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# Carbon disulfide

<b>Method number</b>	2
<b>Application</b>	Air analysis
<b>Analytical principle</b>	Gas chromatography/mass spectrometry
<b>Completed in</b>	March 2005

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## Summary

The analytical method permits the determination of carbon disulfide in workplace air in a concentration range of 2.5 to 63.2 mg/m<sup>3</sup>. For sampling, a defined volume of the ambient air is drawn through a tube filled with charcoal using a suitable pump. For elution the charcoal loaded with carbon disulfide is covered with a mixture of toluene and dichloromethane and shaken. Analysis is carried out with gas chromatography coupled with mass spectrometry. Quantitative evaluation is performed in accordance with the method of an internal standard.

## Characteristics of the method

### Accuracy:

Standard deviation (rel.)	$s = 3.1\%$
Mean variation	$u = 6.9\%$
Measurement uncertainty (rel.)	$U = 6.2\%$ for $n = 10$ determinations and $c = 2.5 \text{ mg/m}^3$
Standard deviation (rel.)	$s = 2.6\%$
Mean variation	$u = 5.8\%$
Measurement uncertainty (rel.)	$U = 5.2\%$ for $n = 10$ determinations and $c = 31.6 \text{ mg/m}^3$
Standard deviation (rel.)	$s = 3.3\%$
Mean variation	$u = 7.5\%$
Measurement uncertainty (rel.)	$U = 6.6\%$ for $n = 10$ determinations and $c = 63.2 \text{ mg/m}^3$

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Limit of quantification:	1.14 mg/m <sup>3</sup> for an air sample volume of 40 liters
Recovery:	$\eta = 0.60 - 0.78$ (60–78%)
Sampling recommendation:	Sampling time: 2 hours Sampling volume: 40 litres

### Carbon disulfide [CAS-No. 75-15-0]

Carbon disulfide is a colourless liquid (molar mass 76.14 g/mol; boiling point 46.24 °C at 1013 mbar; vapour pressure 397 mbar at 20 °C) with an unpleasant sweetish smell. The substance is highly volatile, easily inflammable, less soluble in water, and heavier as water. Its vapour is inflammable and forms highly explosive mixtures with air.

Carbon disulfide is used in viscose industry for the manufacture of fibers. Furthermore, it is used for syntheses of fungicides and as vulcanization catalysts, for the gassing of cereals and soils, and as a solvent and extraction agent for fats, oils, waxes, and resins. Carbon disulfide is absorbed as the vapour via the respiratory tract and as the liquid through the skin. Concerning the toxicity of carbon disulfide, see MAK value documentation [1].

The MAK value of carbon disulfide is 16 mg/m<sup>3</sup> and 5 mL/m<sup>3</sup>, respectively [2]. In the List of MAK and BAT Values, the short-term value for carbon disulfide is classified in peak limitation category II with an excursion factor of 2 [2].

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## Content

- 1 General principles
- 2. Equipment, chemicals and solutions
  - 2.1 Equipment
  - 2.2 Chemicals
  - 2.3 Solutions
  - 2.4 Calibration standards
- 3 Sample collection and preparation
- 4 Operating conditions
- 5 Analytical determination
- 6 Calibration
- 7 Calculation of the analytical results
- 8 Reliability of the method
  - 8.1 Precision
  - 8.2 Recovery
  - 8.3 Limit of quantification
  - 8.4 Shelf-life
  - 8.5 Interferences
- 9 Discussion
- 10 References

## 1 General principles

To determine carbon disulfide in the air of workplaces, a defined air volume is drawn through a charcoal tube using a suitable pump. The adsorbed carbon disulfide is desorbed with a mixture of toluene and dichloromethylene. Qualitative and quantitative

analysis is performed by gas chromatography using a mass selective detector (MSD). Quantitative evaluation is carried out using a calibration graph.

