrm{d}}} \tag{5}$$

where

$\rho_{\mathrm{Se,dry}}$	is the mass concentration of total selenium expressed as elemental selenium in the flue gas on a dry basis at STP (µg/m^3);
$\rho_{\mathrm{G,Se,dry}}$	is the mass concentration of gaseous selenium expressed as elemental selenium in the flue gas on a dry basis at STP (µg/m^3);
$\rho_{\mathrm{S,Se,dry}}$	is the mass concentration of particulate selenium expressed as elemental selenium in the flue gas on a dry basis at STP (µg/m^3);
$C_{\mathrm{A1,Se}}$	is the concentration of selenium in prepared sample of the first and second absorber solutions (µg/ml);
$C_{\mathrm{A2,Se}}$	is the concentration of selenium in prepared sample of the third absorber solution (µg/ml);
$C_{\mathrm{R,Se}}$	is the 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 (see 9.2.1 or 9.3.1) (µg/ml);
$C_{\mathrm{S,Se}}$	is the concentration of selenium in prepared sample solution for particulate selenium analysis (see 9.2.2 or 9.3.2) (µg/ml);
v_{A1}	is the volume of recovered sample of the first and second absorber solutions (see 8.9.1) (ml);
v_{A2}	is the volume of recovered sample of the third absorber solution (see 8.9.1) (ml);
v_{R}	is the volume of recovered sample of rinse solution that washed transfer line from the filter housing to the first impinger nozzle in main-stream sampling (see 8.9.1) (ml);
v_{S}	is the volume of prepared sample solution for particulate selenium analysis (see 9.2.2 or 9.3.2) (ml);
$V_{G,\mathrm{d}}$	is the volume of dry flue gas sample for gaseous selenium analysis, normalized to STP (m^3);
$V_{S,\mathrm{d}}$	is the volume of dry flue gas sample for particulate selenium analysis, normalized to STP (m^3).

For the side-stream arrangement,

$$\rho_{\mathrm{G,Se,dry}} = \frac{C_{A1,Se} \times v_{A1} + C_{\mathrm{A2,Se}} \times v_{\mathrm{A2}} + C_{\mathrm{R2,Se}} \times v_{\mathrm{R2}}}{V_{side,\mathrm{d}}} + \frac{C_{\mathrm{R1,Se}} \times v_{\mathrm{R1}}}{V_{main,\mathrm{d}} + V_{side,\mathrm{d}}} \tag{6}$$

$$\rho_{\mathrm{S,Se,dry}} = \frac{C_{\mathrm{S,Se}} \times v_{\mathrm{S}}}{V_{main,\mathrm{d}} + V_{side,\mathrm{d}}} \quad (7)$$

where

$C_{\mathrm{A1,Se}}$	is the concentration of selenium in prepared sample of the first and second absorber solutions (µg/ml);
$C_{\mathrm{A2,Se}}$	is the concentration of selenium in prepared sample of the third absorber solution (µg/ml);
$C_{\mathrm{R1,Se}}$	is the 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);
$C_{\mathrm{R2,Se}}$	is the 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);
$C_{\mathrm{S,Se}}$	is the concentration of selenium in prepared sample solution for particulate selenium analysis (µg/ml);
v_{A1}	is the volume of recovered sample of the first and second absorber solutions (see 8.9.1)(ml);
v_{A2}	is the volume of recovered sample of the third absorber solution (see 8.9.1)(ml);
v_{R1}	is the volume of recovered sample of rinse solution that washed transfer line from the filter housing to the T-piece (ml);
v_{R2}	is the volume of recovered sample of rinse solution that washed transfer line after the T- piece to the first impinger nozzle (ml);
v_{S}	is the volume of prepared sample solution for particulate selenium analysis (ml);
$V_{main,\mathrm{d}}$	is the volume of dry flue gas sample in the main stream, normalized to STP (m^3);
$V_{side,\mathrm{d}}$	is the volume of dry flue gas sample in the side stream, normalized to STP (m^3).

11.4 Mass concentration of selenium expressed as elemental selenium in the flue gas on a dry basis at STP and reference oxygen volume fraction, $\rho_{\mathrm{Se,dry,O}}$

Calculate $\rho_{\mathrm{Se,dry,O}}$ using Formula (8):

$$\rho_{\mathrm{Se,dry,O}} = \rho_{\mathrm{Se,dry}} \times \left(\frac{20{,}9 - \varphi_{\mathrm{O,ref}}}{20{,}9 - \varphi_{\mathrm{O,d}}} \right) \quad (8)$$

where

$\rho_{\mathrm{Se,dry,O}}$	is the 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);
$\varphi_{\mathrm{O,ref}}$	is the volume fraction of the reference oxygen (%);
$\varphi_{\mathrm{O,d}}$	is the volume fraction of the average oxygen on a dry basis measured during the sampling (%).

