Organotin compounds
(Species analysis)

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	October 1992

Summary

By means of a sampling pump measured air volumes are drawn from the breathing area through adsorption tubes which are filled with the protonated type of a wet cation exchange resin. Solid particles and aerosols are collected on a preconnected glass fibre filter. The gaseous mono-, di- and trialkyltin compounds are bound ionically and tetraalkyltin is bound adsorptively to the ion exchange resin. After desorption with acidified diethyl ether the mono-, di- and trialkyltin chlorides are reacted with pentylmagnesium bromide to the corresponding tetraalkylstannanes (RPe_3Sn, R_2Pe_2Sn, R_3PeSn). They are transferred to a silica gel column for clean-up and eluted with hexane. The polar compounds remain on the column. The tetraalkylstannanes are separated and determined by means of capillary gas chromatography. If interferring components are present (bad resolution of the peaks in the chromatogram, difficulties in the assignments of peaks) they can be identified and quantified by means of a mass selective detector. Dihexyltin dichloride is used as an internal standard.

Precision:	Standard deviation (rel.) s = 1.4 and 8.6% Mean variation u = 2.9 and 19.4% at concentrations of about 0.15 and 0.015 mg tin per m^3 air and n = 10 determinations (measured for 4 different organotin compounds)
Detection limit:	0.1 µg tin per m^3 air for each individual component (at a sample volume of 100 L)
Recovery rate:	η = 0.56–0.94 (56–94%) (cf. Tab. 1)
Recommended sampling time:	1 h
Recommended sample volume:	360 L

Organotin compounds

Tin compounds with at least one tin-carbon bond in the molecule are named organotin compounds:

R_4Sn	Tetraorganotin compounds
R_3SnX	Triorganotin compounds
R_2SnX_2	Diorganotin compounds
$RSnX_3$	Monoorganotin compounds

Legend:

R = Alkyl-, cycloalkyl-, carbobutoxyethyl-, acrylic hydrocarbon substituents
X = Anionic groups like halogene, –OH, –OR', –SR', –OOCR', $–NR'_2$

The tetraorganotin compounds mainly serve as intermediates for the production of mono-, di- and triorganotin compounds. Triorganotin compounds are used as biocides against mites, fungi, bacteria and algae. The most important fields of application for tributyltin are wood preservatives, textile preservatives, biocide treatment of sealing materials and as antifouling paints for ships. Triphenyltin and tricyclohexyltin are applied as plant protection agents. Di- and monoorganotin compounds (especially methyltin, butyltin and octyltin) are used as PVC stabilizers, as catalysts for polymerizations, esterifications and trans-esterifications. Methyltin chloride is applied in the refinement of glass surfaces.
The MAK value of organotin compounds is 0.1 mg/m^3 (referring to tin) [1]. The symbol "H" in the MAK list indicates the risk of skin absorption. The tri-n-butyltin compounds are an exception. Here the MAK is 0.05 mg/m^3 (referring to TBTO) [1]. This corresponds with a concentration of 0.02 mg/m^3 referring to tin.
The toxicology of the organotin compounds is described in detail in the DFG method “Tin in urine” [2] and in “The evaluation of occupational toxicants” by the DFG [3].

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Contents

1 General principles

By means of a sampling pump measured air volumes are drawn from the breathing area through adsorption tubes which are filled with the protonated type of a wet cation exchange resin. Solid particles and aerosols are collected on a preconnected glass fibre filter. The gaseous mono-, di- and trialkyltin compounds are bound ionically and tetraalkyltin is bound adsorptively to the ion exchange resin. After desorption with acidified diethyl ether the mono-, di- and trialkyltin chlorides are reacted with pentylmagnesium bromide to the corresponding tetraalkylstannanes (RPe_3Sn, R_2Pe_2Sn, R_3PeSn). They are transferred to a silica gel column for clean-up and eluted with hexane. The polar compounds remain on the column. The tetraalkylstannanes are separated and determined by means of capillary gas chromatography. If interferring components are present (bad resolution of the peaks in the chromatogram, difficulties in the assignments of peaks) they can be identified and quantified by means of a mass selective detector. Dihexyltin dichloride is used as an internal standard.

