

Environment Agency Method Implementation Document for EN 14385:2004

Stationary source emissions – Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V

The Environment Agency recognises that European and International standards may need supplementing by Method Implementation Documents (MIDs) to ensure they are being implemented consistently.

This document supplements EN 14385:2004. The clause numbers in this document follow those of EN 14385 although the text from the standard is not repeated in this document.

1. Scope

European Standard EN 14385 may be used to determine other metals than those named in the scope of the standard. However, Hg is excluded from the scope of this MID (Hg must be measured using other methods, such as EN 13211).

In order to extend the scope of metals it is necessary for the analytical laboratory to carry out validation for the analysis of the additional metals. The filter, rinsing solutions and absorption solutions can be spiked with certified reference materials and analysed to determine recoveries and limits of detection.

The analysis of Sn may be problematic because of the formation of "tin stone" (a mixed valence oxide). However, validation work carried out by a UK laboratory has shown acceptable results.

EN 14385 has been validated on stacks with a gas composition given in Table 1 of the standard. The standard can be used on processes with other gas compositions.

It is not permitted to combine the measurement of metals and particulates.

MCERTS accredited organisations are required to implement this version of the MID by 31 March 2022.

2. Normative references

EN 13284-1:2001 has been replaced by EN 13284-1:2017.

3. Definitions, symbols and abbreviations

No additional information

4. Principle

No additional information

5. Apparatus, chemicals and gases

5.1 Apparatus

Commercial titanium is made to different specifications based on the purity of the titanium. As the other materials present may contain the specific elements being determined during the measurement it is important that an appropriate grade of titanium is used.

Titanium will degrade in gas streams with a fluoride content of greater than 20 ppm.

Titanium may also degrade at temperatures greater than 350°C.

Absorbers shall be kept below 30°C. This can be done by using ice.

PTFE is not suitable for temperatures in excess of 200°C.

5.2 Chemicals and filter material

5.2.1 General

No additional information

5.2.2 Filter

A batch of filters for sampling metals are those prepared on a single occasion. This may include filters prepared prior to the sampling campaign for use exclusively on that campaign or a greater number of filters prepared on one occasion but stored for use in future monitoring campaigns.

At least one filter per batch should be analysed for metal content prior to use.

5.2.3 Hydrofluoric acid

No additional information

5.2.4 Hydrogen peroxide

No additional information

5.2.5 Nitric acid

No additional information

5.2.6 Hydrochloric acid

No additional information

5.2.7 Water

No additional information

5.2.8 Absorption solution

EN 14385 states that the absorption solution must be freshly made. The diluted nitric acid solution shall be prepared at a permanent laboratory. The addition of peroxide to the acid solution may be carried out at the laboratory or on site.

The elements being determined shall be below 1 µg/l in the absorption solution.

5.2.9 Boric acid solution

No additional information

5.2.10 Chemical blank solution for digestion

At least one digestion blank shall be prepared with each batch of samples.

5.2.11 Rinsing acid

The standard states that the rinsing acid is used for rinsing the digestion equipment. The rinsing acid is used on site to rinse the nozzle probe and filter housing (see section 8.4.2)

EN 14385 specifies the use of 25% mass content nitric acid for rinsing glassware on site. Because of health and safety concerns, nitric acid with a 5% mass content may be used.

The elements being determined shall be below 1 µg/l in this solution. This shall be confirmed before use.

5.2.12 Standard solutions

No additional information

5.2.13 Certified reference material

No additional information

5.2.14 Gases

No additional information

6. Sampling equipment

6.1 General requirements

No additional information

6.2 Isokinetic sampling equipment

No additional information

6.3 Absorbers

The absorber efficiency test compares the concentration of each element found in the third absorber with the concentration of that element in the total sample train.

A number of metals are often measured together as a group and are summed for comparison with an ELV for total metals. For example, metals are typically reported in two groups:

- Cd and Tl
- Sb, As, Pb, Cr, Co, Cu, Mn, Ni, & V

The absorber efficiency test is applied separately to each group of metals.