11.5 Rate of mass discharge of selenium expressed as elemental selenium, $q_{\mathrm{m,Se}}$

The rate of discharge can be determined by finding the product of the concentration of selenium at reference conditions in micrograms per cubic meter by the average flow rate in the duct at reference conditions.

$$q_{\mathrm{m,Se}} = \frac{\rho_{\mathrm{Se},i} \times q_{V,\mathrm{fg},i}}{1\,000} \tag{9}$$

where

$q_{\mathrm{m,Se}}$ is the rate of mass discharge of selenium expressed as elemental selenium (mg/s);

$\rho_{\mathrm{Se},i}$ is the mass concentration of selenium expressed as elemental selenium at conditions i of temperature, pressure, oxygen and moisture conditions (µg/m^3);

$q_{V,\mathrm{fg},i}$ is the volume flow rate of flue gas through the sampling plane at conditions i of temperature, pressure, moisture and oxygen content (m^3/s).

11.6 Mass concentration of selenium expressed as elemental selenium in the flue gas on a wet basis at STP, $\rho_{\mathrm{Se,wet}}$

Calculate $\rho_{\mathrm{Se,wet}}$ using Formula (10):

$$\rho_{\mathrm{Se,\,wet}} = \rho_{\mathrm{Se,dry}} \times \frac{\left(100 - w_{\mathrm{W}}\right)}{100} \tag{10}$$

where

$\rho_{\mathrm{Se,wet}}$ is the mass concentration of selenium expressed as elemental selenium in the flue gas on a wet basis at STP (µg/m^3);

w_{W} is the average moisture content of the flue gas at the sampling plane during the sampling period (%).

11.7 Mass concentration of selenium expressed as elemental selenium in the flue gas on a wet basis at STP and reference oxygen concentration, $\rho_{\mathrm{Se,wet,O}}$

Calculate $\rho_{\mathrm{Se,wet,O}}$ using Formula (11):

$$\rho_{\mathrm{Se,\,wet,O}} = \rho_{\mathrm{Se,wet}} \times \left(\frac{20,9 - \varphi_{\mathrm{O,ref}}}{20,9 - \varphi_{\mathrm{O,d}}} \right) \tag{11}$$

where

$\rho_{\mathrm{Se,wet,O}}$ is the 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);

$\rho_{\mathrm{Se,wet}}$ is the mass concentration of selenium expressed as elemental selenium in the flue gas on a wet basis at STP (µg/m^3);

$\varphi_{\mathrm{O,ref}}$ is the volume fraction of the reference oxygen (%);

$\varphi_{\mathrm{O,d}}$ is the volume fraction of the average oxygen on a dry basis measured during the sampling (%).

12 Performance characteristics

12.1 Detection limits

The detection limit depends on a sampling gas volume and an analysis method. The typical detection limits for gaseous selenium compounds and particulate selenium compounds are shown in Table 1 and Table 2, respectively.

Table 1 — Typical value of detection limit for gaseous selenium compounds

Detection limit (µg/m^3)	Analytical method
47	ICP-OES
1,2	ICP-MS
2,3	HG-ICP-OES
0,3	HG-ICP-MS
47	GFAAS
1,5	HG-AAS
0,1	HG-AFS
Sampling volume of 0,12 m^3; based on a flow rate of 1,2 l/min for a sampling period of 100 min.	

Table 2 — Typical value of detection limit for particulate selenium compounds

Detection limit (µg/m^3)	Analytical method
0,25	ICP-OES
0,006	ICP-MS
0,012	HG-ICP-OES
0,001 2	HG-ICP-MS
0,25	GFAAS
0,007	HG-AAS
0,000 5	HG-AFS
Sampling volume of 2,0 m^3; based on a flow rate of 20 l/min for a sampling period of 100 min.	

12.2 Evaluation of measurement uncertainty

Calculate the measurement uncertainty in accordance with ISO 20988 or ISO/IEC Guide 98-3 (see Annex A).