2 Equipment, chemicals and solutions

2.1 Equipment

Capillary gas chromatograph equipped with a flame ionization detector or a mass selective detector, on-column injector, option for the recording and evaluation of chromatograms (e. g. recorder, integrator or work station).

Adsorption tubes: Eppendorf pipette tip (blue) filled with about 0.5 g wet cation exchange resin placed between two stoppers of silanized glass wool inserted in a suction finger (glass tube melted at one end, length about 10 cm, internal diameter about 1 cm, equipped with olive adapter and screw closure with hole (cf. Fig. 1).

Glass fiber filter, diameter 13 mm, thickness 550 µm, pore size about 50–60 µm (e.g. Sartorius SM 6, # S 13 400)

Suction pump, pumping capacity about 6 L/min

Gasmeter

Thermometer

Barometer

Glass tube (length 15 cm, diameter 2 cm) equipped with glass frit bottom and delivery cock (chromatography column)

Solid phase extraction system (e. g. VacElut of ICT)

10 mL Medical disposable syringes with Luer tip (e.g. of Henke-Sass, Wolf GmbH)
Eppendorf pipettes, variable
Eppendorf pipette tips, blue, for 100–1000 µL pipettes
1 and 100 mL Bulb pipettes
100 mL Volumetric flasks
50 mL Ampoules
5 mL Injection vials with aluminium closure caps and PTFE coated septa
Crimper
1 µL Liquid syringe for gas chromatography
Ultrasonic bath
Analysis balance

2.2 Chemicals

Cation exchange resin Amberlite CG 120 I (Rohm & Haas, Philadelphia, USA; e.g. EGA Chemie), grain size 100–200 mesh, counter-ion: Na^+
Butyltin trichloride, 95% e.g. from Aldrich [20, 105-7]
Dibutyltin dichloride, 97% e.g. from Aldrich [20, 549-4]
Tributyltin chloride, 96% e.g. from Aldrich [T 5, 020-2]
Tetrabutyltin, 96% e.g. from Aldrich [T 600-8]
Dihexyltin dichloride as internal standard, e.g. from Acima, CH-9470 Buchs
Pentylmagnesium bromide, 2.0 M in diethyl ether, e.g. from Aldrich [29, 099-8]
2-Propanol, analytical grade, e. g. from Merck
Diethyl ether, analytical grade, e. g. from Merck
t-Butyl methyl ether, residue analysis, e. g. from Merck
n-Hexane, analytical grade
Hydrochloric acid, highest purity, w = 30% (e.g. Suprapur from Merck)
Sulfuric acid 0.5 M, analytical grade
Sodium hydroxide, 2 M, analytical grade
Hydrochloric acid, 2 M (prepared from the hydrochloric acid 30% as mentioned)
Silica gel 60, grain size 0.063–0.200 mm, 70–230 mesh, for column chromatography (e. g. from Merck)
Glass wool, silanized

2.3 Solutions

Diethyl ether (hydrochloric):
Add 100 mL diethyl ether and 5 mL of 30% hydrochloric acid to a separating funnel. After shaking the flask, the aqueous phase is separated and disposed of.

2.4 Calibration standards

The following experimental procedure is generally applied for all organotin compounds (except the estertin compounds). The preparation of the calibration standards for the butyltin compounds is described as an example.

Initial solution:
300–400 mg each of tetrabutyltin, dibutyltin dichloride and butyltin trichloride and 800–1000 mg tributyltin chloride are exactly weighed into a 100 mL volumetric flask and diluted up to the mark with *t*-butyl methyl ether.

