Tetraethyl orthosilicate

Application	Air analysis
Analytical principle	Gas chromatography
Completed in	June 1985

Summary

Air containing tetraethyl orthosilicate is drawn consecutively through two wash bottles each containing 20 mL 2-propanol as absorbent. The 2-propanol collecting phases are transferred separately into 25 mL volumetric flasks and analysed by gas chromatography with flame ionization detection. The quantitative evaluation makes use of a calibration curve in which the tetraethyl orthosilicate concentrations of calibration standards are plotted versus the peak areas.

Precision:	Standard deviation (rel.)	s = 6.5 - 0.8%
	Mean variation	u = 16.2 - 1.9%
	at concentrations ranging fro	m 25–200 mL/m ³ (ppm)
	for a sample volume of 50 L	where
		n = 8 determinations
Detection limit:	4.9 mL/m^3 (ppm) equivalent with a sample volume of 50	to 42.0 mg/m ³ L
Recovery rate:	$\eta = 0.96 (96\%)$ using two wa	ash bottles
Recommended sampling tim	ne:	30 min
Recommended sample volu	me:	50 L

Tetraethyl orthosilicate (tetraethoxysilane, silicic acid, tetraethyl ester)

Si (OC₂H₅)₄

Tetraethyl orthosilicate is a colourless inflammable liquid (molar mass 208.2 g/mole, b.p. 165–166°C, density 0.9356 g/mL). The substance hydrolyzes slowly in water. It is miscible with ethanol [1].

Tetraethyl orthosilicate is used industrially as a binder for materials with high melting points and moulds, for the production of weather and acid resistant mortars, as an ad-

ditive together with powdered zinc colours in anticorrosive paints, and as an intermediate in the production of organosilicon compounds [2]. The current MAK value (1990) is 20 mL/m³ or 170 mg/m³. The substance is listed in a Peak Limitation Category I, the local irritants [3].

Tetraethyl orthosilicate causes irritation of the eyes and of the respiratory tract. High doses affect the lungs and other inner organs [4].

Author: *K. Flick* Examiner: *M. Kuck*

Tetraethyl orthosilicate

Application	Air analysis
Analytical principle	Gas chromatography
Completed in	June 1985

Contents

- 1 General principles
- 2 Equipment, chemicals and solutions
- 2.1 Equipment
- 2.2 Chemicals
- 2.3 Calibration standards
- 3 Sample collection and preparation
- 4 Operating conditions for gas chromatography
- 5 Analytical determination
- 6 Calibration
- 7 Calculation of the analytical results
- 8 Reliability of the method
- 8.1 Precision
- 8.2 Recovery rate
- 8.3 Detection limit
- 9 Discussion of the method
- 10 References

1 General principles

Air containing tetraethyl orthosilicate is passed consecutively through two wash bottles each containing 20 mL 2-propanol as absorbent. The 2-propanol collecting phases are transferred separately into 25 mL volumetric flasks and analysed by gas chromatography with flame ionization detection. The quantitative evaluation makes use of a calibration curve in which the tetraethyl orthosilicate concentrations of calibration standards are plotted versus the peak areas.

2 Equipment, chemicals and solutions

2.1 Equipment

Gas chromatograph equipped with a flame ionization detector, recorder and integrator

Steel column:	Length 2 m, inner diameter 2.7 mm
Stationary phase:	20% SP-2100 + 0.1% Carbowax 1500 on 100/120 Supelcoport
Alternative:	15% UCON LB 550X on Chromosorb W or 10% silicone rubber UC W 982 on Chromosorb W-AW/DMCS, 80–100 mesh

Sampling apparatus consisting of a suction pump with a regulating valve, gas flow meter (dry gas meter) equipped with a manometer and thermometer, two wash bottles each with frit G2, as receivers Barometer Thermometer 25 and 50 mL Volumetric flasks 1, 2, 5mL Graduated pipettes

1 μ L Syringe for gas chromatography

2.2 Chemicals

Tetraethyl orthosilicate (tetraethoxysilane), purum (Fluka) 2-Propanol (isopropyl alcohol), for spectroscopy Nitrogen, prepurified (99.999%) Hydrogen (99.90%) Synthetic air

2.3 Calibration standards

Stock solution:

A volume of 1 mL of tetraethyl orthosilicate is pipetted into a 50 mL volumetric flask and diluted to the mark with 2-propanol (935.6 mg/50 mL). The following calibration standards are prepared in 25 mL volumetric flasks from the stock solution:

Volume of the stock solution mL	Final volume of the calibration standards mL	Mass of tetraethyl orthosilicate in 25 mL 2-propanol mg
4	25	74.9
2	25	37.4
1	25	18.7
0.5	25	9.4

The stock solution and the calibration standards must be freshly prepared.

