MARKES international

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Radiello

Application Compendium

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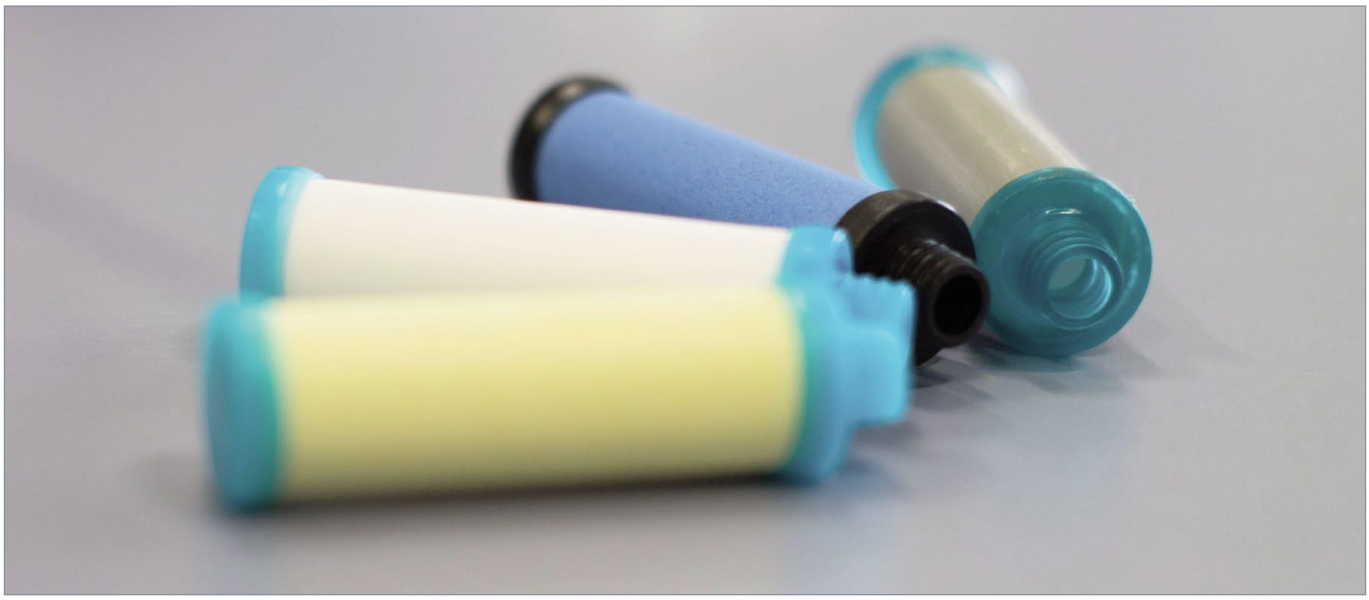
Subject Index



How does the diffusive sampler work?

The diffusive sampler is a closed box, usually cylindrical. Of its two opposite sides, one is “transparent” to gaseous molecules which cross it, and are adsorbed onto the second side. The former side is named diffusive surface, the latter is the adsorbing surface (marked with ***S*** and ***A*** in the figure).

Driven by the concentration gradient ***dC/dl***, the gaseous molecules cross ***S*** and diffuse towards A along the path l, parallel to the axis of the cylindrical box. The molecules, which can be trapped by the adsorbing material, are eventually adsorbed onto ***A*** according to the equation:

$$\frac{dm}{dt} = D\,S\,\frac{dC}{dl} \qquad [1]$$

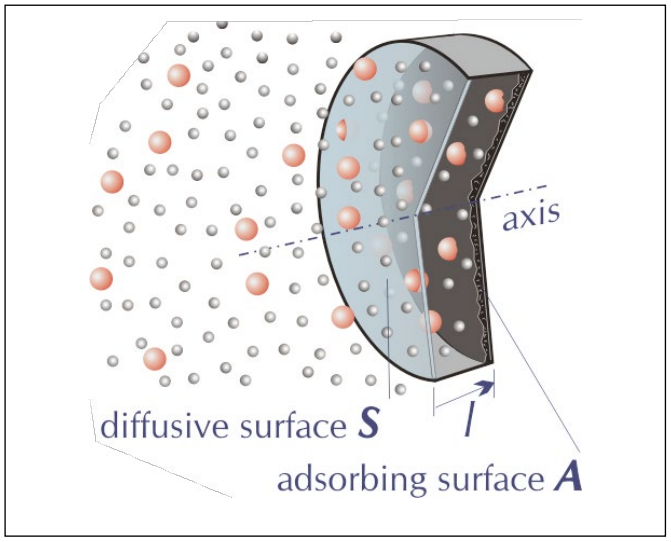
where dm is the adsorbed mass during time dt and D is the diffusion coefficient.

Let C be the concentration at the diffusive surface and C0 the concentration at the adsorbing surface, the integral of [1] becomes

$$\frac{m}{t} = D\,\frac{S}{l}\,(C - C_0) \qquad [2]$$

If the concentration at the adsorbing surface is negligible, the equation can be approximated to

$$\frac{m}{t\,C} = D\,\frac{S}{l} = Q \quad \text{and then} \quad C = \frac{m}{t\,Q} \qquad [3]$$



In the diffusive sampler, the adsorbing and the diffusive surfaces are two opposing plane of a closed box. Driven by the concentration gradient, the gaseus molecules (coloured in the figure) pass through the diffusive surface and are trapped from the adsorbing surface.

Q is the ***sampling rate*** and has the dimensions of a gaseous flow (if m is expressed in µg, t in minutes and ***C*** in µg·l-1, ***Q*** is expressed in l·min-1).

Therefore, if ***Q*** is constant and measured, to calculate the ambient air concentration you need only to quantify the mass of analyte trapped by the adsorbing material and to keep note of the time of exposure of the diffusive sampler.

To improve the analytical sensitivity the collected mass m should be increased by enlarging ***Q***. As ***D*** is a constant term, one can only try to improve the ***S/l*** ratio, namely the ***geometrical constant*** of the sampler. Unfortunately, in the common axial simmetry sampler, if ***S*** is enlarged, the adsorbing surface ***A*** must be enlarged too, in order to keep the two parallel surfaces at a fixed distance. Since the analytes can be recovered from the axial sampler only by solvent extraction, any increase of ***A*** lead to a proportional increase of the extraction solvent volume, thus the improvement of ***Q*** is canceled out by the effect of dilution.

The value of distance l could also be reduced, but under the critical value of about 8 mm the diffusion law is no longer valid in the case of low air velocity values, since adsorption rate becomes higher than supplying rate of analyte molecules at the diffusive surface.

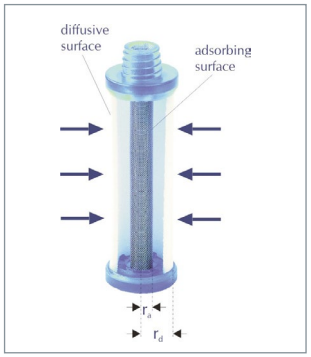
Cannot we improve ***Q*** then?

The answer is to improve the sampler geometry to a ***radial*** design.

From this idea the radiello sampler has been developed, its cylindrical outer surface acting as diffusive membrane: the gaseus molecules move axially parallel towards an adsorbent bed which is cylindrical too and coaxial to the diffusive surface.

When compared to the axial sampler, radiello shows a much higher diffusive surface without increase of the adsorbing material amount. Even if the adsorbing surface is quite smaller then the diffusive one, each point of

Section of radiello. Diffusive and adsorbing surfaces are cylindrical and coaxial: a large diffusive surface faces, at a fixed distance, the small surface of a little concentric cartridge.



The diffusive layer faces the diffusion barrier at the same distance. Section of radiello. Diffusive and adsorbing surfaces are cylindrical and coaxial: a large diffusive surface faces, at a fixed distance, the small surface of a little concentric cartridge.

As ***S=2vrh*** (where h is the height of the cylinder) and the diffusive path is as long as the radius ***r***, we can then express equation [1] as follows

$$\frac{dm}{dt} = D2\nu hr \frac{dC}{dr} \qquad [4]$$

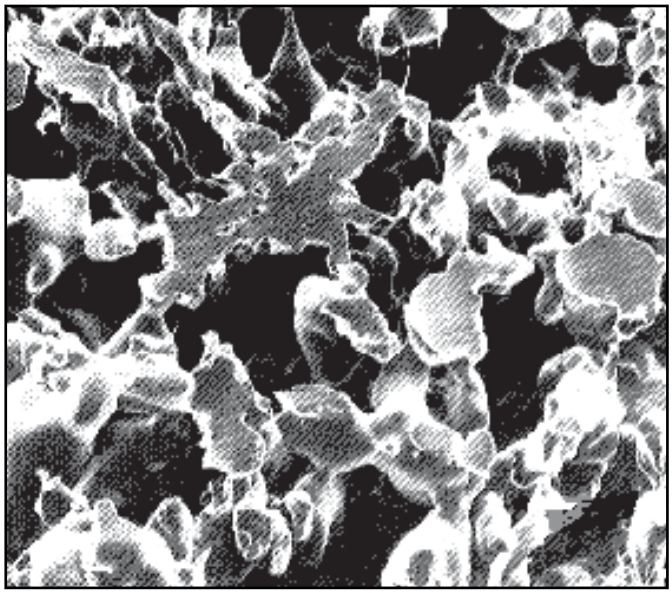
The integral of equation [4] from rd (radius of the diffusive cylindrical surface) to ra (radius of the adsorbing surface) becomes

$$\frac{m}{tC} = D \frac{2\nu n}{\ln \frac{r_d}{r_a}} = Q \qquad [5]$$

the ratio

$$\frac{2\nu h}{\ln \frac{r_d}{r_a}}$$

is the geometrical constant of radiello. The calculated uptake rate [5] is therefore proportional to the height of the diffusive cylinder and inversely proportional to the logarithm of the ratio of diffusive vs adsorbing cylinder radii.