If one of the individual metal elements in the last impinger (e.g. Sb) is more than 10% of the total combined metals for that individual element (i.e. the filter, probe rinse and impingers) collected, then the result for all the metals in that group shall be rejected.

However, for each group the requirement to pass the absorber efficiency check shall not apply:

- to individual metal element(s), where the individual mass of the element in the final result is less than 1% of the result for the total mass of metals in the group; or
- if the total combined result for the metals in the group is less than 30% of the ELV.

The absorber efficiency check becomes less effective as the concentration of the pollutant in a stack gas decreases.

For example:

- Cd and Tl combined – 0.05 mg/m³
- Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V combined – 0.5 mg/m³

For Cd and Tl combined it would not be necessary to comply with the less than 10% in the last impinger criteria, if the overall combined Cd and Tl result for the sample train was below 0.015 mg/m³ (i.e. <30% of the ELV).

For combined metals (Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V) it would not be necessary for each individual element to comply with the less than 10% in the last impinger criteria, if the overall combined result for the sample train was below 0.15 mg/m³ (i.e. <30% of the ELV).

7. Cleaning of the sampling equipment prior to sampling

The following is a proven cleaning procedure:

- Rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water,

followed by three additional rinses with HPLC water. Then soak all glassware in a 10 percent (v/v) nitric acid solution for a minimum of 4 hours, rinse three times with water and then rinse a final time with acetone and allow to air-dry. Cover all glassware openings until the sampling train is assembled for sampling (this procedure is specified in US EPA method 29).

The above procedure also includes glass and titanium probe liners. However, it may not be practical to soak probe liners for 4 hours in a nitric acid solution. An alternative is to circulate the rinsing solution for 15 minutes.

It is permissible to use an alternative cleaning procedure, if an analytical laboratory provides evidence to UKAS that the procedure is equivalent to the procedure specified above.

A consistently low field blank results help demonstrate that an alternative cleaning procedure is effective.

Although it is acceptable to re-use glassware on different stacks, it may not be advisable because of the risk of contamination.

8. Procedure

8.1 General requirements

EN 14385 states that the sampling probe and out-stack filter shall be maintained at a temperature of at least 20°C above stack gas temperature. However, due to limitations on the equipment, it is not necessary to heat the sampling probe and out-stack filter to temperatures above 180°C.

Details of the probe and filter temperature shall be included in the report.

8.2 Preparation and installation of equipment

No additional information

8.3 Performance of the sampling

No additional information

8.4 Disassembling the equipment

Aluminium foil shall not be used to cap sample trains.

8.5 Field blanks

A blank shall be taken at each stack during a sampling campaign. A campaign is defined as one site visit.

8.6 Requirements for storage of the samples

Samples shall be stored during transport in a cool dark place, such as a cool box packed with ice or plastic freezer packs. An appropriate temperature measurement / indication device shall be used to confirm that the temperature is maintained below 25°C.

Note: this approach is based on the requirements in US EPA M29 and VDI 3869.

8.7 Pre-treatment before analysis

No additional information

8.8 Analysis

Linearity shall be checked and the correlation coefficient should be 0.98 or better. Analyte additions can be used as an alternative calibration technique and internal standards may be added to correct for transport effects and instrument drift.

Suitable quality checks (QCs) should be prepared and measured with each batch of samples. For filters, a suitable certified reference material (CRM) can be used if available. If no CRMs are available then a spiked filter may be exposed to the digestion process instead. For adsorption and rinsing solutions, spiked solutions can be used. For all QCs a recovery of 100 ± 20 % of the expected or certified value is acceptable. If any QC results are outside this range then this must be highlighted in the final report. If recoveries are outside the required range sampling and analysis stages may have to be repeated.

Adsorption and rinsing solutions are tested as part of the blank solution for digestion and, consequently, do not need to be done separately.

9. Expression of results

If results are at or below the limit of detection then they shall be reported as being at the detection limit.

10. Test report

No additional information

Annexes

No additional information