

Method for the determination of antimony trioxide

Method tested and recommended by the Berufsgenossenschaften for the determination of antimony and its compounds in working areas after discontinuous sampling. For the assessment of working areas, both personal and stationary sampling are possible.

- 1 Sampling with a pump and collection on a particle filter,
atomic absorption spectrometry with the flame technique.
(Issue: August 1987. This method replaces that of August 1985)
Cancelled, April 2002
- 2 Sampling with a pump and collection on a particle filter,
atomic absorption spectrometry with the hydride technique.
(Issue: August 1987)
“Antimony trioxide-2-AAS”

IUPAC name:
antimony(III)-oxide

CAS No.:
1309–64-4

2 Sampling with a pump and collection on a particle filter, atomic absorption spectrometry (AAS) with the hydride technique

Principle: With a pump a measured air volume is drawn through a filter. Antimony and its compounds contained in the dust collected are transformed after wet-ashing into antimony hydride and determined by atomic absorption spectrometry (hydride technique).

Technical data:

Quantification limit for antimony using cellulose ester membrane filter:

Air sample volume	Volume of the sample solution	Filter diameter	Quantification limit	
			relative (air)	sample solution
(m ³)	(ml)	(cm)	(µg/m ³)	(µg/l)
0,42 ¹	25	3,7	1,8	30
45 ²	100	15	0,07	30

¹ personal sampling (e. g. PGP with suitable pump) [1]

² stationary sampling (e. g. Gravikon VC 25 G) [2, 3]

Selectivity: Highly selective for antimony, not really selective for antimony trioxide

Advantages: Personal sampling possible.

Disadvantages: Time-consuming,
high sophisticated apparatus.

Apparatus: Sampling device,
consisting of particle filter,
if necessary with suction probe,
pump with gas meter or flow meter,
atomic absorption spectrometer with an accessory unit for the
hydride technique.

Detailed description of the method

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Summary

This method permits the determination of the concentrations of particulate antimony and its compounds in dust from working areas averaged over the sampling time after personal or stationary sampling.

With a pump carried by a person during working hours or used in a stationary position, a measured air volume is drawn through a particle filter. The antimony and its compounds collected by the filter is determined after wet-ashing by the hydride AAS technique.

The relative quantification limit is 2 $\mu\text{g}/\text{m}^3$ antimony trioxide for a 420-litre air sample.

2 Equipment, chemicals and solutions

2.1 Equipment

For sampling:

Dust collecting device: Suitable are sampling devices which collect the inhalable dust fraction in accordance to DIN EN 481 [1, 2].

Pumps must be used whose flow rate is sufficiently independent of the pressure drop at the filter.

Glass-fibre filters,
membrane filters:

3,7 cm diameter for personal, 15 cm diameter for stationary sampling.

With the test aerosol, paraffin oil mist, the filters should have a transmission rate of max. 0.5 % [3, 4, 5].

Membrane filters with 0.8 µm pore size are preferable used.

Binder-free glass-fibre filters can also be used in particular with large air sample volumes ($> 1 \text{ m}^3$).

For sample preparation and analysis:

Filter: Paper filter (Class 2) or PTFE-Membrane-filter.

Atomic absorption
spectrometer:

Commercially available apparatus, hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL) for antimony, heated quartz cuvette.

Hydride system:

Accessory unit for the reduction of the dissolved antimony to gaseous antimony hydride with sodium borohydride (NaBH_4).

Evaluation unit
Glass equipment:

The glass equipment must be made of borosilicate or quartz glass.

Beakers, 50 ml, 250 ml.

Volumetric flasks, 25 ml, 100 ml, 1000 ml.

Microlitre pipettes.

Before use, the glass equipment must be washed with a ten-side solution and rinsed with distilled water. Then it is cleaned with hot concentrated nitric acid and again rinsed with distilled water.

2.2 Chemicals

Sodium hydroxide, analytical grade

Sodium borohydride, NaBH_4 , analytical grade

Sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$, analytical grade

Nitric acid, analytical grade, 65 %

Potassium iodide, analytical grade

Hydrochloric acid, analytical grade, 36 %

2.3 Solutions

Sodium hydroxide solution:	Solution of 2 g sodium hydroxide/100 ml water 20 g sodium hydroxide dissolved in water is placed in a 1000 ml volumetric flask. The flask is filled to the mark with water. (NaOH concentration = 0.5 mol/l).
Reduction solution:	Solution of 5 g sodium borohydride/100 ml sodium hydroxide solution 5 g sodium borohydride is dissolved in sodium hydroxide solution in a 100 ml volumetric flask which is then filled to the mark with sodium hydroxide solution.
Hydrochloric acid:	Hydrochloric acid 1,5 % resp. 3 % 40 ml resp. 80 ml hydrochloric acid 36 % is placed in a 1000 ml volumetric flask which is then filled to the mark with water.
Antimony stock solution*:	Standard solution containing 1000 µg antimony/ml (as SbCl ₃ in hydrochloric acid (HCl concentration = 5 mol/l)).
Antimony calibration solution:	Solution of 1 µg antimony/ml 1 ml antimony stock solution is pipetted into a 1000 ml volumetric flask which is then filled to the mark with 1.5 % hydrochloric acid. This solution must be freshly prepared each day when needed.
Inert gas:	Argon or Nitrogen as inert gas and for rinsing the quartz cuvette.