The microporous sintered polyethylene diffusive barrier of radiello photographed at the electron microscope; the path length is much longer than the membrane thickness due to the tortuosity of the pores.

While r_a can be easily measured, r_d can only be calculated by exposure experiments. Actually the diffusive membrane has been designed with a thick tubular microporous layer. The actual diffusive path length is therefore much longer than the distance among the diffusive and adsorbing surfaces due to the tortuosity of the path through the pores. A diffusive cylinder of external diameter 8 mm, thickness 1.7 mm and average porosity of 25 µm, coupled to an adsorbing cartridge with radius 2.9 mm creates a diffusive path of 18 mm instead of the straight line path estimation of (8-2.9) = 5.1 mm.

The sampling rate ***Q*** is function of diffusive coefficient ***D***, which is a thermodynamic property of each chemical substance. ***D*** varies with temperature ***(T)*** and pressure ***(p)***; therefore also the sampling rate is a function of those variables according to

Q values that will be quoted in the following have been measured at 25 °C and 1013 hPa. As a consequence, they should be corrected so as to reflect the actual sampling conditions.

$$Q = f(T, p)$$

The correction of ***Q*** for atmospheric pressure is usually negligible since its dependence is linear and very seldom we face variations of more than 30 hPa about the average value of 1013 hPa. In the worst case, if corrections for pressure are ignored you make an error of ±3%, usually it is within ±1.5%.

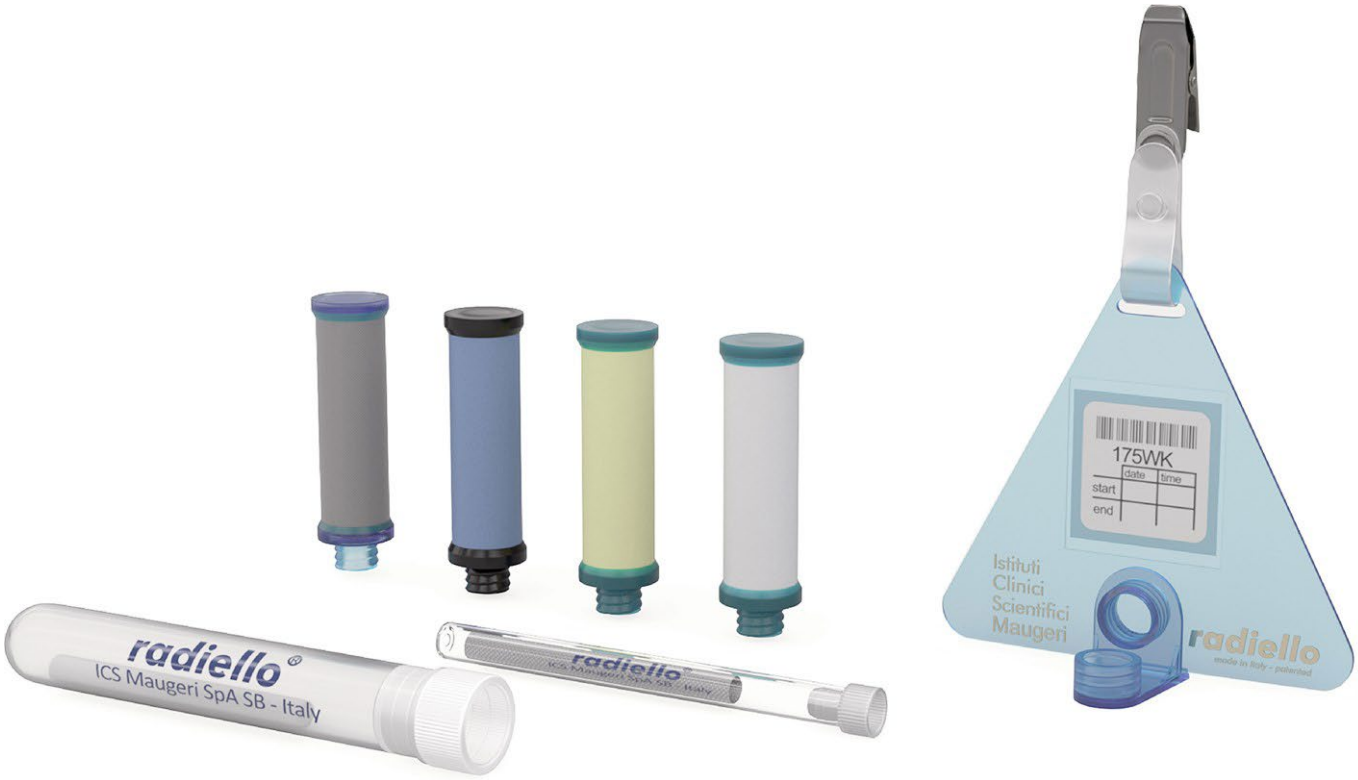
On the other hand, ***Q*** depends exponentially on temperature variations, therefore more relevant errors can be introduced if average temperature is significantly different from 25 °C. Moreover, when chemiadsorbing cartridge are used kinetic effects (variations of reaction velocities between analyte and chemiadsorbing substrate) can be evident, apart from thermodynamic ones (variation of ***D***).

It is therefore very important to know the average temperature in order to ensure accuracy of experimental data. See how you can perform on-field temperature measurements on page 18.

Even if some cartridges adsorb large quantities of water when exposed for a long time in wet atmosphere, generally this does not affect sampling by radiello. Some consequences, neverthless, can sometimes be felt on the analysis. As an example, a very wet graphitised charcoal cartridge could generate ice plugs during cryogenic focusing of thermally desorbed compounds or blow out a FID flame.

It is therefore important to protect radiello from bad weather. See page 16 how this can be easily done.

Why radiello is so special?



The diffusive sampling does not involve the use of heavy and encumbering pumping systems, does not have energy power supply problems, does not require supervision, is noiseless, is not flammable and does not represent an explosion hazard, can be performed by everybody everywhere and with very low costs.

Moreover, it is not subject to the breakthrough problem, which can be serious when active pumping is performed.

Why diffusive sampling has not been so extensively adopted up to now?

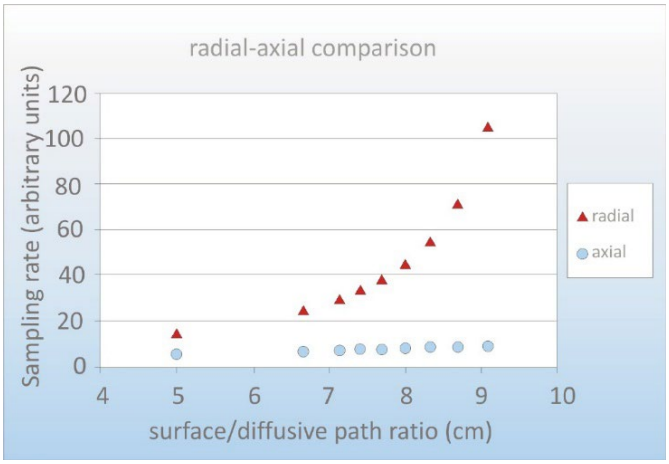
This is due to the fact that the traditional axial symmetry sampler has generally poor sensitivity and reproducibility because of the limits set by its geometry. On one side, uptake rate values are generally low, on the other, they often vary depending on environmental conditions.

These limitations have been overcome by radiello.

By virtue of radial symmetry, uptake rate is:

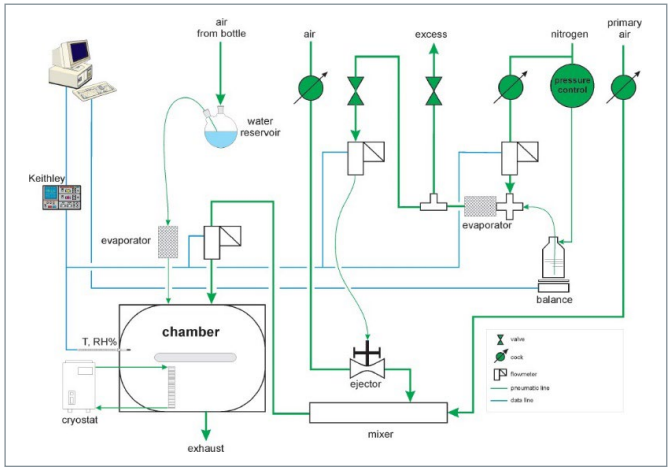
- ***High,*** with the same dimensions, radiello's uptake rate is at least three times higher than that of any axial diffusive sampler;
- ***Constant,*** due to the great adsorbing capacity of the adsorbing

Substrates;



For a traditional axial symmetry sampler the uptake rate increases linearly with the ratio of diffusive surface vs diffusive path length, while for the radial symmetry sampler, the corresponding increase is exponential. This means that, let the diffusive surface vs diffusive path length ratio be 8:1, for the axial sampler the uptake rate value is 8 (regardless of dimensions) while for the radial one it is 45.