## 2 Equipment, chemicals and solutions

### 2.1 Equipment

*For sampling:*

- Pump, suitable for flow rates of 33 mL/min, e.g. DU Pont Alpha 1 from DEHA-Haan & Wittmer GmbH, D-71296 Heimsheim
- Adsorptions tubes filled with charcoal (standardised, consisting of two sections filled with about 300 mg (sampling section) and 700 mg (backup section) of charcoal and separated by porous polymer material), type B, e.g. from Dräger Safety, D-23560 Lübeck
- PTFE-caps for the opened adsorption tubes

*For sample preparation and analysis:*

- 5, 10, and 500 mL volumetric flasks
- 2 and 20 mL glass vials with PTFE-coated septa and crimp caps
- Crimper
- 10 and 50 mL pipettes
- 5, 10, 25, 50, 100, 250, and 500  $\mu$ L injection syringes
- 5 mL disposable syringes with disposable filter holders (13 mm/0.45  $\mu$ m)
- Mechanical shaker
- Gas chromatograph with a mass selective detector (MSD) and a data system (Hewlett-Packard Model HP 6890/HP 5973)

### 2.2 Chemicals

- Toluene, purity 99.9%, e.g. from Riedel-de Haen, D-30926 Seelze
- Dichloromethane, purity 99.9%, e.g. from Merck, D-64271 Darmstadt
- Carbon disulfide, purity 99.9%, e.g. from Riedel-de Haen, D-30926 Seelze
- Ethanol-d, degree of deuteration 99.9%, from Merck, D-64271 Darmstadt

### 2.3 Solutions

*Desorption solution* (mixture of toluene/dichloromethane (9 + 1 v/v)):

50 mL of dichloromethane are placed into a 500 mL volumetric flask and the flask is filled to the mark with toluene.

*Internal standard solution* (178 mg of ethanol-d<sub>6</sub> per mL standard solution):

100  $\mu$ L of ethanol-d<sub>6</sub> and 400  $\mu$ L of the desorption solution are pipetted into a 2 mL crimp-vial and shaken after sealing the vial.

*Carbon disulfide stock solution* (Solution of 5 mg CS<sub>2</sub>/mL desorption solution): 50 mg of carbon disulfide (with an accuracy of 0.1 mg) are placed in a 10 mL volumetric flask which already contains a few mL of the desorption solution. The flask is filled to the mark with the desorption solution and shaken afterwards.

## 2.4 Calibration standards

Calibration standards containing 5 to 300 µg carbon disulfide/mL are prepared from the stock solution according to the pipetting scheme shown in Table 1.

**Table 1.** Pipetting scheme for the preparation of the calibration standard solutions.

Calibration solution No.	Volume of the stock solution [µL]	Volume of the internal standard solution [µL]	Finale volume of the calibration standard solution [mL]	Concentration of CS <sub>2</sub> [µg/mL]
1	10	10	10	5
2	20	10	10	10
3	40	10	10	20
4	60	10	10	30
5	100	10	10	50
6	200	10	10	100
7	300	10	10	150
8	400	10	10	200
9	500	10	10	250
10	600	10	10	300

With these solutions and a 40-litre air sample volume (shift average limit) a concentration range from 1.25 to 75 mg/m<sup>3</sup> is covered. By using an air sample volume of 5 L (short-time value) a concentration range between 10 and 600 mg/m<sup>3</sup> will be covered.

## 3 Sample collection and preparation

### *Sampling:*

A charcoal tube is opened and connected to the pump in a way that during sampling the collection phase is loaded at first. The flow rate is set at 0.33 L/min. A sample collection time of 2 h (shift average value) and of 15 min (short-term value), corresponds to an air sample volume of 40 and 5 L, respectively. The pump and collection tube are carried by a person during working hours or used in a stationary position. After sampling, the adsorption tubes are sealed tightly with PTFE caps and the sampling conditions are documented (temperature, sampling duration, and volume flow).

*Sample preparation:*

The content of the loaded charcoal tubes is transferred to a 20 mL volumetric flask. After adding 10 mL desorption solution, the flask is sealed tightly and shaken for 30 min. A part of the sample solution is removed with a 5 mL disposable syringe and filtered through a disposable filter holder into a 5 mL volumetric flask until the mark. Afterwards, 5 µL of internal standard are added to the sample solution and shaken thoroughly to ensure complete mixing. From this solution, a part is pipetted into a 2 mL sample vial. In order to check whether the desorption solution and/or the charcoal contain interfering contaminants, an unloaded charcoal tube is prepared in the same way as the sample tubes (blank experiment).

