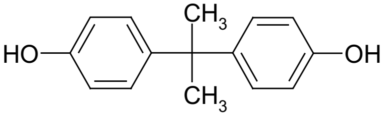
Method for the determination of bisphenol A

German Social Accident Insurance
Deutsche Gesetzliche Unfallversicherung
Analytical Subcommittee of the Chemistry Board of Experts*

Carcinogenic substances	Order number:	BGI 505-75-01
Established methods:	Issued:	May 2009

This method has been tested and recommended by the German Social Accident Insurance for the determination of bisphenol A at workplaces.
Both personal and stationary sampling can be performed for assessment of workplaces.

Sampling is carried out with a pump and collection on a glass fiber filter. Analysis is performed by high-performance liquid chromatography (HPLC) after desorption.

Chemical names:	Bisphenol A; 4,4′-dihydroxy-2,2-diphenylpropane; 2,2-bis-(4-hydroxyphenyl)propane
CAS number:	80-05-7
Molecular formula:	$C_{15}H_{16}O_2$
Molar mass:	228.28 g/mol
Structural formula:	

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Summary

This method permits determination of the bisphenol A concentration at workplaces averaged over the sampling time after personal or stationary sampling.

Principle: A pump draws a defined volume of air through a GSP sampling system equipped with a glass fiber filter. The collected bisphenol A is desorbed with acetonitrile and analyzed by means of liquid chromatography.

Limit of quantification: Absolute: 1.4 ng of bisphenol A
Relative: 5 µg/m^3 of bisphenol A for an air sample of 200 L, a sample solution of 3 mL and an injection volume of 4 µL.

Selectivity: Elevated values may be caused by interferents. Interference in general can be avoided by selecting different separation conditions.

Advantages: Personal and selective measurements are possible.

Disadvantages: No indication of peak concentrations.

Apparatus: Pump with volumetric flow meter, GSP sampling system with an intake cone for a flow rate of 1 L/min, glass fiber filter, liquid chromatograph with UV/VIS or diode array detector (DAD).

Detailed description of the method

Contents

1

Equipment, chemicals and solutions

1.1

Equipment

For sampling:

- Pump, suitable for a flow rate of 1 L/min, e.g. BUCK-GENIE VSS5, from Ravebo Supply B.V., t'Woud 2, 3232 LN Brielle, Netherlands
- Gas meter or volumetric flow meter
- Glass fiber filter, diameter 37 mm, e.g. GF 6, MACHEREY-NAGEL, 52355 Düren, Germany
- GSP sampling system with an intake cone for a flow rate of 1 L/min, from DEHA, Haan & Wittmer, 71296 Heimsheim, Germany

For sample preparation and analysis:

- Volumetric flasks, 1 mL, 10 mL, 100 mL
- Sample vials with sealing caps (PTFE-coated sealing caps), 10 mL
- Sample vials, 1 mL

- Adjustable piston pipettes with a volume range from 100 µL to 1000 µL, suitable for solvents, e.g. Micromar, from Abimed, 40764 Langenfeld, Germany
- Microliter syringes, 1 µL, 10 µL, 100 µL
- HPLC instrument with gradient pump control and a UV/VIS or diode array detector (DAD)
- Water purification unit, e.g. Milli-Q plus, Millipore, 65760 Eschborn, Germany
- Shaker, e.g. MTS 4, IKA, 79219 Staufen, Germany

1.2
Chemicals and solutions

Bisphenol A, purity of at least 99%, e.g. Aldrich, 82024 Taufkirchen, Germany
For operation of the HPLC:

- Ultrapure water
- Acetonitrile, purity of at least 99%, e.g. Promochem, 46485 Wesel, Germany

Stock solution:	Solution of approx. 1000 µg of bisphenol A per mL acetonitrile. Approx. 20 mg of bisphenol A are weighed exactly to the nearest 0.1 mg into a 20 mL volumetric flask. Then the flask is filled to the mark with acetonitrile and shaken.
Calibration solutions:	Solutions of 2.05 to 410 mg of bisphenol A per L acetonitrile. The volumes of the stock solution shown in Table 1 are each pipetted into six separate 10 mL volumetric flasks, the flasks are filled to the mark with acetonitrile and shaken.

Table 1 Calibration solutions.

Solution	1	2	3	4	5	6
Stock solution added in µL	20	200	500	1000	2000	4000
Bisphenol A in mg/L	2.05	20.5	51.3	103	205	410

For an air sample volume of 200 L, a concentration range from approx. 0.03 to 6 mg/m^3 is covered by these solutions.

2
Sampling procedure

For sampling the GSP sampling system is connected to the pump. The flow rate is adjusted to 1 L/min. Thus the definition of inhalable dust according to DIN EN 481 [2] is fulfilled. The pump and the sampling system are either worn by a person at the workplace or set up for stationary sampling. The maximum air sample volume is 200 L.