- ***Reproducible***, for the continuous control of the homogeneity of the materials used and of all the production lots of radiello;
- ***Precisely measured***, because the flow rate is not estimated but calculated experimentally, measured in a dynamic atmosphere controlled chamber in a wide range of conditions of concentration, temperature, humidity, air velocity, presence of interfering…



Moreover, radiello

- Is able to work properly also with bad weather conditions due to the water-repellent diffusive body
- Has blank values lower than three times the instrumental noise due to the complex conditioning procedures of the bulk adsorbing (or chemiadsorbing) materials and to the repeated quality controls along the whole production
- Has low detection limits and high adsorbing capacities that allow exposure time duration from 15 minutes to 30 days and concentration measurements from 1 ppb to over 1000 ppm
- Offers high precision and accuracy over a wide range of exposure values
- Allows thermal desorption and HRGC-MS analysis without interferents
- Is suited to the sampling of a vast range of gaseous pollutants
- Is though and chemically inert, being made of polycarbonate, microporous polyethylene and stainless steel
- Is indefinitely reusable in all of its components apart from the adsorbing cartridge; the latter can be recovered if thermal desorption is employed
- *It comes from the efforts of one of the mail European scientific research institutions that produces it directly by high technology equipment and continuously submits it to severe tests and performs research and development in its laboratory in Padova*

All the images in the manual concern the Environmental Research Center of the Istituti Clinici Scientifici Maugeri

The components of radiello

The essential parts of radiello are the adsorbing cartridge, the diffusive body, the supporting plate and the adhesive label with the bar code indication. Apart from the adsorbing cartridge, if not differently stated, all of the other components can be repeatedly used for several sampling experiments.

The adsorbing cartridge

Depending on the polluting compound to be sampled, many different adsorbing or chemiadsorbing cartridges have been developed. Their dimensions are nevertheless the same for all: 60 mm length and 4.8 or 5.8 mm diameter.

They are contained in glass or plastic tubes wrapped up in a transparent polyethylene thermowelded bag.

The code number, printed onto the bag along with the lot number and expiry date indicates the kind of cartridge.

Apart from the thermal desorption cartridges, all of the other kinds are for single use only.

Available in 5 or 20 pieces per package.

The cartridge has to be introduced into the diffusive body.

C-RAD1203	C-RAD120	C-RAD1201	C-RAD1202

The diffusive body

Four kinds of diffusive bodies are available, with like outer dimensions: 60 mm height and 16 mm diameter.

The ***white*** diffusive body, ***C-RAD120***, of general use, is made of microporous polyethylene 1.7 mm thick and average porosity 25 ± 5 µm. Diffusive path length is 18 mm.

The ***blue*** diffusive body, ***C-RAD1201***, has the same properties of the white one but is opaque to light: It is suited to the sampling of light-sensitive compounds.

The ***yellow*** diffusive body, ***C-RAD1202***, should be used whenever the sampling rate must be reduced; it is made of microporous polyethylene 5 mm thick and average porosity 10 ± 2 µm. Diffusive path length is 150 mm.

The ***permeative*** diffusive body, ***C-RAD1203***, is a 50 µm thick silicone membrane strengthened by a stainless steel net and a microporous polyethylene cylinder. It is employed for anesthetic gases and vapours sampling.

Available in 20 pieces per package only.

The diffusive body has to be screwed onto the supporting plate.

C-RAD190

The label

Self-adhesive, with printed barcode number. Since each barcode number has been printed in only one copy, it allows an unmistakable identification of the subsequent analysis.

Each package of 20 adsorbing cartridges contains also 21 labels.

If the labels are ordered separately, they are shipped in 198 pieces per package only.

The supporting plate.

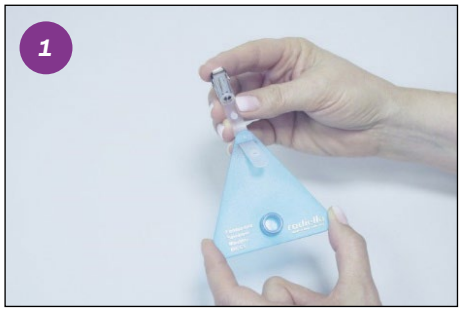
It is identified by the code ***C-RAD121***. Made of polycarbonate, it acts both as closure and support for the diffusive body, which has to be screwed onto the thread. It comes along with a clip and a transparent adhesive pocket to hold the label. The three parts are to be assembled before use (see page 12).

Available in 20 pieces per package only.

How to use radiello

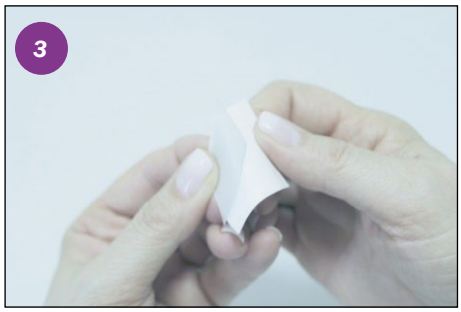
Assembling the supporting plate before sampling

Before using radiello, you have to assemble the supporting plate with the clip, necessary to suspend it, and the adhesive label pocket.

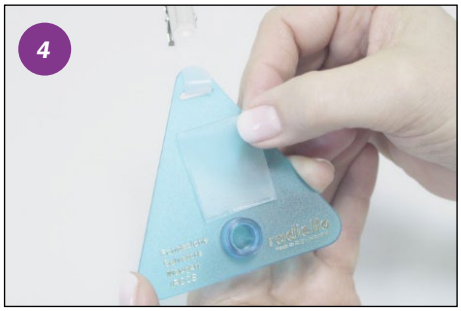


Insert the clip strip in the slot, with the peg facing upwards

Apply the strip and insert the peg into the hole



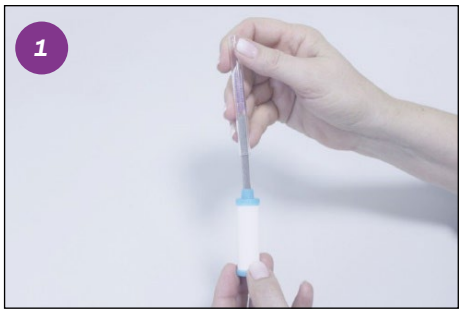
Peel off the transparent pocket and stick it onto the plate in a central position;



If you prefer, the pocket can be applied to the rear of the plate, but BE CAREFUL, always with the label insertion slot on the side (otherwise, if it starts raining the label can get wet)

USER TIP
Assemble the supporting plate in your laboratory before the sampling campaign: on the field they are uselessly time-consuming.

On-field to start the sampling



Open the plastic bag, draw the cartridge out from the tube and put it in the diffusive body. ***Keep the glass or the plastic tube and stopper in the original plastic bag***.

The lower part of the diffusive body holds a seat for the central positioning of the cartridge.

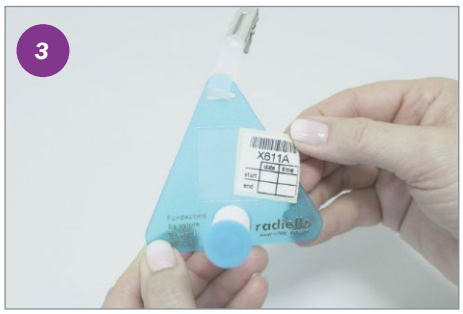
A correctly centered cartridge should not stick out even by half a millimeter. If it is not so, the cartridge is not correctly positioned and is out of axis.

As a consequence, when the diffusive body is screwed onto the supporting plate the cartridge is bent, the geometry of the sampler is disturbed and the results obtained become unreliable.

To place the cartridge centrally you need only to tap on the diffusive body.

How to use radiello

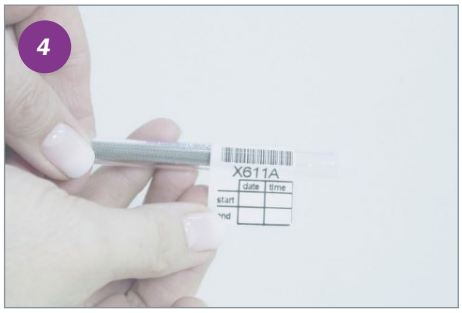
Keeping the diffusive body in a vertical position, screw it onto the supporting plate.



BE CAREFUL:
Do not hold the diffusive body horizontally when you screw it onto the plate, otherwise the cartridge could come out from its seat and stick out. Insert a label in the pocket without peeling it off. Keep note of the date and time and expose radiello. Sampling has started.

USER TIP
Even if you can write date and time of the sampling start and end on the adhesive label, we suggest you to keep note of these parameters also separately: after a week exposure with bad weather conditions, your writings could become illegible!

DO NOT USE MARKING PENS to write on the label: they contain solvents that are sampled by radiello!



After the sampling

Keep note of the date and time of the end of exposure.

Place the cartridge into the tube, peel off the label and stick it onto the tube such that the barcode is parallel to the axis of the tube.

If you have performed the sampling of different polluting compounds at the same time, BE CAREFUL NOT TO MIX UP THE TUBES: place the exposed cartridge in its original tube, identified by the code printed on the plastic bag.

IMPORTANT:
Always stick the label such that the barcode is parallel to the axis of the tube: any other position will compromise the barcode automated reading by the optic reading device.