## 4 Operating conditions

*GC working conditions:*

Apparatus:	Gas chromatograph HP 6890 with autosampler combi PAL (from CTC Analytics AG)
Column:	Material: Quartz capillary
Length:	60 m
Internal diameter:	0.32 mm
	Stationary phase: Poly (6% cyanopropylphenyl- 94% dimethyl-)siloxane (Rtx-624 from Restex)
	Film thickness: 1.8 µm
Detector:	Mass selective detector (MSD)
Temperatures	Injector: 250 °C
	Oven: 50 °C (9 min) $\xrightarrow{10\text{ °C/min}}$ 180 °C (8 min)
Injection volume:	1 µL
Sample injection:	Split
Split flow:	20 mL/min
Split ratio:	20 : 1
Septum purge flow:	3 mL/min
Carrier gas:	Helium (99.999%)
Carrier gas flow:	1 mL/min

*MS working conditions:*

Apparatus:	Mass selective detector HP 5973
Temperatures:	Ion source: 230 °C
	Quadrupole: 150 °C
	Interface: 280 °C
Ionisation mode:	Electron impact ionization (EI)
Pressure in the ion source	$1.2 \times 10^{-5}$ kPa
Electron current	35 µA
Ionization energy:	70 eV

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Registration mode:	Selected ion monitoring (SIM)
	carbon disulfide: 76 and 44 m/e
	Ethanol-d <sub>6</sub> : 33 and 51 m/e
Dwell time:	100 ms

## 5 Analytical determination

1 µL of each sample solution and blank experiment is injected in at least repeated determination into the gas chromatograph and analysed under the conditions as described in Section 4. In Figure 1, an example of a chromatogram is shown as obtained under the described conditions. Evaluation is carried out using the calibration graph (Figure 2) according to the method of the internal standard. In Figure 3 the EI mass spectrum of ethanol-d<sub>6</sub> is shown.

## 6 Calibration

The calibration standards of each solution (Section 2.4, Table 1) are analysed in repeated determination under the operating conditions described in Section 4. The calibration graph, which is evaluated computer-aided, is linear in the concentration range between 50–3000 µg of carbon disulfide/10 mL desorption solution.

## 7 Calculation of the analytical results

The computer-aided evaluation provides the concentration value  $\rho$  of the carbon disulfide mass in mg/m<sup>3</sup> directly, if automatically the air sample volume and the recovery are accounted with the carbon disulfide mass in the desorption solution. When evaluation is carried out manual, the corresponding carbon disulfide mass is determined from the quotient of the peak areas of carbon disulfide and the internal standard from the calibration graph. The concentration by weight of carbon disulfide in the air sample in mg/m<sup>3</sup> is calculated according to Equation (1):

$$\rho = \frac{X}{V \times \eta} \quad (1)$$

At 20 °C and 1013 hPa:

$$\rho_0 = \rho \times \frac{273 + t_a}{293} \times \frac{1013}{p_a} \quad (2)$$

The corresponding volume concentration  $\sigma$  (independent of the state variables pressure and temperature) is:

$$\sigma = \rho_0 \times \frac{V_m}{M} \quad (3)$$

$$\sigma = \rho \times \frac{273 + t_a}{p_a} \times \frac{1013}{293} \times \frac{V_m}{M} \quad (4)$$

For the calculation of the carbon disulfide concentration by volume  $\sigma$  in mL/m<sup>3</sup> follows with  $t_a = 20$  °C and  $p_a = 1013$  hPa:

$$\sigma = \rho \times 0.317 \quad (5)$$

Where:

- $X$  is the mass of carbon disulfide in the sample solution as determined from the appropriate calibration graph in  $\mu\text{g}$
- $V$  is the air sample volume in L (calculated from the flow rate and the sampling time)
- $\eta$  is the recovery
- $\rho$  is the mass concentration of carbon disulfide in the workplace air related to  $t_a$  and  $P_a$  in  $\text{mg/m}^3$
- $\rho_0$  is the mass concentration of carbon disulfide in the workplace air related to 20 °C and 1013 hPa in  $\text{mg/m}^3$
- $t_a$  is the temperature during sampling in °C
- $P_a$  is the atmospheric pressure during sampling in hPa
- $\sigma$  is the concentration by volume of carbon disulfide in the workplace air in  $\text{mL/m}^3$
- $V_m$  is the molar volume of carbon disulfide in L/mol
- $M$  is the molar mass of carbon disulfide in g/mol

## 8 Reliability of the method

The characteristics of the method were determined according to EN 482 [3].

### 8.1 Precision

In order to determine precision, each ten adsorption tubes filled with charcoal were loaded with different masses of carbon disulfide by using injection syringes. For that procedure 20  $\mu\text{L}$  of a solution of 50 mg carbon disulfide/10 mL toluene/dichloromethane as well as 1  $\mu\text{L}$  and 2  $\mu\text{L}$  of pure carbon disulfide were used.