Stock solution:
10 mL of the initial solution are pipetted into a 100 mL volumetric flask and diluted up to the mark with *t*-butyl methyl ether. This stock solution contains
102.6–136.8 mg Sn/L as tetrabutyltin
291.8–364.7 mg Sn/L as tributyltin chloride
117.2–156.2 mg Sn/L as dibutyltin dichloride
126.2–168.3 mg Sn/L as monobutyltin trichloride

Calibration standard solutions:
The calibration standard solutions are prepared from the stock solution by dilution with *t*-butyl methyl ether (Bu_4Sn).

Table 1. Pipetting scheme for the preparation of calibration standards.

Stock solution No	mL	Final volume mL	Concentration Bu_4Sn mg Sn/L	Bu_3SnCl mg Sn/L	Bu_2SnCl_2 mg Sn/L	$BuSnCl_3$ mg Sn/L
1	10.00	100	10.26 –13.68	29.18 –36.47	11.72 –15.62	12.62 –16.83
2	5.00	100	5.13 – 6.84	14.59 –18.24	5.86 – 7.81	6.31 – 8.42
3	2.00	100	2.05 – 2.74	5.84 – 7.29	2.34 – 3.12	2.52 – 3.27
4	1.00	100	1.03 – 1.37	2.92 – 3.65	1.17 – 1.56	1.26 – 1.68
5	0.75	100	0.77 – 1.03	2.19 – 2.74	0.88 – 1.17	0.95 – 1.26
6	0.50	100	0.52 – 0.69	1.46 – 1.83	0.59 – 0.78	0.63 – 0.84

A volume of 200 µL of the working solution of the internal standard is added to 200 µL of the prepared calibration standard solutions as mentioned before. Then 5 mL of hexane are added and the solution is alkylated and treated according to Sect. 3.6. 1 µL of each solution is analysed for the determination of the peak area correction factor referring to the internal standard.

Preparation of the solution of the internal standard:
400–500 mg dihexyltin dichloride are weighed into a 100 mL volumetric flask and diluted up to the mark with *t*-butyl methyl ether (stock solution).
1 mL of the stock solution are pipetted into a 100 mL volumetric flask and diluted up to the mark with *t*-butyl methyl ether. The solution (working solution) prepared in this way contains 13.2–16.5 mg Sn/L as dihexyltin dichloride.

3 Sample collection and preparation

3.1 Cleaning of the vessels (glass ware)

After the normal cleaning procedure of the laboratory vessels all glass ware has to be cleaned with acidified 2-propanol until no more tin is detectable in the wash solution. The glass ware is dried at air.

3.2 Preparation of the exchange resin

The Na^+ type of the exchange resin is allowed to swell in deionized water for 24 hours. The turbid water phase (due to the content of fine grained resin) is decanted and the resin is washed until the water is clear. The resin is filled into a chromatographic column up to a height of about 5 cm, washed slowly with 50 mL NaOH (2 M) and then with deionized water until the eluate is neutral. The resin is converted into the H^+ type with 50 mL HCl (2 M) and eluted with deionized water until chloride is not detectable in the eluate. The resin prepared in this way is stored under water. Before use it has to be washed again with water.

3.3 Preparation of the adsorption unit

A small piece of silanized glass wool is placed in the conical end of an Eppendorf pipette tip (blue) and the treated exchange resin added to a height of 25 mm. It is closed with silanized glass wool and first washed with 1 mL acidified 2-propanol (5 mL 30% hydrochloric acid in 100 mL 2-propanol) and then with 1 mL of deionized water. The prepared pipette tip is positioned into the glass vessel and sealed with aluminium foil until use.

3.4 Sampling and sample storage

For one hour and at a flow rate of 6 L/min air is drawn through an adsorption tube containing exchange resin by means of a flow-stabilized pump or a sampling device controlled by a gasmeter. A glass fibre filter is mounted before the inlet of the adsorption tube. If necessary two exchanger tubes have to be connected in series. The decisive parameters for the concentration determination like sample volume, temperature in the gasmeter as well as ambient pressure and ambient temperature at the measuring location have to be determined.
Loaded adsorption tubes can be stored at least for one week without loss. The tubes should be closed with plastic caps (free of tin) and kept in the dark (if possible in a refrigerator).