Maintenance

When exposed outdoors or in a workplace environment, the diffusive body may get dirty from airborne dust. Fine particles (PM10) are especially harmful to yellow diffusive bodies since they can obstruct the pores. When the diffusive bodies are dirty you can wash them as follows.

Immerse the diffusive bodies in a beaker with a soapy solution (e.g. dish detergent) and sonicate them for 20 minutes. As the diffusive bodies float, you may make them sink by putting a smaller beaker on them, with water inside enough to dip it a few centimeters.

Rinse the diffusive bodies with plenty of water and then deionized water; let them finally dry in the air.

IMPORTANT:
Never use solvents to clean the diffusive body

After four or five washings, diffusive bodies need replacing: repeatedly adsorbed dust may have penetrated the pores such deeply to be undisturbed by washing.

The following table shows the advised washing schedule:

PM_{10} concentration ($\mu g \cdot m^{-3}$)	< 30	40	> 50
Washing after days of exposure	45	30	15

Radiello Ready-to-use

The ready-to-use version may be advantageous when you prefer not to assemble all of the components on field. It can be purchased as it is or in separate parts to be assembled by the customer.

Left: radiello-ready-to-use

Centre: the diffusive body with the polycarbonate cap and the adsorbing cartridge inside

Right: The special snapping adapter

The supporting plate with the vertical snapping adapter

In the as-it-is version the adsorbing cartridge is already contained in a diffusive body closed with a polycarbonate screw-thread cap. The whole is closed in a polypropylene airtight container. Just before use draw the diffusive body out of the container and fit it to the special snapping vertical adapter fixed to the supporting plate. After the end of exposure, the diffusive body with its content is placed again in the poly- propylene airtight container to be shipped to the laboratory for analysis. The ready-to-use as-it-is radiello (polycarbonate cap, glass or plastic tube, special vertical adapter, barcode label and polypropylene container comprised for each type) is available for the sampling of the following compounds:

CODE	SAMPLING OF	CONTAINS
C-RAD1231	BTEX and VOCs	White diffusive body and cartridge code C-RAD130
C-RAD1232	BTEX and VOCs	Yellow diffusive body and cartridge code C-RAD145
C-- RAD1233	NO_2, SO_2 and HF	Blue diffusive body and cartridge code C-RAD166
C-RAD1233	Aldehydes	Blue diffusive body and cartridge code C-RAD165
C-RAD1235	Ozone	Blue diffusive body and cartridge code C-RAD172
C-RAD1236	Hydrogen Sulfide	White diffusive body and cartridge code C-RAD170
C-RAD1237	Ammonia	Blue diffusive body and cartridge code C-RAD168
C-RAD1238	HCl	White diffusive body and cartridge code C- RAD169

IMPORTANT:
In the ready-to-use version the supporting plate is not provided.

If you prefer to assemble it by yourselves, you should order:

- ✓ Diffusive bodies (of the required type, see following chapters)
- ✓ Adsorbing cartridges (of the required type, see following chapters)
- ✓ Polycarbonate caps, ***code C-RAD1241***
- ✓ Special snapping adapters, ***code C-RAD1221***
- ✓ Polypropylene containers, ***code C-RAD1242***
- ✓ Supporting plates, ***code C-RAD121***

USER TIP
The ready-to-use version of radiello is very useful in the workplace sampling campaigns but is not advised if very low concentrations in outdoor or domestic environments are to be measured.

Fit the diffusive body to the adapter by pushing it till you hear a clicking sound.

Draw the diffusive body by tilting it with decision.

Accessories

Vertical adapter

Code C-RAD122

Available in 20 pieces per package only

The diffusive body can be fitted to the supporting plate either in a vertical or horizontal position, the vertical one being more comfortable when radiello is used for personal sampling.

To assemble radiello in vertical position you have to screw it to the vertical adapter code C-RAD122, fitted to the supporting plate.

Place the vertical adapter over the mounting point on the plate

Press the adapter onto the plate with your thumbs till the ridge fits the edge of the plate.

Shelter

Code C-RAD196

For outdoor exposures a mountable polypropylene shelter is available which can be hanged to lamp posts.

Available in 10 pieces per package only

It has been designed to be mounted easily and without any tool on field, so that it is not cumbersome when you transport it from your laboratory. Once assembled, it ensures the best compromise between protection against bad weather and ventilation.

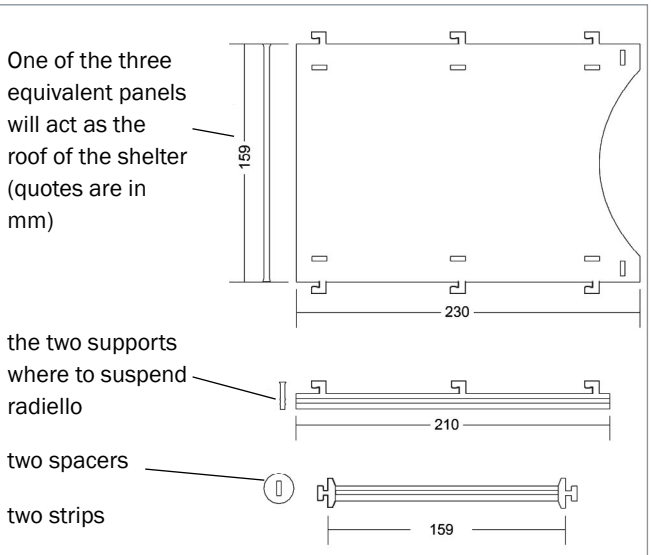
It can house up to four radiello and is able to fit a wide range of pole diameters.

Its colour is quite similar to that of the majority of lampposts: being less visible, it is less subject to acts of vandalism.

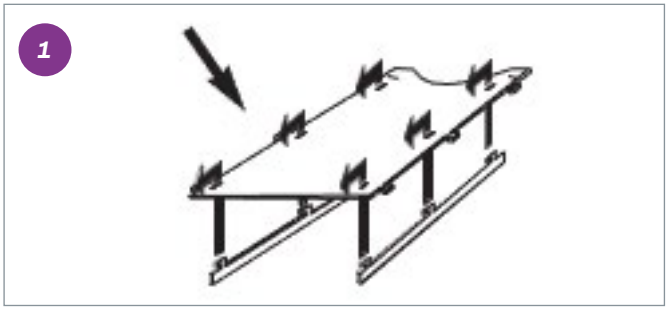
USER TIP
The adapter can be removed from the plate by lifting the ridge.

IMPORTANT:
When mounting the diffusive body be careful to keep it vertical with the thread upside (see page 12).

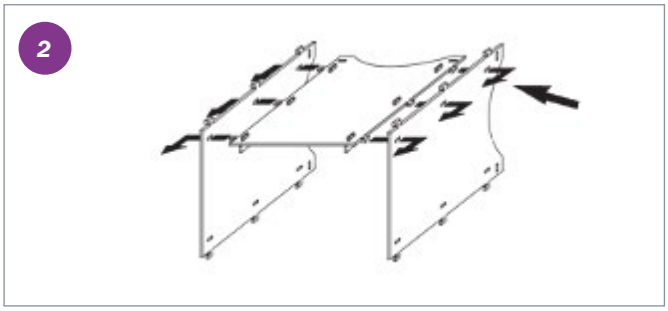
How to assemble the shelter



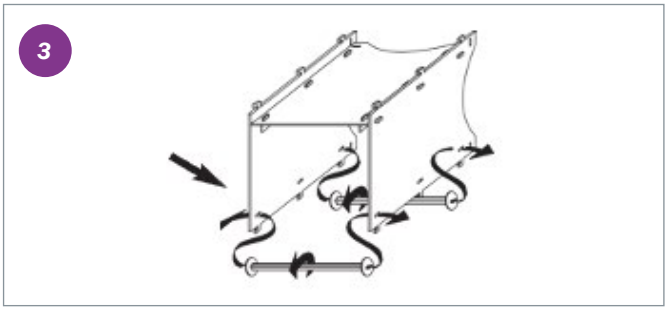
All of the components are snap-on assemble



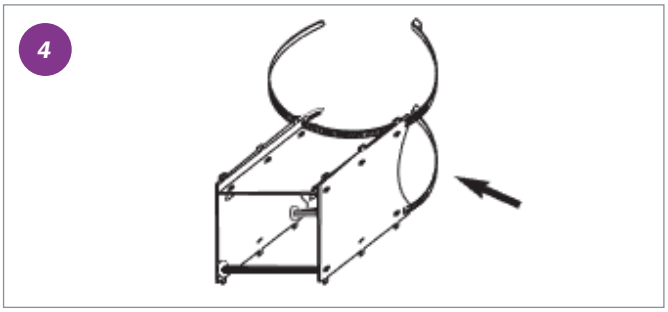
First of all, insert on this panel (the roof) the two supports that will be used to suspend the samplers.



Then fix the two walls on the sides of the roof panel.



The whole becomes rigid by insertion of the two spacers. Fit them to the slots on bottom of the side panels and turn them by 90° (performing this rotation you may feel some resistance, but go on until you hear a clicking sound).