40 L of laboratory air were drawn through the tubes as described in Section 3. Subsequently, the samples were analysed as described in Section 5. The following data were obtained (Table 2):



**Table 2.** Standard deviation (rel.), mean variation  $u$ , and measurement uncertainty  $U$  at  $n = 10$  determinations.

Concentration [mg/m <sup>3</sup> ]	Standard deviation (rel.) [%]	Mean variation [%]	Relative measurement uncertainty [%]
2.5	3.1	6.9	6.2
31.6	2.6	5.8	5.2
63.2	3.3	7.5	6.6

## 8.2 Recovery

In order to determine the recovery, the results of the calculation of precision were used. The recovery of each concentration was averaged from the results of ten measurements. The results are listed in Table 3.

**Table 3.** Recovery  $\eta$  at  $n = 10$  determinations per concentration.

Concentration [mg/m <sup>3</sup> ]	Recovery $\eta$
2.5	0.60 (60 %)
31.6	0.77 (77 %)
63.2	0.78 (78 %)

## 8.3 Limit of quantification

After carrying out a 10-point calibration within the concentration range from 1.25 to 75 mg/m<sup>3</sup>, the limit of quantification was calculated according to DIN 32645 [4]. For a sampled air volume of 40 L the limit of quantification for carbon disulfide is 1.14 mg/m<sup>3</sup>.

## 8.4 Shelf-life

To check the shelf-life, charcoal tubes were loaded each with 0.1, 1.26 and 2.52 mg of pure carbon disulfide using injection syringes. Subsequently, 40 L of laboratory air was drawn through the tubes as described in Section 3. The samples were stored at room temperature. After 7, 14, and 28 days, each three tubes loaded with different masses of carbon disulfide were analysed as described in Section 5. No significant loss of the measured carbon disulfide concentration could be observed after 7 and 14 days of storage. After a storage time of 28 days, a minor decrease of the calculated carbon disulfide concentration could be ascertained.

## 8.5 Interferences

The used analytical system, consisting of a gas chromatograph coupled with a mass selective detector, represents a very high selectivity. If however interferences occur, the sample should be analysed by mass spectrometry without the presence of the internal standard.

## 9 Discussion

The analytical determination of carbon disulfide is very sensitive and selective by using GC/MS. Moreover, the recovery of carbon disulfide can be significantly improved by using toluene/dichloromethane (9 + 1 v/v) as desorption solution for the adsorbed carbon disulfide on charcoal. On the other hand the recovery decreases with increasing concentration in the lower concentration range.