3 Sample collection and preparation

Before sampling begins, 20 mL of 2-propanol are placed in each of the two wash bottles. The second bottle is cooled with ice-water. The bottles are then connected to the suction device (Fig. 1). The gas meter is read and then the sample is collected at a gas flow rate of 1.5–1.7 L/min. It takes 29–33 min to collect an air sample of 50 L. During this time the pressure (negative at the pressure gauge and ambient at the barometer) and the temperatures (of the ambient air and of the air in the gas meter) are measured. After the pump has been switched off, the gas meter is read again and the collecting phases are quantitatively transferred from the two wash bottles into numbered 25 mL volumetric flasks.

The volumetric flasks are each filled to the mark with 2-propanol in the laboratory and the samples are subsequently analysed by gas chromatography.

Column: Material: Steel Length: 2 m Inner diameter: 2.7 mm Column packing: 20% SP-2100 + 0.1% Carbowax 1500 on 100/120 Supelcoport Alternative: 15% UCON LB 550 X on Chromosorb W or 10% silicone rubber UC W 982 on Chromosorb W-AW/DCMS, 80-100 mesh Detector: Flame ionization detector Attenuation: 10 - 80**Temperature:** Column: 100 °C 230 °C Injection block: Detector: 230 °C Carrier gas: Nitrogen, prepurified (40 mL/min) Detector gases: Synthetic air (250 mL/min) Hydrogen (40 mL/min) Integrator: Storage integrator or Calculating integrator Injected volume: 0.5 µL A typical chromatogram is shown in Fig. 3

4 Operating conditions for gas chromatography

5 Analytical determination

Volumes of 0.5 μ L of the sample solution are injected repeatedly into the gas chromatograph with the microliter syringe. The analysis is carried out under the specified operating conditions. The peak areas are determined. In addition, the calibration function is regularly tested by injecting calibration standards of comparable concentration into the gas chromatograph.

6 Calibration

Volumes of 0.5 μ L of the calibration standards and the sample solutions are analyzed repeatedly. The peak areas for tetraethyl orthosilicate are calculated and plotted against the injected mass of tetraethyl orthosilicate (in mg per 25 mL 2-propanol), cf. Fig. 2. The calibration function is linear from 9.4 to 74.9 mg per 25 mL solution.

7 Calculation of the analytical results

The concentrations of tetraethyl orthosilicate (in mg per 25 mL 2-propanol) corresponding to the peak areas are obtained from the calibration curve. The corresponding concentration $\rho_{\rm T}$ (mg tetraethyl orthosilicate per m³ ambient air) is calculated according to the following equation:

$$\rho_{\rm T} = \frac{X}{V_{\rm z} \cdot \eta} \cdot \frac{273 + t_{\rm g}}{273 + t_{\rm a}} \cdot \frac{p_{\rm a}}{p_{\rm a} - \Delta p}$$

The concentration at 20°C and 1013 hPa is calculated as follows:

$$\rho_{0, T} = \rho_{T} \cdot \frac{273 + t_{a}}{293} \cdot \frac{1013 \text{ hPa}}{p_{a}} = \rho_{T} \cdot \frac{273 + t_{a}}{p_{a}} \cdot 3.46 \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

The corresponding concentration σ in mL/m³ (independent of pressure and temperature) is:

$$\sigma = \rho_{0, T} \cdot \frac{24.1 \text{ L} \cdot \text{mole}^{-1}}{208.2 \text{ g} \cdot \text{mole}^{-1}}$$

$$= \rho_{\rm T} \cdot \frac{273 + t_{\rm a}}{293} \cdot \frac{1013 \text{ hPa}}{p_{\rm a}} \cdot \frac{24.1 \text{ L} \cdot \text{mole}^{-1}}{208.2 \text{ g} \cdot \text{mole}^{-1}}$$

$$= \rho_{\rm T} \cdot \frac{273 + t_{\rm a}}{p_{\rm a}} \cdot 0.4 \frac{\rm hPa \cdot mL}{\rm mg}$$