Finally, insert two plastic strips in the rear vertical slots of the side panels. The strips are also available as spare parts, in 100 pieces per package, identified by the ***code C-RAD198.***

Suspend the shelter to the pole by closure of the strips, but ***DO NOT DRAW SO MUCH THAT THE SHELTER IS DEFORMED***. If the pole has diameter larger than 20 cm, the shelter leans on the curved edges on the rear of the sidewalls. If the pole has a smaller diameter, it leans against the curved edge of the roof panel and the rear spacer. If the diameter is very small the shelter bows down, the wind may make it go round, or the shelter may even slip down to ground. It is then advisable to choose another pole.

USER TIP

If the pole diameter is larger than the strip length, you can put two or more strips together to extend the fastening system.

If the sampling site is very windy, do not introduce more than two radiello samplers in each shelter, otherwise rain could dampen the outermost samplers.

On-field temperature measurements

Thermometer code C-RAD126

Available in 3 pieces per package only

C-RAD126

C-RAD127

Since the uptake rate values of radiello depend on temperature, the concentration values obtained will be more accurate if precise temperature measurements are performed during the sampling.

To get reliable temperature data you may ask the local weather station, if there is one, and if the measurements are performed nearby your sampling sites. Bear in mind that you should take into the account the urban heat island: did you know that there can be a difference of even 4-5 °C between the center and the suburbs of a big town?

With radiello you can create your own temperature measurement station.

A thermometer with precision ± 0,5 °C between -20 and 80 °C and equipped with a data logger capable of recording 2048 data points has been fixed to a vertical adapter (***code C-RAD126)***.

It is tiny enough (< 1 cm^3) to go perfectly unobserved.

It has no battery to replace, needs no maintenance and works properly even with bad weather conditions.

Its memory allows you to record one temperature value every 15 minutes for 22 days, or every 30 minutes for 43 days, or every 60 minutes for 85 days, or... it lasts ten years or a million readings!

The thermometer is fitted to the supporting plate of radiello: use the sampler normally and measure temperature and pollution at the same time.

Reader code RAD127

A very simple ***reader (code C-RAD127)***, connected to your PC by a USB port, allows you to program the temperature sensor for the measurements on field, to download the acquired data and to perform data statistical and graphic processing by a very user-friendly software.

USER TIP

When performing urban monitoring install a thermometer every ten sampling sites. If this may help you, contact us to discuss sampling strategies..

Calibration solution for H_2S

Code C-RAD171

Code C-RAD171 relieves you from the task of preparing the sodium sulfide standard solution for the calibration curve used for the determination of H_2S by the cartridge code C-RAD170 (see page 46).

Since sodium sulfide is deliquescent, its weight is not a primary standard and sodium sulfide solution need titration once prepared. Moreover, titration must be repeated often due to the instability of diluted solution (one hour time is sufficient to decrease sulfide content by 10%).

Solution	mL ofmL of water		equivalent to $\mu g \cdot ml^{-1}$ of S=
A	2 di codice 171	98	1.145
B	25 di A	25	0.572
C	10 di A	40	0.229
D	5 di A	45	0.115

Code C-RAD171 is a methylene blue concentrated solution that, once diluted 1:50, provides the same absorbance value at 665 nm of a sodium sulfide solution of with concentration 1.145 $\mu g \cdot ml^{-1}$ sulfide ions.

This concentration value has been chosen to obtain the highest absorbance value within the linearity range of the spectrophotometer.

To obtain a complete calibration curve, just dilute the mother solution as shown in the table.

Code C-RAD171 allows you to prepare as many as 50 calibration curves.

Kept closed at room temperature, code C-RAD171 solution is stable for at least one year.

Filtration kit

Code C-RAD174

Code C-RAD174 filtration kit is composed by 20 single use plastic syringes and 20 single use micropore hydrophilic polypropylene filters with diameter 13 mm and 0.45 µm porosity.

Both filter and syringe are suited to filtration of aqueous solutions with pH in the range of 0 to 12 with commonplace eluents for ion chromatography and reverse phase HPLC.

Calibration solutions for aldehydes

Code C-RAD302

Calibration curves for aldehydes are obtained with standard solutions of the corresponding 2,4-dinitrophenylhydrazones (see page 22). Although their synthesis is straightforward, their purification is tricky and time-consuming. Code C-RAD302 offers a certified and convenient choice: a solution of nine 2,4-dinitrophenylhydrazones in a solvent compatible with HPLC eluents and with concentrations suitable for the preparation of calibration curves in the range usually spanned by radiello samples.

Code C-RAD302 is delivered as 10 ml of acetonitrile solutions of the nine 2,4-dinitrophenylhydrazones formed by the aldehydes listed in the table, contained in a pierceable-septum crimped cap vial. The listed concentration values are indicative, actual ones are cer tified for each lot.

Kept tightly capped in a dark place at 4 °C, the solution is stable for at least four months.

2,4-DNPH of	$\mu g \cdot ml^{-1}$ as aldehyde
Formaldehyde	50
Acetaldehyde	50
Acrolein	10
Propanal	50
Butanal	50
Isopentanal	50
Pentanal	50
Hexanal	50
Benzaldehyde	50

Calibration solutions for BTEX (CS_2 desorption)

Code C-RAD405

Code C-RAD405 calibration kit has been conceived for the analysis of BTEX sampled in urban environments by the cartridge code C-RAD130 and chemically desorbed by carbon disulfide (see page 27).

The kit may be used both for routine calibration and for scheduled quality control of the calibration procedure described on page 31.

Code	Simulated concentrations in $\mu g \cdot m^{-3}$ C-RAD405 (7 days exposure equivalent)		
C-RAD405	**Group 1**	**Group 2**	**Group 3**
Benzene	1	10	50
Toluene	2	20	100
Ethylbenzene	1	10	50
M-xylene	1	10	50
P-xylene	1	10	50
O-xylene	1	10	50

It is composed of 12 code C-RAD130 cartridges, three of which are blanks and nine, divided into three groups of three, preloaded with BTEX to simulate 7 days exposures (10,080 minutes) o the concentrations listed in the table. The values shown are ndicative, actual ones are certified for each lot.

The mass of each analyte deposited onto the cartridge spans he whole range of concentrations usually found in urban envionments, extreme values included.

BTEX loading is performed by injection of precisely known amounts of vaporized standard solutions in CS_2 of the five

compounds under nitrogen flow.

Kept at 4 °C, the cartridges are stable for at least four months.

Calibration solutions for VOCs in workplace environments

Code C-RAD406

The code C-RAD406 kit has been conceived for scheduled quality control of the calibration procedure for the analysis of volatile organic compounds (VOCs) sampled by code C-RAD130 cartridges in workplace environments (see page 30).

It is composed of 12 code C-RAD130 cartridges, three of which are blanks and nine, divided into three groups of three, preloaded with VOCs to simulate 8 hours exposures (480 minutes) to the concentrations listed in the table. The values shown are indicative, actual ones are certified for each lot.

The composition of the mixture is simple but it includes compounds with different polarity. The loaded mass is calculated in order to represent exposures to 0.5, 1 and 2 times the TLV value for the mixture.

VOCs loading is performed by injection of precisely known amounts of calibrated mixtures of the eight compounds under nitrogen flow.

Kept at 4 °C, the cartridges are stable for at least four months.

Code	Simulated concentrations in $mg \cdot m^{-3}$ C-RAD406 (8 hours exposure equivalent)		
C-RAD406	**Group 1**	**Group 2**	**Group 3**
Benzene	0.1	0.2	0.4
Toluene	19	38	76
Ethylbenzene	12	24	48
M-xylene	12	24	48
P-xylene	12	24	48
O-xylene	12	24	48
Butanol	15	30	60
2-etoxyiethyl acetate	2.5	5	10

Calibration solutions for BTEX (thermal desorption)

Code C-RAD407

Code	Simulated concentrations in µg·m^{-3} (7 days exposure equivalent)		
C-RAD407	**Group 1**	**Group 2**	**Group 3**
Benzene	1	5	25
Toluene	2	10	50
Ethylbenzene	1	5	25
M-xylene	1	5	25
P-xylene	1	5	25
O-xylene	1	5	25

Code C-RAD407 calibration kit has been conceived for the analysis of BTEX sampled in urban environments by the cartridge code C-RAD145 and thermally desorbed (see VOCs - thermal desorpion).

The kit may be used both for routine calibration and for scheduled quality control of the calibration procedure described on page 38. t is composed of 12 code C-RAD145 cartridges, three of which are blanks and nine, divided into three groups of three, preloaded with BTEX to simulate 7 days exposures (10,080 minutes) to the concentrations listed in the table.

The values shown are indicative, actual ones are certified for each lot.

BTEX loading is performed by injection of precisely known amounts of vaporized standard solutions in methanol of the five compounds under nitrogen flow. During the analysis the chromatographic peak of methanol will be visible. Kept at 4 °C, the cartridges are stable for at least four months.

The spare parts

Barcode adhesive label

Codice C-RAD190

Available in 198 pieces per package only

Barcode adhesive label

Code C-RAD190

Available in 198 pieces per package only.

Strip

Code C-RAD198

Useful for repositioning of radiello shelter. Length 75 cm.
Available in 100 pieces per package only.

Tubes

Available in 20 pieces per package only.