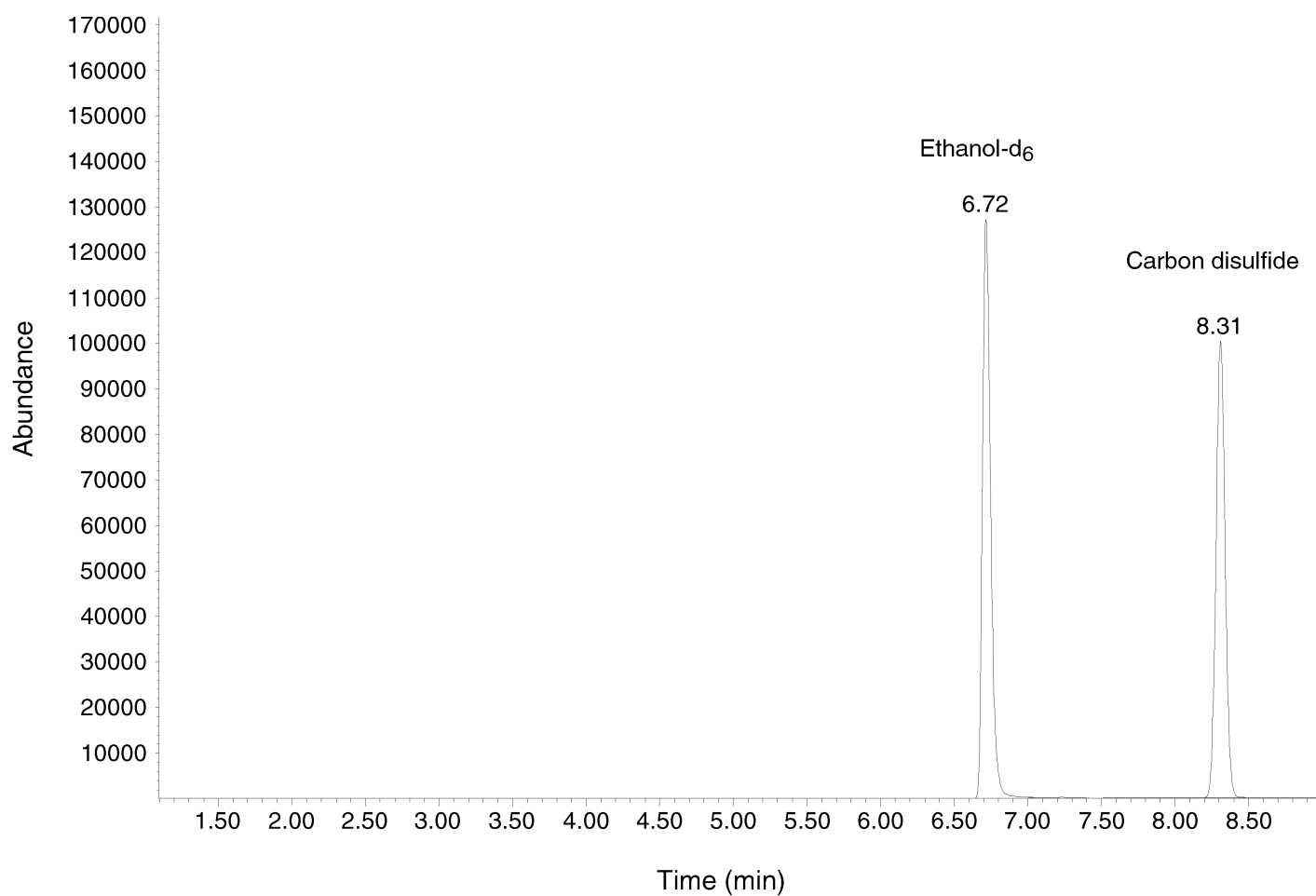
By means of a careful determination of the recovery in the expected range of concentration, systematic errors can be widely avoided.

## 10 References

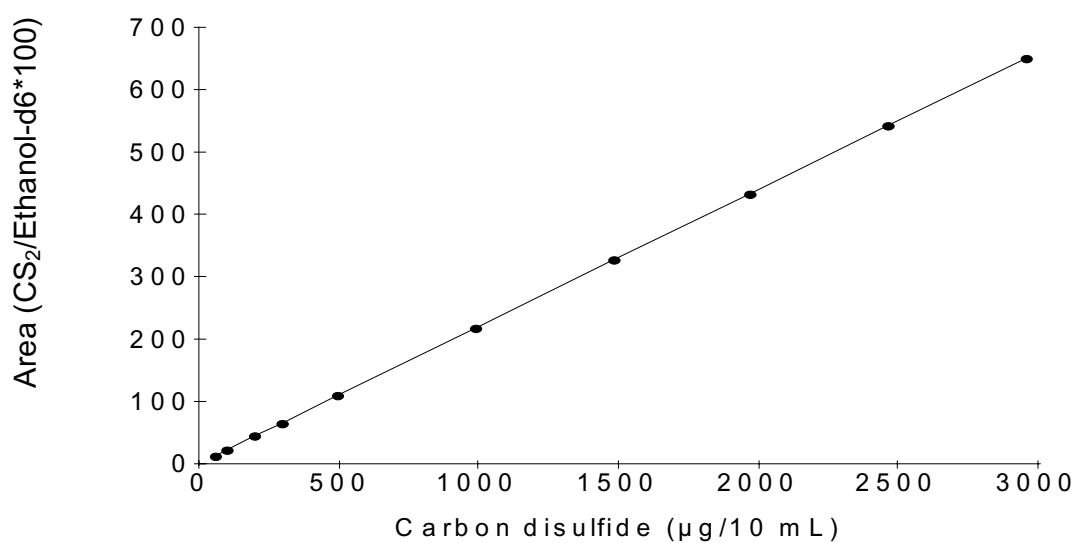
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- [2] DFG (Deutsche Forschungsgemeinschaft) (2008) List of MAK and BAT Values 2008. Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 44. Wiley-VCH, Weinheim.
- [3] EN 482 Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents, European Standard. Issue: October 2006, Beuth Verlag, Berlin.
- [4] DIN 32645 – Chemical analysis; decision limit; detection limit and determination limit. Issue: May 1994, Beuth Verlag, Berlin.

