# Lead

Application	Air analysis
Analytical principle	Flame and electrothermal Atomic absorption spectrometry
Completed in	June 1985

## Summary

Airborne lead collected from workplaces is deposited on particle filters using suitable dust collectors. For this purpose defined air volumes are sucked through cellulose nitrate membrane filters by a pump which samples the ambient air from the breathing zone of exposed persons or a stationary monitoring pump. After wet chemical treatment the particulate lead in the collected dust is determined by means of flame atomic absorption spectrometry or in a graphite furnace, depending on the workplace concentration, the analysis time and the type of dust collector.

a) Flame AAS

Precision:	Standard deviation (rel.) $s = 4.6-2.7 \%$ Mean variation $u = 10.4-6.1 \%$ at concentrations of 100 and 200 µg of lead/m <sup>3</sup> air where $n = 10$ determinations
Detection limit:	33 $\mu$ g lead/m <sup>3</sup> air, (for a sample volume of 480 L and a sampling time of 4 h)
Recovery rate:	$\eta = 0.96 - 0.99 \; (96 - 99 \; \%)$
b) Electrothermal AAS	
Precision:	Standard deviation (rel.) $s = 8.7-6.3 \%$ Mean variation $u = 19.4-12.7 \%$ in a concentration range from 1 to 2 µg of lead/m <sup>3</sup> of air and $n = 10$ or 5 determinations
Detection limit:	1 $\mu$ g of lead/m <sup>3</sup> of air (for a sample volume of 480 L, a sampling time of 4 h and an injection volume of 50 $\mu$ L)
Recovery rate:	$\eta = 0.94 - 0.92 \; (94 - 92 \; \%)$

	Personal sampling	Permanent monitoring station
Recommended sampling time:	4 h	10 min
Recommended sample volume:	480 L	$3,75 \text{ m}^3$

## Lead

Lead is a soft, pliable, bluish-grey heavy metal (density 11.34 g/cm<sup>3</sup>, atomic mass 207.2 g/mole) with a melting point of 327 °C and a boiling point of about 1750 °C. Elementary lead is extracted by smelting various lead ores, among which lead glance (galenite) PbS is of particular importance.

Lead and the majority of its compounds have wide-spread industrial applications. For example, it is used in the manufacture of accumulators. Organolead compounds are used as additives in fuel refineries and in the production of pigments as well as anticorrosive materials.

It must be assumed that health hazards exist where dust or smoke containing lead (the element itself vaporizes markedly at temperatures as low as 550 to 600 °C, forming lead dioxide) or its compounds are present.

In the MAK list [1] lead is classified in Peak Limitation Category III, substances with systemic effects and strongly cumulative properties. The peak exposure level may reach ten times the MAK value (average value during 30 min) only once in an 8 hour shift. Absorption into the organism occurs mainly through the respiratory tract or the gastro-intestinal tract. However, in the case of exposure to organolead compounds absorption through the skin must also be taken into account. The target organs for intoxication by lead and its inorganic compounds are the smooth muscles, the motor nervous system and the haematopoietic system. The most serious consequences of extreme over-exposure to lead are dysfunction of the cranial nerves and encephalopathy. Correlation between blood lead concentrations (Pb-B), the excretion of lead in the urine (Pb-U) and the airborne lead concentrations (Pb-A) at workplaces has been reported [2–5].

These investigations show that the relationship between the external (airborne lead) and the internal (blood lead) concentrations may be subject to great variation. If the current MAK value of 0.1 mg of lead /m<sup>3</sup> of air is not exceeded [1], blood lead concentrations of 60  $\mu$ g/100 mL should be reached [5, 6] only in exceptional cases. The present BAT-value is 70  $\mu$ g/100 mL or 45  $\mu$ g/100 mL (for women <45 years) [5].

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# **1** General principles

Airborne particles of lead or its compounds are deposited on cellulose membrane filters by a pumping device. After a wet chemical treatment of the loaded filters with nitric acid, the lead concentration is determined from a calibration curve by atomic absorption spectrometry. Depending on the concentration in the air and on the sampling period, flame or electrothermal AAS in combination with the standard addition procedure is used.

# 2 Equipment, chemicals and solutions

#### 2.1 Equipment

Dust collectors:

The working capacity of the pumps with a suction velocity of  $1.25 \text{ m/s} \pm 10 \%$  should be independent of the pressure drop at the filter. For personal as well as for stationary sampling, the dust collector heads must be suitable for collecting total dust [7].