3.5 Preparation and conditioning of the silica gel cartridges

Silica gel is doped with 5% deionized water and allowed to swell for 24 h. 10 mL disposable syringes are 3/4 filled with the conditioned silica gel.

3.6 Desorption, derivatization and clean-up

After sampling the exchange resin and the glass fibre filter are transferred into a 50 mL vial and 200 µL of internal standard solution are pipetted into the vial. Desorption is effected by treatment with 2 mL acidified diethyl ether in an ultrasonic bath for 2 min. 5 mL *n*-hexane is added and the solution is alkylated dropwise with 1 mL pentylmagnesium bromide solution in an ice bath. After the reaction has subsided, a further 1 mL pentylmagnesium bromide solution is used to complete the reaction for another 5 min in the ultrasonic bath. In an ice bath 0.5 M sulfuric acid (2–3 mL) is dropped into the solution until two clear, colourless phases are formed. The organic phase is transferred into a 50 mL vial using an Eppendorf pipette and the solvent is evaporated carefully in a nitrogen flow to a residual volume of 200 µL. Thus removes the diethyl ether which interferes with the following clean-up with silica gel. 1 mL *n*-hexane is added to the residue and the clean-up is carried out by use of a conditioned silica gel cartridge. It is desorbed with 15 mL hexane and the eluate is concentrated to 200 µL in a nitrogen flow. Losses of organotin species may occur during the concentrating process. 1 µL of this solution is injected into the gas chromatograph.

3.7 Determination of the blank value

An unloaded adsorption tube is treated as described in Sect. 3.6. If tetraalkylstannanes are found in the chromatogram (and the characteristic isotopic pattern of tin in the mass spectrum) either the source of pollution has to be detected and removed (e. g. traces of tributyl-pentyl-tin were sometimes found in the pentylmagnesiumbromide) or the blank value has to be considered in the analysis.

4 Operating conditions for capillary gas chromatography equipped with flame ionization detector or mass selective detector

4.1 Operating conditions for gas chromatography

Column:	used silica capillary column	
	Length:	2 m
	Internal diameter:	0.31 mm
Stationary phase:	Methylsilicone rubber	
	Film thickness:	1.05 µm

Precolumn:	Fused silica capillary column
	Length: 1 m
	Internal diameter: 0.53 mm
	desactivated, uncoated
Detector:	Flame ionization detector or
	mass selective detector
Temperatures:	Column: 60 °C 1 min isothermal then
	with 15 °C/minute up to 280 °C
	Flame ionization detector: 300 °C
	Transfer-line from the ion source
	to the mass spectrometer: 280 °C
Carrier gas:	Helium 5.0 (99.999% by volume helium)
	Column head pressure: 1020 hPa
	Column flow: 1 mL/min
Sample injection:	On column
Injection volume:	1 µL

An example of a gas chromatogram is represented in Fig. 3.

4.2 Operating conditions for the mass selective detector

Both detection modes SCAN mode and Multiple Ion Detection (MID) are necessary for detection by the mass selective detector. The ionization energy is 70 eV in both cases. First a total ion current chromatogram of the alkylated and prepared calibration solutions (cf. Sect. 2.4 and 3.6) is recorded in the SCAN mode. Significant masses and the ratios of intensities of two ions or ion groups for each tin compound are taken from the obtained mass spectra. (Normally for tetraalkylstannanes the significant ions of the isotopic clusters R_3Sn^+ or $R_2R'Sn^+$ are preferred because they are very intense and interferences are not expected). The identification and quantification of the alkyltin compounds in the sample occurs by use of the MID technique based on the retention time, the mass number and the correct relationship mass number/intensity. The following parameters for the SCAN mode and the MID mode were selected for the data acquisition:

SCAN
Mass range: 100–550 amu
Rate: 0.82 scans/s

MID

Component	Significant ions m/z	Qualifier ion m/z
Bu_4Sn	291, 289, 235, 233	289
Bu_3SnPe	305, 303, 235, 233	303
Bu_2SnPe_2	319, 317, 249, 247	317
$BuSnPe_3$	319, 317, 249, 247	317
Pe_4Sn	333, 331, 263, 261	331
Hex_2SnPe_2	347, 345, 277, 275	345

Dwell time (measuring time)/ion: 50 ms each
Electron multiplier voltage: 1800 V

5 Analytical determination

5.1 Analysis by means of a flame ionization detector

By means of a suitable GC injection syringe, 1 µL of the sample solution (prepared according to Sect. 3) are injected into the gas chromatograph and analysed as described in Sect. 4.1. To check the results, repeated analyses are performed and the peak areas of the alkyltin compounds relative to the internal standards are determined. Calibration standards are analysed with each batch of sample and also regularity for quality control.

5.2 Analysis by means of a mass selective detector

In order to define the significant masses, to determine the ratio mass number/intensity and to check the retention times of the tetraalkyltin compounds exactly 1 µL of the alkylated and prepared calibration standard solution No 4 (cf. Sect. 2.4 and 3.6) is analysed in the SCAN mode of the mass spectrometer under the operating conditions mentioned in Sect. 4.2. By use of the mass spectrometric parameter which are determined this way 1 µL of the sample solution obtained according to Sect. 3 is injected into the gas chromatohgraph and analysed in the MID mode.
To check the results, repeated analyses are performed and the peak areas of the alkyltin compounds relative to the internal standards are determined. Calibration standards are analysed with each batch of sample and also regularity for quality control.

6 Calibration

The quantitative evaluation occurs in accordance with the method of the internal standard (dihexyltin dichloride). To make the calibration curve the calibration standards 1–6 (prepared according Sect. 2.4 and alkylated according to Sect. 3.6) are analysed by gas chromatography corresponding with the methods described in Sect. 5.1 and 5.2. The peak areas of the alkyltin compounds relative to the internals standard are determined. The linearity of the detector was tested for the following concentrations:

Bu_4Sn:	12.0 µg – 0.24 µg	Sn/mL
Bu_3SnX:	30.5 µg – 0.60 µg	Sn/mL
Bu_2SnX_2:	17.5 µg – 0.34 µg	Sn/mL
$BuSnX_3$:	15.0 µg – 0.30 µg	Sn/mL
Pe_2SnX_2:	16.0 µg – 0.32 µg	Sn/mL
Hex_2SnX_2:	5.2 µg – 0.26 µg	Sn/mL

Referring to a sample volume of 100 L of air this corresponds with the range of 0.02–1.5 fold of the currently valid MAK value for organotin.

7 Calculation of the analytical result

On the basis of the obtained peak area relationships of the tetraalkyltin compounds and the internal standard the quantity of tin in milligram of the tetraalkyltin compound used can be taken from the calibration curve, if the same weighed sample of the internal standard in the calibration solutions and in the sample solutions are used.
The concentration by weight ρ (µg tin per m^3 air) is calculated as follows:

$$\rho = \frac{X}{V_Z \cdot \eta} \cdot \frac{273 + t_g}{273 + t_a}$$

At 20 °C and 1013 hPa:

$$\rho_0 = \rho \, \frac{273 + t_a}{293} \cdot \frac{1013\,\text{hPa}}{p_a}$$

The corresponding concentration by volume σ – independent of pressure and temperature – is:

$$\sigma = \rho_0 \, \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{M} = \rho \cdot \frac{273 + t_a}{p_a} \cdot \frac{1013\,\text{hPa}}{293} \cdot \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{M}$$

For tin (M= 118.7 g mole^{-1}):

$$\sigma = \rho \cdot \frac{273 + t_a}{p_a} 0.702 \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