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**Figure 1.** Gas chromatogram of carbon disulfide and ethanol-d<sub>6</sub> in toluene/methylenechloride (9 + 1 v/v).



**Figure 2.** Calibration graph of carbon disulfide.

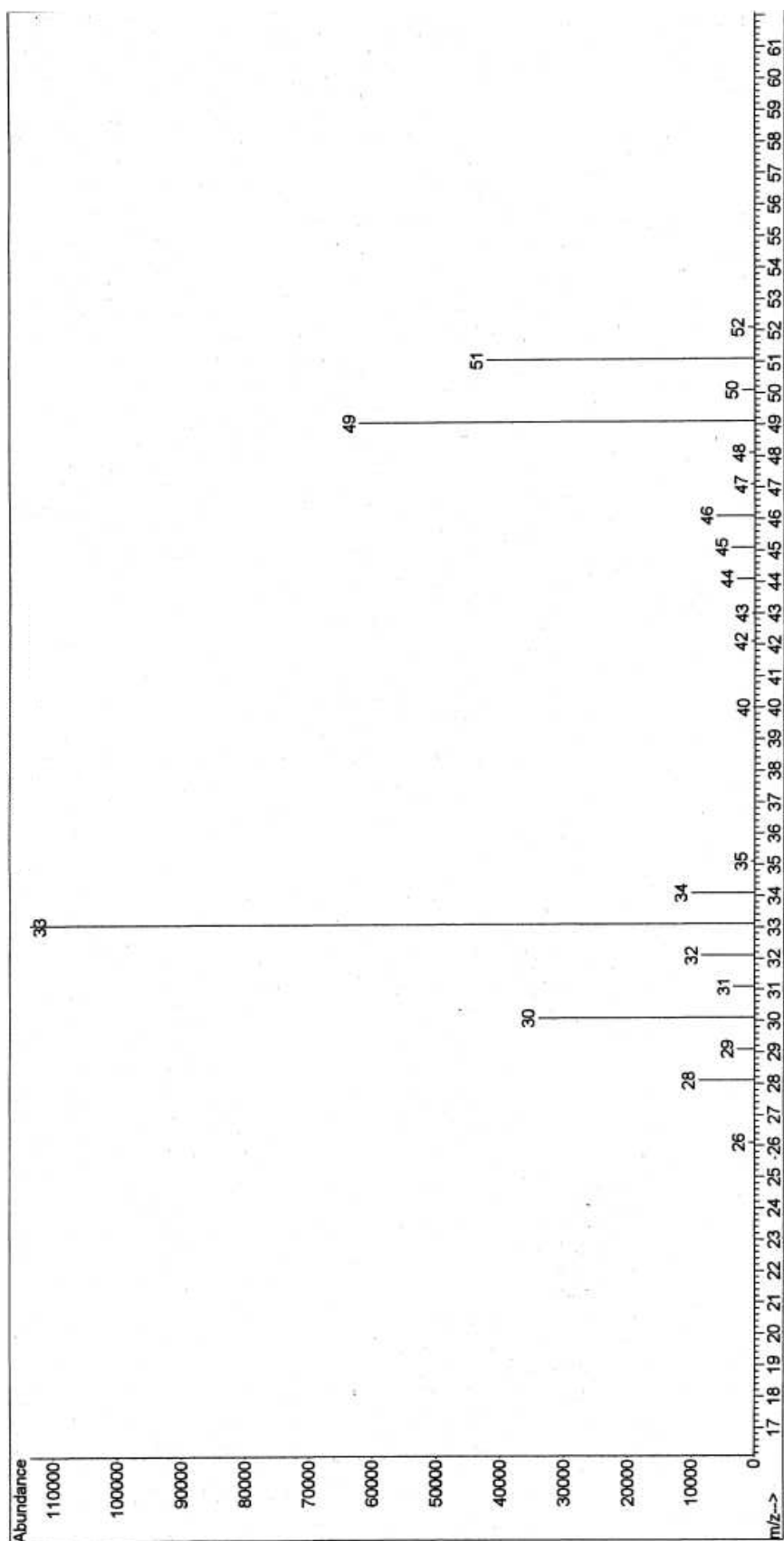


Figure 3. EI mass spectrum of ethanol-d<sub>6</sub>.