Personal sampling: Personal air sampler with air flow adjustable from 1.2 to 240 L/h and a dust collector head with an air flow of 2 L/h

Stationary sampling: Dust collector with an air flow of 22.5 m<sup>3</sup>/h

Cellulose nitrate membrane filter with a pore size of 8  $\mu$ m or 0.8  $\mu$ m and a filter diameter of 150 mm or 37 mm, respectively

Heated magnetic stirrer, adjustable

Magnetic stirring bars

Atomic absorption spectrophotometer with the option of background correction at the measuring wavelength and laminar burner as well as a graphite furnace Recording unit

Lead ED lamp including power supply unit or lead concave cathode lamp

Graphite tubes, normal, uncoated

Centrifuge

Beakers, 150 or 250 mL

50, 100, 500 and 1000 mL Volumetric flasks

5 mL Graduated pipettes

Disposable polyethylene tubes with stoppers

10–100 and 100–1000 µL Adjustable automatic pipettes

Disposable tips

Plastic forceps

## 2.2 Chemicals

Lead standard solution (e. g. Titrisol) containing 1 g lead in the form of lead(II)nitrate Nitric acid (65 %) of the highest purity (e.g. Suprapur from Merck) Highly purified water (ASTM type 1), or double-distilled water Argon, 99.998 % Acetylene, 99 % Compressed air

#### 2.3 Solutions

1 M nitric acid for cleaning the vessels

#### 2.4 Calibration standards

Initial solution:

The standard solution (1.0 g lead) is diluted with highly purified water in a 1 L volumetric flask (1 g/L)

Stock solution:

From the initial solution 5 mL are pipetted into a 500 mL volumetric flask and diluted with highly purified water (10 mg/L). Calibration standards or standard addition solutions are prepared by diluting the stock solution with highly purified water. The stock solution and the standards should be freshly prepared for each series of analyses.

Calibration standards for flame AAS

Volume of the initial solution mL	Final volume of the calibration standards mL	Concentration of the calibration standards mg/L
0.1	100	1
0.2	100	2
0.3	100	3
0.4	100	4
0.5	100	5

Standard addition	solution f	for electrothermal	AAS
Standard addition	solution		11110

Volume of the	Standard add	lition solution	No.
stock solution	Final volume	Concentration	
mL	mL	µg/L	
1	100	100	I
2	100	200	II
3	100	300	III

## 3 Sample collection and preparation

In order to avoid any exogenous lead contamination, all glassware and polyethylene vessels used for sampling and sample treatment must be cleaned with 1 M nitric acid, thoroughly washed with highly purified water and dried at room temperature. The membrane filters should be taken out of their packaging and inserted into the holder on the dust collector only at the sampling location.

#### 3.1 Sampling

The measurement strategy, i.e. sampling of the air inhaled by an exposed worker or monitoring with a stationary device, is selected according to the problem to be investigated. The former sampling method gives more representative results for workplaces at which the emission source is concentrated at one point [8, 9] e.g. during welding processes, while monitoring with a stationary device has proved to be practicable for sampling when the emission source is more extensive. In the latter case, samples can be collected at one or several locations, according to the size of the work area and distribution of the expected workplace concentrations, in order to obtain representative results for the exposure to the hazardous material.

The sampling time must be selected to ensure that the samples collected are representative of the exposure. The objective is always to determine the average exposure for the whole shift. If the sampling time practicable with the analytical procedure is shorter than a shift, the minimum number of measurements required for the given sampling time must be established by consulting TRGS 402 [10]. According to these regulations, the present method must be able to determine concentrations of lead and its compounds in the range between one tenth of and three times the MAK value.

For personal sampling, the flow rate is adjusted at the pump to 2 L/min, to correspond with the intake velocity specified for the personal dust collector. For stationary sampling at an air intake velocity of 22.5 m<sup>3</sup>/h, a 10 minute sampling period is sufficient (sample volume  $3.75 \text{ m}^3$ ).

After sampling is completed, the exposed filters are stored in closed containers, if possible in those in which further sample treatment will be carried out (e.g. 150 mL beakers for filters of 37 mm diameter and 250 mL beakers for filters of 150 mm diameter).

## 3.2 Sample treatment

The filters are treated with highly purified water and nitric acid in a ratio of 1:1. The final volume should be 10 mL in the case of the smaller filters and 50 mL for the 150 mm filters. The samples are concentrated to a volume of 3 or 15 mL, respectively, on a hot plate at 180 °C with a magnetic stirrer. This procedure is repeated after adding 3 or 25 mL, respectively, of concentrated nitric acid. The solution is transferred into a 50 mL volumetric flask; the beakers are rinsed and the rinsings added to the flask which is then filled up with highly purified water. After mixing thoroughly, the insoluble components are removed by centrifugation and the clear solution is decanted into polyethylene tubes for further analysis. Unused filters from the same batch are treated in the same way to determine the blank value.

## 4 Operating conditions for atomic absorption spectrometry

Atomic absorption spectrophotometer:Wavelength:283.3 nmBackground compensation:Deuterium lamp

Spectral slit width:0.7 nmLamp current:According to the manufacturer's instructions

Electrothermal AAS:

Decomposition and atomization temperatures and times must be selected by the operator for each individual instrument. The following temperature/time schedule is only intended as a guide.