13 Test report

The test report shall refer to this International Standard and shall include at least the following information:

a) identification of the sampling site, including:

— the date,

— time and duration of sampling,

— the sampling and analytical personnel;

b) description of the plant or process operation conditions, including:

— any variation to the process that occurred during sampling,

— the load on the plant during monitoring,

— the maximum loading conditions of the plant;

c) identification of the sampling location, including:

— duct dimensions,

— sampling position,

— number and position of sampling points;

d) flue gas characteristics at the sampling location, including:

— flue gas velocity,

— flue gas static pressure,

— temperature and oxygen profiles,

— flue gas water vapour content;

e) measurement procedure:

— whether sampling was carried out isokinetically, at sampling points according to ISO 9096 or ISO 12141 with justification or at a single point with justification,

— entry nozzle diameter,

— location of filter,

— filtration temperature,

— duration of each sample;

f) test results:

— sampled flue gas volume at sampling conditions,

— average sample gas flow rate, any special circumstances or incidents,

— the volume of sample submitted for analysis,

— the concentration of selenium in the sample measured in the laboratory,

— the corrected concentration at standard conditions;

g) quality assurance:

— leak test result,

— equipment field blank,

— information on measurement uncertainty,

— absorption efficiency;

h) comments:

— any special circumstances that may have influenced the results,

— report of any modification to the method.

Annex A
(informative)

Results of evaluation of measurement uncertainties

The standard uncertainty and the expanded uncertainty of the measurement were calculated from the results of paired measurements for coal combustion flue gases using Formula (A.1) in accordance with ISO 20988:2007, Table 1, type A6 (paired measurement of two identical measurement systems). Both sampling probes were placed at adjacent points in a sampling plane and the sampling were carried out simultaneously.

$$u(y) = \sqrt{\frac{1}{2n}\sum_{j=1}^{n}(y_{1,j} - y_{2,j})^2} \qquad \text{(A.1)}$$

where

$u(y)$ is the standard uncertainty;

$y_{1,j}$ is the j th concentration value of the first measuring system;

$y_{2,j}$ is the j th concentration value of the second measuring system;

n is the number of paired measured values.

The results of uncertainty analysis for gaseous selenium are described in Table A.1. The evaluated input data are given in Table A.2.

Table A.1 — Work steps and results for gaseous selenium analysis

Step	Element	Instruction	Result
1	**Problem specification**		
	Evaluated quantity	Result of measurement	y
	Required uncertainty parameters	Standard uncertainty of y Expanded 95 % uncertainty of y	$u(y)$ $U_{0,95}(y)$
	Input data	Series of observation $y_{1,j}$ and $y_{2,j}$ with j = 1 to n obtained in paired application of two identical measuring systems operated independently of each other.	See Table A.2
	Reference values	Mean values $y_{Rj} = (y_{1,j} + y_{2,j})/2$	See Table A.2
	Additional information	Standard uncertainty $u(y)$ Standard uncertainty of the unbiased reference values $u(y_R) = u(y)/\sqrt{2}$	constant constant
	Representativeness	The input data evaluated are considered representative for application of the considered method of measurement at two types of stationary sources	-

Table A.1 *(continued)*

Step	Element	Instruction	Result
2	**Data treatment**		
	Model equation	$y_{1,j} = y_{Rj} + e_{1,j}$ with deviation $e_{1,j} = (y_{1,j} - y_{2,j})/2$	-
	Variance equation	$\mathrm{var}(y_{1,j}) = \mathrm{var}(y_{1,j})/2+$ $\frac{1}{4n}\sum_{j=1}^{n}(y_{1,j} - y_{2,j})^2$ $\mathrm{var}(y_{2,j}) = \mathrm{var}(y_{1,j})$	-
	Covariance	$\mathrm{cov}(y_{Rj}, e_{k,j})$	0
	Bias	$u_B(y) = \frac{1}{n}\sum_{j=1}^{n}(y_{1,j} - y_{2,j})$	0,7 µg/m³
3	**Results of uncertainty analysis**		
	Standard uncertainty of y	$u(y) = \sqrt{\frac{1}{2n}\sum_{j=1}^{n}(y_{1,j} - y_{2,j})^2}$	1,6 µg/m³
	Number of degree of freedom	$v = n$ since $u_B(y) \leqq 0{,}5 \cdot u(y)$	23
	Coverage factor	$k_{0,95}$	2,1
	Expanded uncertainty of y	$U_{0,95}(y) = k_{0,95} \cdot u(y)$	3,4
	Range of application	$\min(y) \leqq y \leqq \max(y)$	$0{,}5\ \mu g/m^3 \leqq y \leqq 27{,}2\ \mu g/m^3$