At t_a = 20 °C and p_a = 1013 hPa:

$$\sigma = \rho \cdot 0.203 \frac{\text{mL}}{\text{mg}}$$

Legend:

V_z Sample volume in m^3
η Recovery rate
t_g Temperature in the gasmeter in °C
t_a Temperature of the ambient air in °C
p_a Ambient pressure in hPa
ρ Tin concentration by weight per tin compound in the ambient air in µg/m^3 referring to t_a and p_a
ρ_0 Tin concentration by weight per tin compound in the ambient air in µg/m^3 at 20°C and 1013 hPa
σ Tin concentration by volume per tin compound in the ambient air in µL/m^3
X Weight of tin per tin compound in the desorption solution in mg

8 Reliability of the method

8.1 Precision

In order to determine the precision for the complete method volumes of 200 µL each of solutions of two different concentrations of tetrabutyltin, tributyltin chloride, dibutyltin dichloride and butyltin trichloride in *t*-butyl methyl ether (concentration of the individual components cf. Tab. 2) were pipetted twenty times into small tubes by means of a precise dosing device (schematic representation of the apparatus cf. Fig. 2). 100 L air were drawn through each tube and another tube with the exchange resin connected behind. At the selected concentrations this corresponds with about 0.15 mg Sn/m^3 or 0.015 mg Sn/m^3 airborne organotin compounds. Each sample prepared according to Sect. 3.6 was analysed six times by gas chromatography, three times using flame ionization detection and three times using mass selective detection.

Table 2. Standard deviation (rel.) *s,* mean variation *u* and recovery rate η.

Detector	Component	Applied weight of tin	Recovered weight of tin mean of ten individual determinations	Standard deviation (rel.)	Mean deviation	Recovery rate
		X	*X**	*s*	*u*	η
		µg Sn/ 200 µL	µg Sn	%	%	
FID	Bu_4Sn	2.410	2.027	2.4	5.2	0.841
	Bu_3SnCl	6.050	5.553	1.4	3.0	0.918
	Bu_2SnCl_2	3.370	2.870	1.4	3.2	0.852
	$BuSnCl_3$	2.995	2.402	2.1	4.7	0.802
FID	Bu_4Sn	0.234	0.140	6.7	14.3	0.598
	Bu_3SnCl	0.603	0.566	3.2	7.1	0.939
	Bu_2SnCl_2	0.342	0.305	1.4	2.9	0.892
	$BuSnCl_3$	0.299	0.229	1.4	2.9	0.766
MS	Bu_4Sn	2.410	1.784	5.9	13.3	0.740
	Bu_3SnCl	6.050	5.124	5.3	11.9	0.847
	Bu_2SnCl_2	3.370	2.145	4.0	8.9	0.717
	$BuSnCl_3$	2.995	2.376	3.2	7.1	0.793
MS	Bu_4Sn	0.234	0.131 [1)]	8.6	19.4	0.562
	Bu_3SnCl	0.603	0.568 [1)]	3.6	8.0	0.943
	Bu_2SnCl_2	0.342	0.306 [1)]	2.0	4.4	0.896
	$BuSnCl_3$	0.299	0.228 [1)]	4.1	9.1	0.761

[1)] Mean of 9 individual determinations

8.2 Recovery rate

The recovery rate $\eta = X^*/X$ (i. e. the ratio of the real analytically determined quantity X^* to the quantity X in the sample) was determined according to the experiments in Sect. 8.1. The results for the components, concentrations and detectors are given in Table 2.

8.3 Detection limit

The detection limit depends on the used apparatus. The detection limit with the measuring apparatus and the measuring parameter applied is 50 pg tin (measuring value corresponds with the threefold background noise). At a sample volume of 100 L and a final volume of the solution of 200 µL a detection limit of 0.1 µg Sn/m^3 for each individual component can be achieved.