Analysis phase	Duration of the heating phase	Isothermal phase	Temperature	
	s	S	°C	
Drying	2	30	110	
Decomposition	2	30	500	
Atomization	0	5	2300	
Annealing	0	3	2700	

Type of graphite furnace:	Normal, uncoated
Inert gas:	Argon, internal gas flow 300 mL/min
Injected volume:	50 μL
Flame AAS:	
Detector gases:	Acetylene/compressed air

# **5** Analytical determination and calibration

## **5.1 Electrothermal AAS**

The following pipetting plan has proved to be suitable for the analysis by electrothermal AAS:

Sample identification	Sample volume	Highly purified water	Standard a 100 µg/L I	addition sol 200 µg/L II	lution 300 µg/L III	Lead concen- tration added to the sample solution
	μL	μL	μL	μL	μL	µg/L
no addition	800	200	_	_	_	_
1st addition	800	_	200	_	_	25
2nd addition	800	_	_	200	_	50
3rd addition	800	_	_	_	200	75
Reagent blank	800	200	_	_	_	_

 $50 \ \mu L$  of the sample solution is injected into the graphite furnace. The extinction of the sample without any standard addition solution should not exceed a value of 0.06. Otherwise the injected volume must be reduced or the sample solution must be diluted.

## 5.2 Flame AAS

After the burner, the fuel gas and the sprayer have been adjusted to optimum conditions, the calibration standards and the sample solution are sucked directly into the flame and measured. The results are evaluated from the maximum extinction values for each concentration of the calibration standards.

# 6 Calculation of the analytical result

Reference standards with known lead concentrations are measured for calibration (cf. Section 2.4). After subtraction of the reagent blank, the extinctions are plotted against the concentration (Fig. 1).

The graphic determination of the lead concentration in air using the standard addition method is shown in Fig. 2. The peak heights (if necessary, with the reagent blank sub-tracted) are plotted against the added lead concentration. The intersection of this line with the abscissa (concentration axis) is a measure of the lead concentration in the sample.

In both cases the lead concentration  $(mg/m^3 \text{ or } \mu g/m^3)$  is calculated by multiplying the graphically determined result  $(mg/L \text{ or } \mu g/L)$  by the factor obtained on dividing the volume of the sample solution (mL) by the collected air volume (L) (example: 50 mL sample solution, 480 L air volume  $\rightarrow$  factor 0.104).

# 7 Reliability of the method

## 7.1 Precision

In order to determine the precision in the flame AAS series, filters with a simulated airborne lead concentration of 100 and 200 µg lead/m<sup>3</sup> were analyzed. A total of n = 10 determinations gave a relative standard deviation of s = 4.6-2.7% with a range of mean variation of u = 10.4-6.1%.

The electrothermal AAS method gave a standard deviation (rel.) of s = 8.7-6.3 % with a mean variation of u = 19.4-12.7% when the filters bore quantities of lead equivalent to 1 and 2 µg of lead/m<sup>3</sup> of air.

# 7.2 Recovery rate

On the basis of n = 10 determinations, the recovery rate for flame AAS ranged from 96 to 99 % and in the case of the electrothermal AAS method from 92 to 94 %. The

simulated lead loading of the filters was equivalent to the current MAK value of  $0.1 \text{ mg/m}^3$  for lead.

#### 7.3 Detection limit

A concentration of 33  $\mu$ g lead/m<sup>3</sup> was detected in an air volume of 480 L by means of flame AAS. The detection limit of the atomic absorption spectrometric method with the same volume of air and an injection volume of 50  $\mu$ L was 1  $\mu$ g lead/m<sup>3</sup>.

#### 7.4 Sources of error

When the conditions for sampling, calibration and analysis are observed, no interference is to be expected.

## 8 Discussion of the method

The method described permits the reliable determination of airborne lead concentrations. When the air inhaled by exposed workers was sampled with personal samplers for 4 h, which is a representative time for assessing an 8 hour shift [10], about a third of the lead MAK value can be accurately detected with flame AAS. For electrothermal AAS under the same conditions, the value is  $1 \mu g/m^3$  (1/100 MAK).

With stationary sampling and the above-mentioned detection limit, the sampling time decreases. With a sampling time of about 10 min and an air flow rate of 22.5 m<sup>3</sup>/h, concentrations lower than a tenth of the MAK value can be detected by means of flame AAS.

The method described here is suitable for routine monitoring of workplaces where health is endangered by fumes and dust containing lead compounds. At lead concentration levels > 10% of the MAK value, it is advisable to use flame AAS. On the one hand, application of flame AAS is more economical, on the other, if ETAAS is used when higher concentrations of lead are present at the workplace, the analyte solutions must be diluted (up to two factors of ten). Experience shows that this leads to large errors in practice.

Apparatus:

Atomic absorption spectrophotometer 400 with a graphite furnace HGA 76 and burner device (batwing burner) and autosampler AS 1 from Perkin-Elmer

10 mV Recorder (Perkin-Elmer)

Pump: personal air sampler P 4000 (Du Pont Instruments) equipped with a head for total dust collection BIA\* (Ströhlein)

Dust collector: VS 25 G (Ströhlein)

Filter: cellulose nitrate membrane filter, 37 mm diameter, 0.8  $\mu$ m pore size (Sartorius); cellulose nitrate membrane filter, 150 mm diameter, pore size 8  $\mu$ m (Sartorius)

<sup>\*</sup> BIA = Berufsgenossenschaftliches Institut für Arbeitssicherheit

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Fig. 1. Calibration curve for the determination of lead by means of flame AAS.



Fig. 2. Graphic determination of the lead concentration by means of ETAAS using the standard addition procedure.