Code C-RAD1991

Glass tube, working volume 2.8 ml

Code C-RAD1992

Polypropylene tube, working volume 12ml

Aldehydes

What you need

Blue diffusive body code C-RAD1201

Supporting plate code C-RAD121

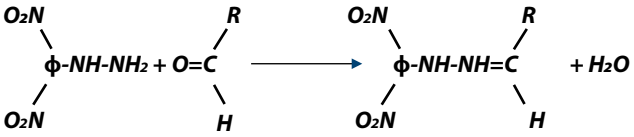
Vertical adapter code C-RAD122

(Optional) chemiadsorbing cartridge code C-RAD165

Filtration kit code C-RAD174 (only for analysis)

Principle

Code C-RAD165 is a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated Florisil®. Aldehydes react with 2,4-DNPH to give the corresponding 2,4-dinitrophenylhydrazones



2,4-DNPH ***aldehyde*** ***2,4-DNPhydrazone***

The 2,4-dinitrophenylhydrazones are then extracted with acetronitrile and analyzed by reverse phase HPLC and UV detection.

Sampling rates

Sampling rates values at 298 K (25 °C) and 1013 hPa are listed below:

	Sampling rate ml·min^{-1}	Linearity range µg·m^{-3}·min	Limit of quantitation1 µg·m^{-3}	Uncertainty % at 2a-%
Acetaldehyde	84	1,000÷12,000,000	0.1	15.9
Acrolein	33	3,000÷3,000,000	0.3	16.5
Benzaldehyde	92	1,000÷8,000,000	0.1	17.2
Butanal	11	9,000÷10,000,000	0.9	23.5
Hexanal	18	5,000÷15,000,000	0.6	20.2
Formaldehyde	99	1,000÷4,000,000	0.1	13.8
Glutaric Aldehyde	90	1,000÷3,000,000	0.1	14.5
Isopentanal	61	1,500÷12,000,000	0.2	17.0
Pentanal	27	4,000÷12,000,000	0.4	22.9
Propanal	39	3,000÷8,000,000	0.3	17.1

1after 7 days exposure

Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298}\right)^{0.35}$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. This produces a variation of ± 1% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 m·s^{-1}.

Calculations

The average concentration C over the whole sampling time (in µg·m^{-3}) is calculated according to the expression:

where:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q\ [ml \cdot min^{-1}] \cdot t\ [min]}\ 1{,}000{,}000$$

m = mass of aldehyde in µg

t = exposure time in minutes

Exposure

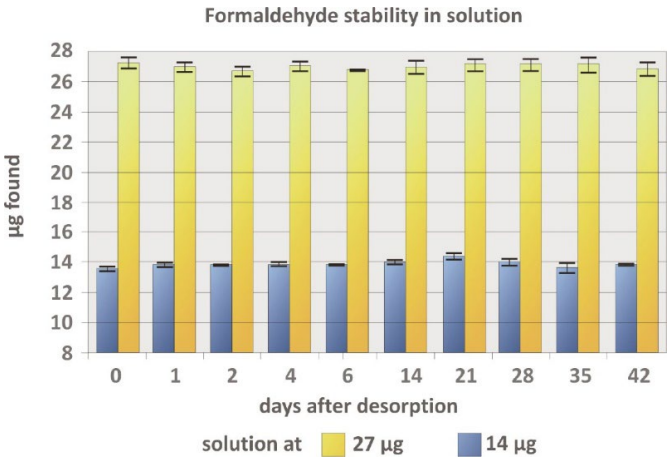
The optimum exposure duration varies with the expected concentration. Taking formaldehyde as an example, concentration values of 5-30 µg·m^{-3} are usually found in outdoor urban measurements while 20-200 µg·m^{-3} are expected in workplace environments. In workplace environments concentrations may be as high as 2,000-3,000 µg·m^{-3} for short time intervals: it can therefore be interesting to evaluate the peak value (usually referred to by STEL). The corresponding advised exposure time is shown in the table below:

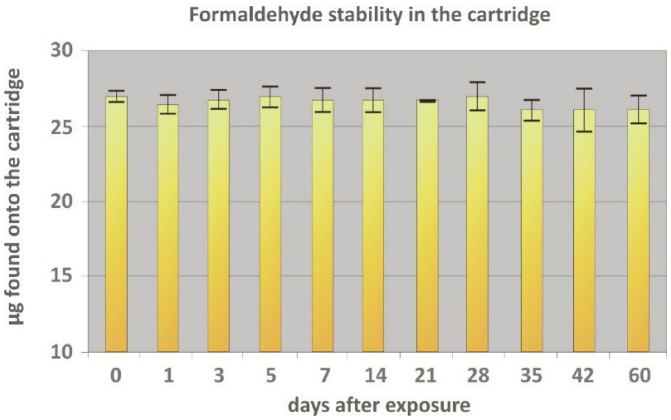
Advised exposure times

	outdoor environment	indoor environment	workplace average conc.	environment peak conc.
minimum	8 h	8 h	2h	15 minutes
maximum	7 days	7 days	8h	1h

Storage

The cartridges need to be kept, properly sealed, in a dark place at 4 °C for ensuring a shelf life (according to EN 13528-2) of six months. If stored at ≤ -18 °C, the shelf life will be twelve months. Each lot is approved for use when the blank value of formaldehyde and acetaldehyde are less than 0.1 µg and 0.3 µg per cartridge, respectively, corresponding to a concentration in air less than 0.1 and 0.25 $\mu g \cdot m^{-3}$ over one week of exposure, respectively. The blank value may increase with time. After exposure keep the cartridges well capped at 4 °C,





Formaldehyde stability in the cartridge after the sampling (on top) and in solution (left). The stability tests were performed upon cartridges exposed for one week in a standard atmosphere chamber at 25 °C and with 50% relative humidity and at two different concentration levels. Each bar in the plot represents the average and error from the analysis of six samples.

they are stable for 60 days. After solvent desorption (see Analysis) discard the cartridge. The resulting solution, well capped and stored at 4 °C, is stable for at least 42 days.

Analysis

Desorption

Materials

- HPLC grade acetonitrile
- Class A volumetric pipette, capacity 2 ml
- Micropore filter membranes, porosity 0.45 µm, solvent resistant

Procedure

Introduce 2 ml acetonitrile directly in the cartridge tube, recap and stir from time to time for 30 minutes. Discard the cartridge. Filter the resulting solution and keep it well capped until analysis time. If analysis has to be delayed, store the solution at 4 °C.

USER TIP

For a reliable and rapid filtration employ the filtration kit code C-RAD174.

To obtain an accurate calibration curve we offer you the calibration solution code C-RAD302.

Instrumental analysis

The method suggested below is only indicative; the analyst can choose an alternative method, on the basis of its personal experience.

IMPORTANT:
verify the presence and the abundance of the 2,4-DNPH chromatographic peak: otherwise, the cartridge could be saturated.

Materials

- Reverse phase C18 HPLC column, length 150 mm, 4.6 mm diameter, 5µm packing particle size

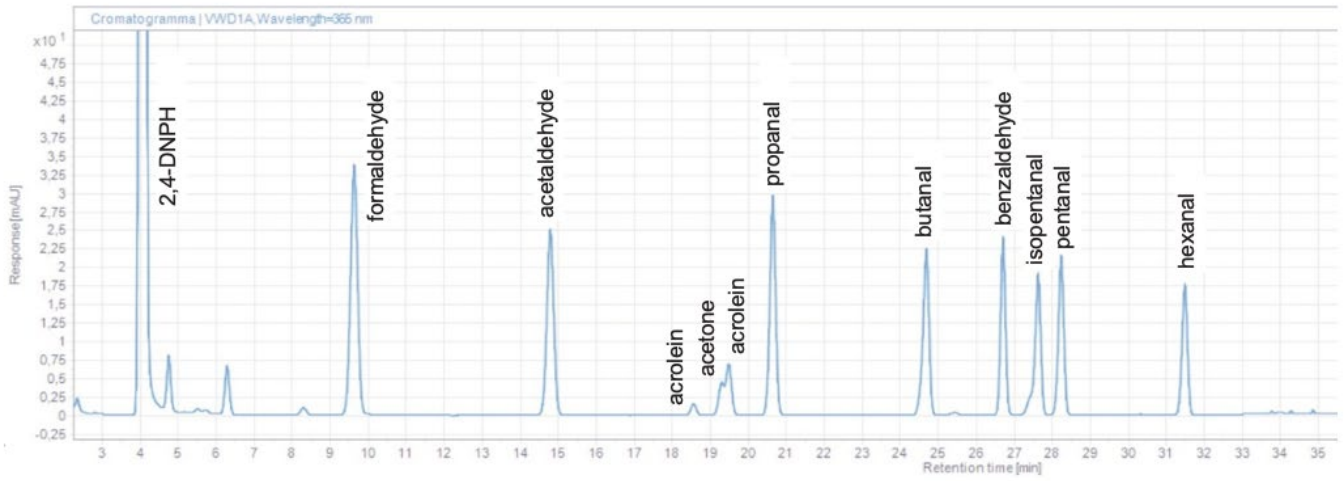
- HPLC apparatus capable of elution gradient and UV detection

Procedure

Set the detector at the wavelength of 365 nm. Inject between 10 and 50 µl of solution and elute as follow:

- Flow: 1.9 ml·min-1
- Isocratic elution with water/acetonitrile 63:37 v/v for 10 minutes, up to water/acetonitrile 31:69 v/v in 20 minutes, isocratic elution with water/acetonitrile 0:100 v/v in 5 minutes, isocratic elution with water/acetonitrile 63:37 v/v in 15 minutes.

On the right: the chromatogram of a real sample analyzed under the described conditions.



IMPORTANT:

Acrolein gives place to three chromatographic peaks, two of them are unresolved. Calculate the concentration basing onto this most abundant peak and ignore the others.