When $t_a = 20$ °C and $p_a = 1013$ hPa

$$\sigma = \rho_{\rm T} \cdot 0.116 \, \frac{\rm mL}{\rm mg}$$

Mass of tetraethyl orthosilicate in mg
Sample volume in m ³
Recovery rate
Temperature in the gas meter in °C
Temperature of the ambient air in °C
Ambient pressure in hPa
Negative pressure in the gas meter in hPa
Concentration of tetraethyl orthosilicate in mg/m ³ at t_a and p_a
Concentration of tetraethyl orthosilicate in mg/m ³ at 20°C and 1013 hPa
Concentration of tetraethyl orthosilicate in mL/m ³

8 Reliability of the method

8.1 Precision

In order to test the reproducibility of the results, four consecutive measurements were carried out with selected volumes of tetraethyl orthosilicate (11.4 μ L, 22.8 μ L, 45.6 μ L and 91.1 μ L) in a gas sampling vessel. Air purified by passing it over activated charcoal was drawn through the electrically heated gas collecting vessel containing the given amount of tetraethyl orthosilicate at a flow rate of 1–2 L/min. The tetraethyl orthosilicate was collected in two wash bottles with frits, containing 20 mL of 2-propanol; the second wash bottle was cooled in ice-water. Sample pretreatment and analytical determination were carried out as described above. The measurements were each repeated to give a total of eight results.

The relative standard deviation was calculated from these measurements: s = 6.5-0.8 %, the range of the mean variation, at a statistical certainty of 95%, u = 16.2-1.9 % in a concentration range from 10.63–85.00 mg/25 mL solution (i.e. 25–200 mL/m³ or 212.5–1700 mg/m³, with a sample volume of 50 L).

8.2 Recovery rate

The recovery rate $\eta = X^*/X$, i. e. the ratio of the amount actually detected in the analysis X^* to the actual amount contained in the sample X, was determined according to Section 8.1. The eight measurements yielded an average recovery rate $\eta = 0.933$ (93.3%) in the first wash bottle, $\eta = 0.025$ (2.5%) in the second wash bottle, a total of $\eta = 0.958$ (95.8%).

8.3 Detection limit

The detection limit is 2.1 mg/25 mL solution. This amount corresponds to a tetraethyl orthosilicate concentration of 42 mg/m³ (4.9 mL/m³) for a sample volume of 50 L.

9 Discussion of the method

This analytical method is suitable for determining the tetraethyl orthosilicate concentration in the air at workplaces.

Apparatus:

Sampling apparatus made by Lange & Rehberg, Bochum

Gas chromatograph F 22 equipped with FID and storage integrator SIP-1 manufactured by Perkin-Elmer or

computerized integrator Chromatopac C-R3A manufactured by Shimazdu

10 References

[1] Römpps Chemie Lexikon. Franckh'sche Verlagshandlung, Stuttgart, 8. Auflage, S. 1209.

- [2] Ullmanns Encyklopädie der technischen Chemie. Verlag Chemie, Weinheim, 4. Auflage, Band 15, p. 762–765.
- [3] *Deutsche Forschungsgemeinschaft:* Maximale Arbeitsplatzkonzentrationen und Biologische Arbeitsstofftoleranzwerte 1987. Mitteilung XXIII der Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe. VCH Verlagsgesellschaft, Weinheim 1987.
- [4] E. Browning: Toxicity and metabolism of industrial solvents. Elsevier Publishing Company, Amsterdam, London, New York 1965, p. 693–695.

Author: *K. Flick* Examiner: *M. Kuck*



Fig. 1. Sampling apparatus.

A₁; A₂ Wash bottles with frits

- B Thermos flask (filled with ice-water mixture)
- G Gas flow meter (dry gas meter) equipped with a thermometer T_g for sample air and a manometer M_a to measure the negative pressure
- V Regulation valve
- P Pump
- Ba Barometer
- Ta Thermometer (ambient air)



Fig. 2. Calibration curve for the gas chromatographic determination of airborne tetraethyl orthosilicate.



Fig. 3. Gas chromatogram of tetraethyl orthosilicate in 2-propanol.