After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discount the measurement (see BGI 505-0 “General Part”, Section 3 [1]).

Then the filter holder is removed from the sampling system and sealed.

3
Analytical determination

3.1
Sample preparation and analysis

The glass fiber filter is transferred to a 10 mL sample vial and covered with 3 mL of acetonitrile. Then the vial is sealed and shaken for two hours (sample solution).

In order to ensure that the acetonitrile used for desorption and the glass fiber filter contain no interfering impurities, a glass fiber filter that was not used for sampling is desorbed with 3 mL of acetonitrile (blank solution).

4 µL each from the blank solution and the sample solution are injected into the liquid chromatograph. Then chromatograms, as described in Section 3.2, are recorded (measurement wavelength 220 nm).

3.2
Operating conditions for HPLC

The characteristics of the method stated in Section 5 were determined under the following experimental conditions:

Apparatus:	Hewlett Packard 1100 with UV/VIS detector and autosampler
Column:	Length: 150 mm; inner diameter: 2.1 mm; stationary phase: GL Sciences Inertsil ODS3 3 µm, MZ-Analysentechnik, 55120 Mainz, Germany
Elution:	Gradient elution (see Table 2) Eluent A: Water Eluent B: Acetonitrile
Flow rate:	0.2 mL/min
Injection volume:	4 µL
Measurement wavelength:	220 nm
Oven temperature:	40 °C

Table 2 Gradient profile.

Time [min]	Eluent A [%]	Eluent B [%]
0	40	60
5	0	100
20	0	100
20.1	40	60
30	40	60

4
Evaluation

4.1
Calibration

4 µL of each of the calibration solutions stated as examples in Section 1.2 are injected into the liquid chromatograph and analyzed. The calibration function is obtained by plotting the areas determined versus the concentrations of bisphenol A in the respective calibration solutions. It is linear in the range investigated.

4.2
Calculation of the analytical result

The concentration of bisphenol A in the air sample in mg/m³ is calculated according to equation (1):

$$c = \frac{m}{V \times \eta} \tag{1}$$

where:

c is the concentration by weight of bisphenol A in the air sample in mg/m³
m is the mass of bisphenol A in the sample solution in µg obtained from the calibration function
V is the air sample volume in L
η is the recovery (see Section 5.1)

5
Reliability of the method

5.1
Precision and Recovery

The precision in the lowest measurement range according to DIN EN 482 [3] and the recovery for three different concentrations (see Table 3) were determined.

In order to determine the relative standard deviation of the method and the recovery, three different glass fiber filters were spiked with 10, 100 and 200 µL of the stock solution respectively. Then 200 L of laboratory air were drawn through the sampling system as described in Section 2. The spiked masses of bisphenol A correspond to concentrations of 0.05, 0.51 and 1.03 mg/m^3 for the investigated air sample volume. After storage in the refrigerator (4 °C) for 24 hours, the glass fiber filters were analyzed as described in Section 3.1. The relative standard deviations and recoveries shown in Table 3 were obtained when the procedure described above was carried out six times in each case.

Table 3 Precision and recovery.

Concentration [mg/m^3]	Standard deviation (rel.) [%]	Recovery
0.05	2.0	0.96
0.51	0.5	0.96
1.03	2.5	0.97

5.2
Limit of quantification

The absolute limit of quantification is 1.4 ng of bisphenol A. It was determined on the basis of the calibration line method as stipulated in DIN 32645 [4] for a calibration range of 4.1 to 51.3 ng, corresponding to a concentration of 15 to 192 µg/m^3 in air.

The relative limit of quantification is 5 µg/m^3 of bisphenol A for an air sample volume of 200 L, a sample solution of 3 mL and an injection volume of 4 µL.

5.3
Selectivity

The selectivity of the method depends above all on the type of separation column used and on the separation conditions. The separation conditions stated here have proved successful in practice.

6
Remarks

The loaded filters can be stored in the refrigerator (4 °C) for 14 days without loss of bisphenol A.

References

1 BGI 505-0 (2003) Von den Berufsgenossenschaften anerkannte Analysenverfahren zur Feststellung der Konzentrationen krebserzeugender Arbeitsstoffe in der Luft in Arbeitsbereichen – A. Allgemeiner Teil. Carl Heymanns Verlag KG, Köln.

2 DIN EN 481 (1993) Workplace atmospheres – Size fraction definitions for measurement of airborne particles. Beuth Verlag, Berlin.

3 DIN EN 482 (2006) Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents. Beuth Verlag, Berlin.

4 DIN 32645 (2008) Chemical analysis – Decision limit, detection limit and determination limit under repeatability conditions; Terms, methods, evaluation. Beuth Verlag, Berlin.

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