Isopentanal appears as two unresolved peaks: its concentration should be obtained by integration of both peaks as a sum.

USER TIP

If you perform several analyses, a barcode reader will greatly improve productivity in your laboratory and will also minimize the possibility of errors in the copying of sample labels.

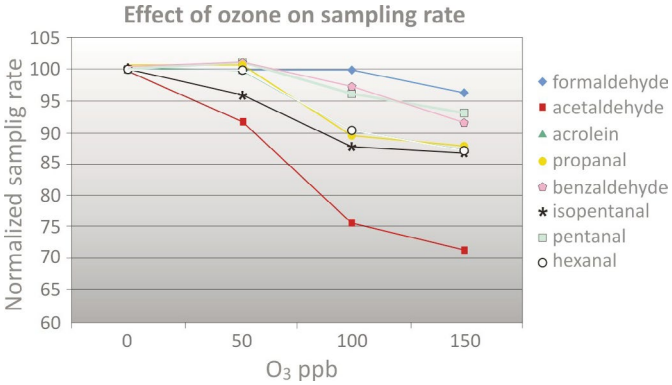
Please contact us to help you in the implementation of the reader.

Interferences

Other carbonyl compounds

All carbonyl compounds, ketones included, react with 2,4-DNPH but do not interfere in the analysis if proper chromatographic parameters are selected.

In the described chromatographic conditions acetone-2,4-DNPH peak is well resolved from acrolein-2,4-DNPH. Nevertheless, if acetone concentration is higher than 50,000 $\mu g \cdot m^{-3}$, acrolein-2,4-DNPH peak intensity is depressed by 25%.



Sampling rate as a function of ozone concentration normalized to 100 for [O₃] equal to zero. Apart from acetaldehyde, ozone effect

becomes relevant only at concentration levels higher than 100 ppb as an average over the whole exposure time interval.

Ozone

Examples of ozonolysis of dinitrophenylhydrazones on active supporting materials as silica gel are found in the literature.

On code C-RAD165 cartridge, packed with coated Florisil®, ozonolysis is much less important than on any other commercial aldehyde sampling device, either diffusive or pumped, and becomes appreciable only if ozone concentration, averaged over the whole exposure time interval, is higher than 100 ppb. Since this is not usually the case, generally no correction is needed to take into account ozone concentration. If there is firm evidence that ozone concentration is equal or higher than 100 ppb over the whole exposure time, make use of the corrected sampling rate values shown in the table below, where [O₃] is ozone concentration in ppb. The listed values are referred to the temperature of

298 K (25 °C), for deviations larger than ± 10 °C substitute the base value (e.g. 99 ml·min-1 for formaldehyde) with the corrected value calculated according to equation on page 22.

No experimental data is available for butanal and glutaric aldehyde.

	Corrected sampling rate $ml \cdot min^{-1}$
Acetaldehyde	84-0.018[O₃]*
Acrolein	33-0.027[O₃]
Benzaldehyde	92-0.05[O₃]
Hexanal	18-0.02[O₃]
Formaldehyde	99-0.02[O₃]
Isopentanal	61-0.06[O₃]
Pentanal	27-0.01[O₃]
Propanal	39-0.03[O₃]

**apply for ozone concentration higher than 50 ppb*

Sampling rate for ozone concentration [O₃] in ppb (apply only if [O₃] >100 ppb)

Volatile organic compounds (VOCs) - chemically desorbed with CS_2

What you need

white diffusive body code C-RAD120

Supporting plate code C-RAD121

Vertical adapter code C-RAD122

(optional) chemiadsorbing cartridge code C-RAD130
Or: radiello-ready-to-use code C-RAD1231

Principle

Codeode C-RAD130 cartridge is a stainless steel net cylinder, with 100 mesh grid opening and 5.8 mm diameter, packed with 530 ± 30 mg of activated charcoal, particle size is 35-50 mesh. Volatile organic compounds are trapped by adsorption and recovered by carbon disulfide displacement, analysis is performed by FID gas chromatography.

Sampling rates

The table on page 28 lists sampling rate values at 298 K (25 °C) and 1013 hPa, experimentally measured in a standard atmosphere chamber. For other compounds whose diffusion coefficient1 is known sampling rate can be calculated according to equation [5] on page 7, taking into account that white diffusive body and code C-RAD130 cartridge give the geometric constant of radiello the value of 14.145 ± 0.110 cm. Several experiments performed in the standard atmosphere chamber demonstrate that the calculated sampling rates seldom deviate by more than

±10% from the experimentally measured values.

Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{1.5}$$

Where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. This produces a variation of ±5% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15 ÷ 90% and with wind speed between 0.1 and 10 $m \cdot s^{-1}$.

[1]Lugg G.A.: Diffusion Coefficients of Some Organic and Other Vapors in Air. Anal. Chem. 40-7:1072-1077 (1968).

Calculations

The listed sampling rate values already take into account for the desorption efficiency with carbon disulfide. The average concentration over the exposure time interval is therefore calculated from the mass of analyte found onto the cartridge and exposure time without introducing any corrective factor, apart from corrections due to average temperature different from 25 °C.

Average concentration (in $\mu g \cdot m^{-3}$) over the whole exposure time is calculated according to the following expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ \mathbf{1{,}000{,}000}$$

where:

m = mass of analyte in µg

t = exposure time in minutes

Volatile organic compounds (VOCs) - chemically desorbed with CS_2

Sampling rate values at 25°C (298 K)				
	sampling rate $ml \cdot min^{-1}$	linearity range $\mu g \cdot m^{-3} \cdot min$	uncertainty 2σ %	Notes
acetone	77	10,000-600·10⁶	7.0	a
acetonitrile	73	10,000-6·10⁶	8.2	b
acrylonitrile	75	1,000-50·10⁶	2.2	
benzyl alcohol	37	1,000-800·10⁶	6.5	
amyl acetate	52	1,000-800·10⁶	3.4	
benzene	80	500-500·10⁶	1.8	
bromochloromethane	70	50,000-1,000·10⁶	1.4	
butanol	74	1,000-500·10⁶	5.0	
sec-butanol	64	1,000-300·10⁶	5.2	
tert-butanol	62	1,000-300·10⁶	5.5	
butyl acetate	60	1,000-1,000·10⁶	3.0	
2-butoxyethanol	56	1,000-100·10⁶	5.7	
2-butoxyethyl acetate	41	1,000-100·10⁶	5.5	
carbon tetrachloride	67	100,000-60·10⁶	9.0	
cyclohexane	54	500-500·10⁶	4.5	
cyclohexanone	68	5,000-120·10⁶	4.2	
cyclohexanol	54	5,000-120·10⁶	4.5	
chlorobenzene	68	1,000-1,000·10⁶	3.6	
chloroform	75	100,000-60·10⁶	9.7	a
n-decane	43	500-1,000·10⁶	1.1	
diaceton alcohol	43	500-1,000·10⁶	4.5	
1,4-dichlorobenzene	51	1,000-1,000·10⁶	7.7	
1,2-dichloroethane	77	1,000-500·10⁶	8.2	
1,2-dichloropropane	66	500-250·10⁶	4.5	
dichloromethane	90	500-60·10⁶	8.7	
N,N-dimetylformamide	82	1,000-200·10⁶	14.5	c
1,4-dioxane	68	1,000-600·10⁶	5.5	
n-dodecane	8	1,000-1,000·10⁶	4.7	
n-heptane	58	5,000-1,500·10⁶	3.0	
n-hexane	66	1,000-1,000·10⁶	2.5	
1-hexanol	52	5,000-120·10⁶	5.5	
ethanol	102	10,000-500·10⁶	7.5	a-b
diethyl ether	78	5,000-500·10⁶	12.0	a
ethyl acetate	78	1,000-1,000·10⁶	1.5	
ethylbenzene	68	1,000-1,000·10⁶	2.4	
2-ethyl-1-hexanol	43	5,000-500·10⁶	10.1	
2-ethoxyethanol	55	500-50·10⁶	6.7	b
2-ethoxyethyl acetate	54	10,000-100·10⁶	2.5	
ethyl-tert-butyl ether (ETBE)	61	500-200·10⁶	3.0	
isobutanol	77	1,000-300·10⁶	2.5	
isobutyl acetate	63	1,000-1,000·10⁶	5.2	
isooctane	55	500-1,000·10⁶	3.2	
isopropanol	52	10,000-400·10⁶	12.0	b
isopropyl acetate	66	1,000-1,000·10⁶	9.9	
isopropylbenzene	58	1,000-1,000·10⁶	2.7	
limonene	43	1,000-1,000·10⁶	10.0	
methanol	125	10,000-250·10⁶	9.2	a-b
methyl acetate	80	1,000-1,000·10⁶	12.0	
methyl-ter-butyl ether (MTBE)	65	500-200·10⁶	2.5	