3 Sampling

Sampling is carried out under the conditions described in Section 2.1. The air sample volume drawn through the filter in one minute should not exceed 2.4 l per cm² filter surface area.

4 Analytical determination

4.1 Sample preparation (wet-ashing)

The loaded particle filter of 3,7 cm diameter [15 cm diameter] is placed in a 50 ml [250 ml] beaker and 25 ml [100 ml] 3 % hydrochloric acid is added. The beaker is carefully heated on a hot plate with temperature control (about 200 °C) until the solution has evaporated to about 20 ml. The solution is filtered (see Section 2.1) and transferred

* Suitable antimony standard solutions are commercially available in this concentration.

to a 25 ml [100 ml] volumetric flask, which is then filled to the mark with 3% hydrochloric acid (sample solution).

To determine the blank value, unloaded filters of the same batch are prepared in the same way.

4.2 Analysis

The atomic absorption spectrometric determination of antimony is carried out at a wavelength of 217.6 nm using 1 ml of the sample solution and 2.5 ml reduction solution per determination.

The temperature of the AAS quartz cuvette for the characteristics given in Section 7 was 900 °C.

5 Evaluation

5.1 Calibration

Volumes of e.g. 10 µl, 50 µl, 100 µl and 200 µl of the antimony calibration solution are each pipetted into a beaker. An unloaded particle filter is added to each. The solution is prepared under the conditions described in Section 4.1.

The calibration curve is obtained by plotting the absorbances, corrected for the blank value, against the corresponding antimony weights.

5.2 Calculation of the analytical result

With the calibration curve, the amount of antimony is determined from the absorbance of the sample solution corrected for the blank value.

The concentration by weight of antimony in the air sample in mg/m³ is calculated according to equation (1):

$$c_w = \frac{w}{V} \quad (1)$$

Where:

c_w Concentration of antimony in the air sample in mg/m³

w Weight of antimony in the sample solution in µg taken from the calibration curve

V Air sample volume in l

To receive the concentration of antimony trioxide the result has to be multiplied with a stoichiometric factor of 1,971.

6 Reliability of the method

6.1 Accuracy

As a result of the different composition and properties of the aerosols in different working areas, it is not possible to make a generally valid statement about the accuracy of the procedure.

Particle filters were loaded each with 250 µl of antimony calibration solution (corresponding to 0,6 mg/m³ antimony for a 420 l air sample) and subjected to the whole procedure (wet-ashing). The relative standard deviation for 12 individual determinations was 1.9%.

6.2 Quantification limit

The quantification limit for antimony depends not only on the quality of the chemicals used, but also on the equipment and its condition.

Air sample volume	Volume of the sample solution	Filter diameter	Quantification limit	
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6.3 Selectivity

Highly selective for antimony, not really selective for antimony trioxide.

7 Discussion

If the described procedure (see Section 4.1) is used only negligible quantities of penta-valent antimony are determined.

For getting the total concentration of antimony different sample preparations have to be used.

8 Suppliers

Pump:	e. g. Du Pont Instruments, supplier in Germany: DEHA-Haan & Wittmer GmbH, Friolzheim
Glass-fibre filter, membrane filter:	e. g. Drägerwerk AG, Lübeck Macherey-Nagel GmbH & Co KG, Düren Millipore, Neu Isenburg Schleicher & Schüll GmbH, Dassel
Dust collector:	e. g. VC 25 G, Ströhlein GmbH & Co, Kaarst
Dust collection head:	e. g. BIA-Gesamtstaubsammelkopf, Ströhlein GmbH & Co, Kaarst
Atomic absorption spectrometer, hydride system:	e. g. AGW Analysen-Geräte GmbH, Leutkirch Beckman Instruments GmbH, Munich Bodenseewerk Perkin Elmer & Co GmbH, Überlingen Varian GmbH, Darmstadt Colora Meßtechnik GmbH, Lorch Philips GmbH, Kassel
Antimony standard solution:	e. g. Merck, Darmstadt Riedel de Haen, Seelze

9 References

- [1] *European Committee for Standardisation (CEN)* (1993) DIN EN 481, Workplace atmospheres-Size fraction definitions for measurements of airborne particles. Brussels. Beuth Verlag, Berlin
- [2] *Siekman H, Blome H* (1994) Auswirkung der Europäischen Norm EN 481 auf die Probenahme von Partikeln in der Luft in Arbeitsbereichen. Staub-Reinhalt. Luft 54: 95–98
- [3] *Coenen W, Meffert K (Eds)* (1989) Messung von Gefahrstoffen – BIA-Arbeitsmappe. Erich Schmidt Verlag, Bielefeld (lose-leaf collection)
- [4] *VDI-Richtlinie 2265* “Feststellung der Staubsituation am Arbeitsplatz zur gewerbehygienischen Beurteilung“
[1] *European Committee for Standardisation (CEN)* (1993)
- [5] *Siekman H, Schwaß D.* Pumpen zur personenbezogenen Probenahme von Gefahrstoffen am Arbeitsplatz, in Coenen W, Meffert K (Eds) (1985) BIA-Handbuch. Erich Schmidt Verlag, Bielefeld (lose-leaf collection)