Table A.2 — Input data of gaseous selenium

Index j	First measuring system $y_{1,j}$ µg/m³	Second measuring system $y_{2,j}$ µg/m³
1	8,8	7,5
2	16,8	14,2
3	14,5	14,6
4	5,9	6,0
5	7,9	7,7
6	11,0	10,7
7	6,8	7,8
8	14,3	14,7
9	24,1	15,3
10	12,0	12,5
11	22,8	22,2
12	20,3	21,4
13	3,2	2,8

Table A.2 *(continued)*

Index j	**First measuring system** $y_{1,j}$ µg/m^3	**Second measuring system** $y_{2,j}$ µg/m^3
14	4,3	5,9
15	7,4	5,0
16	12,2	11,7
17	27,2	23,6
18	0,6	0,5
19	0,7	0,8
20	0,6	0,6
21	0,8	0,7
22	0,8	0,8
23	0,8	0,8

The results of uncertainty analysis for particulate selenium are described in Table A.3. The evaluated input data are given in Table A.4.

Table A.3 — Work steps and results for particulate selenium analysis

Step	Element	Instruction	Result
1	**Problem specification**		
	Evaluated quantity	Result of measurement	y
	Required uncertainty parameters	Standard uncertainty of y Expanded 95 % uncertainty of y	$u(y)$ $U_{0,95}(y)$
	Input data	Series of observation $y_{1,j}$ and $y_{2,j}$ with i = 1 to n obtained in paired application of two identical measuring systems operated independently of each other.	See Table A.4
	Reference values	Mean values $y_{Rj} = (y_{1,j} + y_{2,j})/2$	See Table A.4
	Additional information	Standard uncertainty $u(y)$ Standard uncertainty of the unbiased reference values $u(y_R) = u(y)/\sqrt{2}$	constant constant
	Representativeness	The input data evaluated are considered representative for application of the considered method of measurement at two types of stationary sources	-

Table A.3 *(continued)*

Step	Element	Instruction	Result
2	**Data treatment**		
	Model equation	$y_{1,j} = y_{\mathrm{R}j} + e_{1,j}$ with deviation $e_{1,j} = (y_{1,j} - y_{2,j})/2$	-
	Variance equation	$\mathrm{var}(y_{1,j}) = \mathrm{var}(y_{1,j})/2+$ $\frac{1}{4n}\sum_{j=1}^{n}(y_{1,j}-y_{2,j})^2$ $\mathrm{var}(y_{2,j}) = \mathrm{var}(y_{1,j})$	-
	Covariance	$\mathrm{cov}(y_{\mathrm{R}j}, e_{k,j})$	0
	Bias	$u_B(y) = \frac{1}{n}\sum_{j=1}^{n}(y_{1,j}-y_{2,j})$	−0,9 µg/m^3
3	**Results of uncertainty analysis**		
	Standard uncertainty of y	$u(y) = \sqrt{\frac{1}{2n}\sum_{j=1}^{n}(y_{1,j}-y_{2,j})^2}$	3,1 µg/m^3
	Number of degree of freedom	$v = n$ since $u_{\mathrm{B}}(y) \leqq 0{,}5 \cdot u(y)$	22
	Coverage factor	$k_{0,95}$	2,1
	Expanded uncertainty of y	$U_{0,95}(y) = k_{0,95} \cdot u(y)$	6,5
	Range of application	$\min(y) \leqq y \leqq \max(y)$	0,5 µg/m^3 $\leqq y \leqq$ 61,2 µg/m^3

Table A.4 — Input data of particulate selenium

Index j	First measuring system $y_{1,j}$ µg/m^3	Second measuring system $y_{2,j}$ µg/m^3
1	4,9	5,8
2	6,9	7,3
3	10,9	12,1
4	2,5	2,4
5	2,8	3,5
6	4,0	5,3
7	25,6	26,5
8	27,5	28,3
9	29,2	26,9
10	38,8	37,1
11	32,1	33,6
12	28,4	28,8
13	19,8	17,9

Table A.4 *(continued)*

Index j	**First measuring system** $y_{1,j}$ µg/m^3	**Second measuring system** $y_{2,j}$ µg/m^3
14	21,3	17,7
15	21,9	20,4
16	32,1	43,3
17	45,8	61,2
18	34,6	30,4
19	0,5	0,5
20	0,5	0,6
21	1,0	1,0
22	1,0	0,9

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