9 Discussion

The described analytical method permits the determination of individual airborne organotin compounds in short-term measurements as well as in 8 h average measurements. The airborne organotin compounds are separated quantitatively on glass fibre filters or on membrane filters if they appear as dust (e. g. packing of solid products) or aerosol (e.g. spraying of TBTO containing antifouling paint) [4, 6]. The adsorption of organotin compounds on activated carbon also occurs quantitatively but the desorption is very uncomplete [5, 6]. Silica gel [7] or the organic polymers Chromosorb 102 [8] or Tenax GC and Amberlite XAD-2 [6] are recommended as adsorbents. The desorption with acid containing solvents is complete.
Interferences are possible if the tetraalkyltin compounds which are only bound adsorptively to the ion exchanger are displaced from the exchange resin by organic air pollutants (e. g. solvent vapours). For measurements in working areas impacted to such an extent it is recommended to connect a second adsorption tube (XAD-2 or XAD-4). Other interferences are not known.
The application of ion exchange resins in the gas adsorption is described previously [9, 10]. Desorption, alkylation with alkylmagnesium halogenide and gas chromatographic determination even with mass spectrometric detection were published by Zimmerli [8] in accordance with the analogous procedure in the water analytics.

Apparatus:
Gas chromatograph HP 5880 equipped with flame ionization detector or
Gas chromatograph HP 5890 equipped with mass selective detector (MSD) HP 5970 B of Hewlett Packard
Autosampler HP 7673 A with on-column injection
Chromatogram registration and evaluation:
– FID: HP 5880 GC Terminal, Level 4 of Hewlett Packard
– MSD: HP 9816, Series 200, Workstation of Hewlett Packard
Pump: AMA PN 7300 of AMA, Hilden

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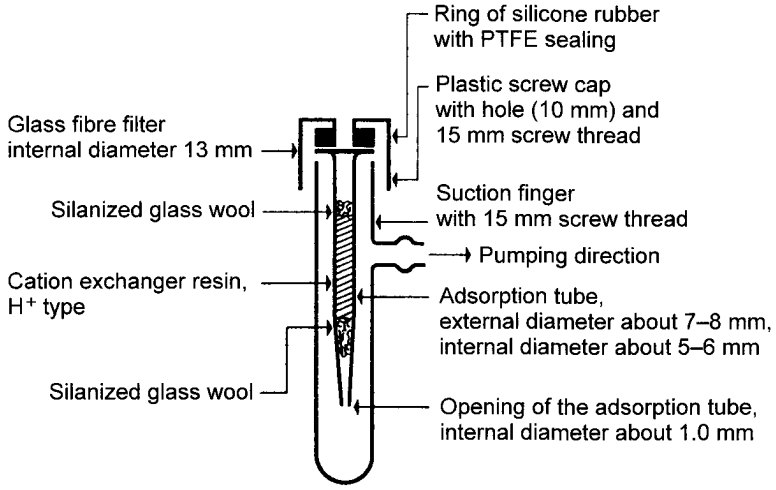

Fig. 1. Sampling apparatus.

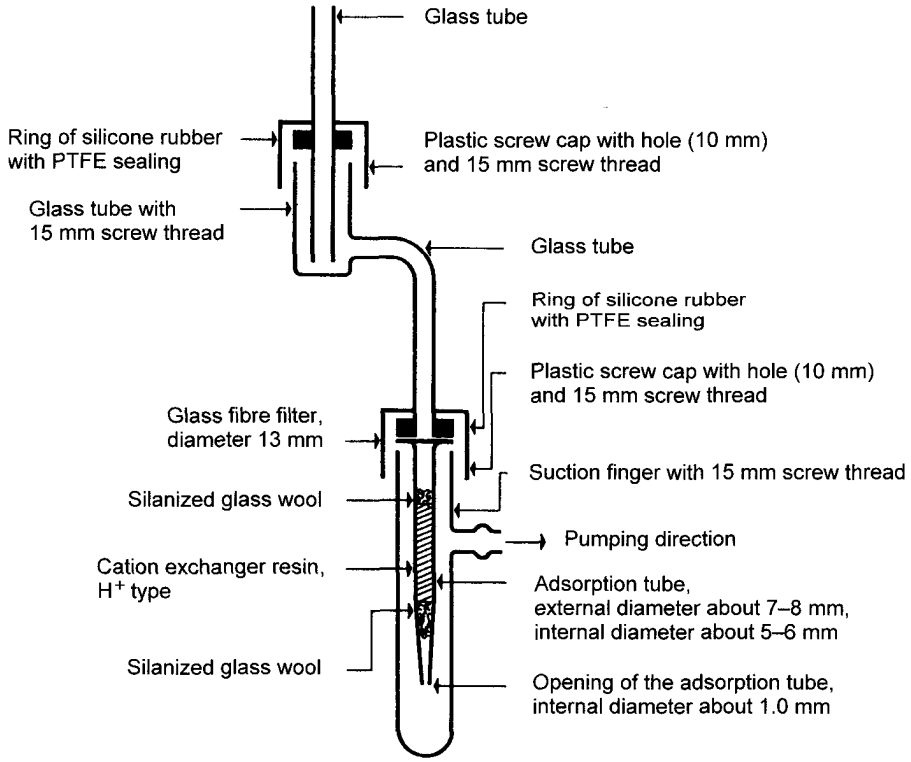

Fig. 2. Apparatus for the determination of the recovery rate.

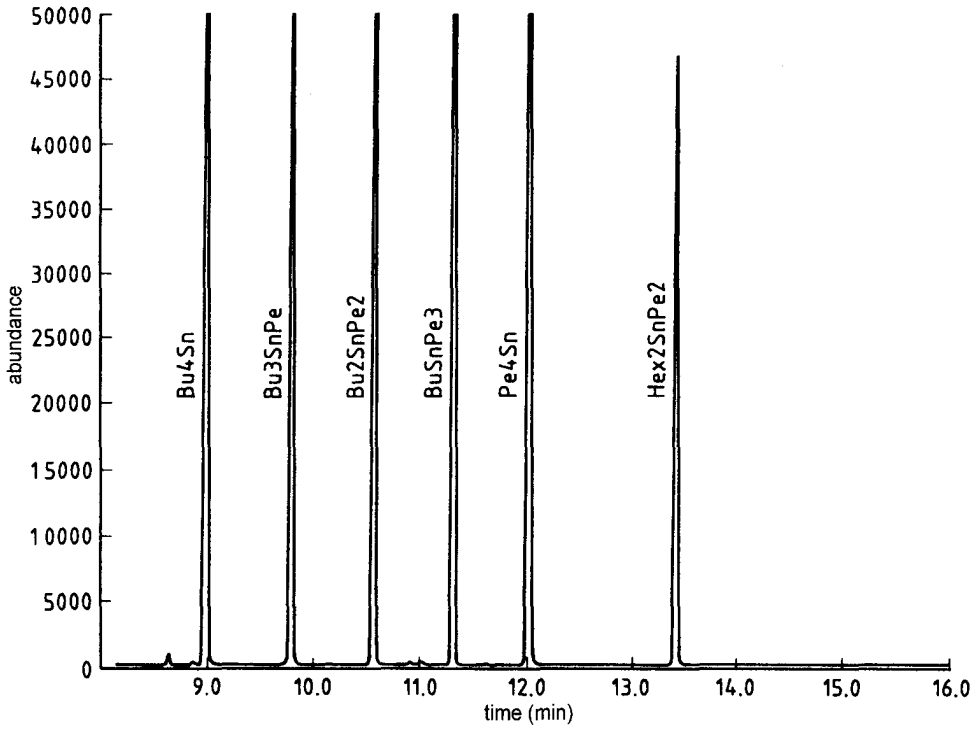

Fig. 3. Gas chromatogram.