Sampling rate values at 25°C (298 K)				
	sampling rate $ml \cdot min^{-1}$	linearity range $\mu g \cdot m^{-3} \cdot min$	uncertainty 2σ %	Notes
methylcyclohexane	66	$1{,}000\text{-}1{,}000 \cdot 10^6$	6.5	
methylcyclopentane	70	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.5	
methylethylketone	79	$1{,}000\text{-}500 \cdot 10^6$	1.6	
methylisobutylketone	67	$1{,}000\text{-}250 \cdot 10^6$	8.7	
methyl metacrylate	68	$1{,}000\text{-}500 \cdot 10^6$	2.5	
2-methylpentane	70	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.5	
3-methylpentane	70	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.5	
2-methoxyethanol	35	$5{,}000\text{-}100 \cdot 10^6$	11.0	b
2-methoxyethyl acetate	56	$2{,}000\text{-}100 \cdot 10^6$	3.0	
1-methoxy-2-propanol	55	$1{,}000\text{-}350 \cdot 10^6$	6.0	
1-methoxy-2-propyl acetate	60	$2{,}000\text{-}350 \cdot 10^6$	6.2	
naphtalene	25	$1{,}000\text{-}1{,}000 \cdot 10^6$	7.0	
n-nonane	48	$1{,}000\text{-}1{,}000 \cdot 10^6$	5.4	
n-octane	53	$500\text{-}1{,}000 \cdot 10^6$	3.2	
pentane	74	$1{,}000\text{-}1{,}000 \cdot 10^6$	1.9	
-pinene	53	$1{,}000\text{-}1{,}000 \cdot 10^6$	7.0	
propyl acetate	65	$500\text{-}1{,}000 \cdot 10^6$	7.5	
propylbenzene	57	$1{,}000\text{-}1{,}000 \cdot 10^6$	2.9	
styrene	61	$1{,}000\text{-}500 \cdot 10^6$	3.0	
tetrachloroethylene	59	$10{,}000\text{-}500 \cdot 10^6$	2.5	
tetrahydrofuran	74	$2{,}000\text{-}250 \cdot 10^6$	11.0	b
toluene	74	$500\text{-}1{,}000 \cdot 10^6$	1.5	
1,1,1-trichloroethane	62	$5{,}000\text{-}1{,}000 \cdot 10^6$	5.5	
trichloroethylene	69	$5{,}000\text{-}1{,}000 \cdot 10^6$	2.4	
1,2,4-trimethylbenzene	50	$500\text{-}1{,}000 \cdot 10^6$	6.6	
n-undecane	24	$1{,}000\text{-}1{,}000 \cdot 10^6$	10.0	
m-xylene	70	$500\text{-}1{,}000 \cdot 10^6$	2.5	
o-xylene	65	$500\text{-}1{,}000 \cdot 10^6$	2.5	
p-xylene	70	$500\text{-}1{,}000 \cdot 10^6$	2.5	

Notes:

a = weakly adsorbed compound. If its concentration is higher than the TLV for the workplace environments it may be partially displaced by other compounds that are more strongly trapped if their concentration is also high. If this is the case, it is advisable to reduce sampling time under 8 hours.

b = prolonged exposure of charcoal cartridges at relative average humidity higher than 80% causes adsorption of up to 100 mg of water. Water does not interfere with adsorption mechanisms but is displaced by carbon disulfide and gives raise to a separate layer. Some very water soluble polar compounds will distribute between the two solvents, thus provoking an underestimation of the actual air concentration since only the carbon disulfide is injected in the gas chromatograph. When the concentration of polar compounds has to be determined, the calibration curve should be prepared by spiking 50 µl of water in each tube containing the cartridge and the 2 ml of carbon disulfide standard solution (see Analysis).

c = better reproducibility obtained by use of methanol as extraction solvent instead of carbon disulfide.

Limit of quantitation

The limit of quantitation depends on the instrumentation and on the analytical conditions. The minimum revealable environmental concentration can be estimated on the basis of the equation on chapter Calculations, where m is the minimum revealable mass, experimentally measured for each compound. Under the analytical conditions described on the following chapter Analysis, the limit of quantitation for 7 days exposure usually ranges from 0.05 and 1 $\mu g \cdot m^{-3}$, depending on the compound.

In any case, the limit of quantitation can never be lower than the inferior limit of the linearity range indicated in the previous table.

Exposure

Code C-RAD130 cartridge has a very large loading capacity: about 80 mg, corresponding to an overall VOCs concentration of 3,000 - 3,500 $mg \cdot m^{-3}$ sampled for 8 hours or 70,000 - 80,000 $\mu g \cdot m^{-3}$ sampled for 14 days. Nevertheless, if the quantified overall adsorbed mass should be near 80 mg, sampling rate could have deviated from linearity. If this is the case, it is advisable to repeat the sampling experiment reducing exposure time.

Workplace environment

In workplace environments complex mixtures of airborne solvent vapours are often found at concentrations 2,000- 3,000 $mg \cdot m^{-3}$. The outstanding adsorbing capacity of code C-RAD130 cartridges allows you to sample them for the whole working shift of 8 hours. On the other hand, the very high values of sampling rates for a variety of compounds allow you to perform accurate concentration measurements even after very short exposures. For example, 15 minutes are enough to measure 0.1 $mg \cdot m^{-3}$ of benzene.

radiello can therefore be employed to evaluate both TWA and STEL concentrations.

Other indoor sampling experiments and outdoor campaigns

High sampling rates of radiello ensure very low limits of detection also for short exposure time intervals. For example, you may measure benzene concentrations as low as 2 $\mu g \cdot m^{-3}$ with an error not exceeding 4% after 8 hours of exposure. If radiello is exposed for 7 days, limit of quantitation becomes 0.1 $\mu g \cdot m^{-3}$.

Generally speaking, we suggest exposure time duration ranging from 8 hours to 30 days, the ideal value being 7 days.

Storage

The activated charcoal cartridges have undergone a complex conditioning process that ensures an outstanding chromatographic blank level, never exceeding three times the instrumental noise of a FID detector at the lowest attenuation.

Kept in a cool place and away from volatile organic compounds, the cartridges maintain unchanging blank level and adsorbing capacity for at least two years. Expiry day and lot number are printed onto the plastic bag wrapping each cartridge: its integrity stands as warranty seal.

After exposure the cartridges, well capped and kept in a cool and solvent-free place, maintain their content unalterated for at least six months.

Analysis

Extraction

Introduce 2 ml of CS_2 and 100 µl of internal standard solution (see next) directly in the radiello glass tube without drawing out the cartridge. Always use class A volumetric pipettes or dispensers. Stir from time to time for 30 minutes. If analysis is not performed soon after, draw out the cartridge and discard it.

Calibration

outdoor environment sampling

If benzene, toluene, ethylbenzene and xylenes (BTEX) have to be analyzed, prepare three or four standard solutions in CS_2 having decreasing concentrations of the analytes in the following ranges (in $mg \cdot l^{-1}$):

benzene	0.04 ÷ 17.6	ethylbenzene	0.04 ÷ 17.7
toluene	0.09 ÷ 34.8	m-xylene	0.04 ÷ 17.2
o-xylene	0.04 ÷ 17.6	p-xylene	0.04 ÷ 17.2

IMPORTANT:
always use high purity grade CS_2.

BE CAREFUL
even refrigerated, CS_2 permeates the tube plastic cap: its volume decreases by 4-5% a day. If the internal standard has been added, it is only a matter of unpleasant odour...

Analysis of unknown samples

Identify the sample that has been exposed for the longest time or at the highest expected concentration. Introduce 2 ml of CS_2 but do not add the internal standard, stir and let the sample stand for 30 minutes. Without discarding the cartridge, inject the CS_2 solution in the gas chromatograph with FID detector (see below), identify the compounds appearing in the chromatogram and make an estimation of the order of magnitude of their concentrations.

Prepare a CS_2 solution of the identified compounds with doubled concentration with respect to the sample. Dilute this solution in order to obtain standard solutions of concentration respectively about 0.1, 0.5 and 1 times the concentration estimated in the sample. Introduce 2 ml of each standard solution onto a blank code C-RAD130 cartridge in its glass tube, along with the chosen internal standard solution.

The chosen internal standard should have a retention time that does not cause interference with other compounds in the chromatogram. Compatibly with this requirements, we suggest to employ a solution of 2-fluorotoluene in CS_2 with concentration of 100 $\mu l \cdot l^{-1}$ for outdoor samples and 2 $ml \cdot l^{-1}$ for workplace samples.

Add 2 ml of CS_2 and the internal standard to all of the samples, stir, let the samples stand for 30 minutes and discard the cartridges prior to the analysis.

USER TIP

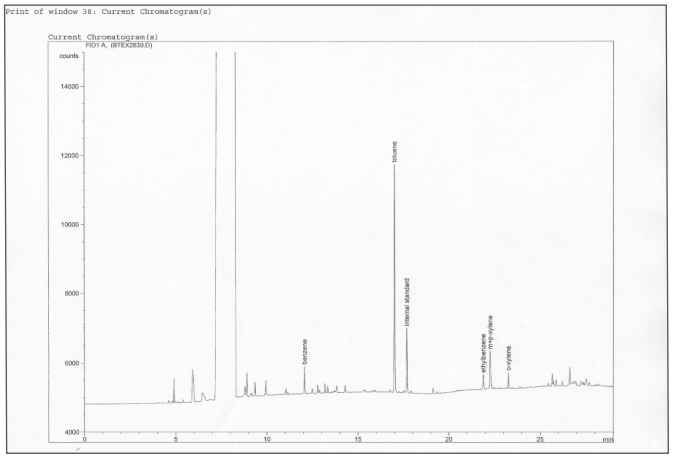
For a very accurate calibration we offer the preloaded cartridges code RAD405 (outdoor environment) and code C-RAD406 (workplace environment).

Instrumental analysis (advised)

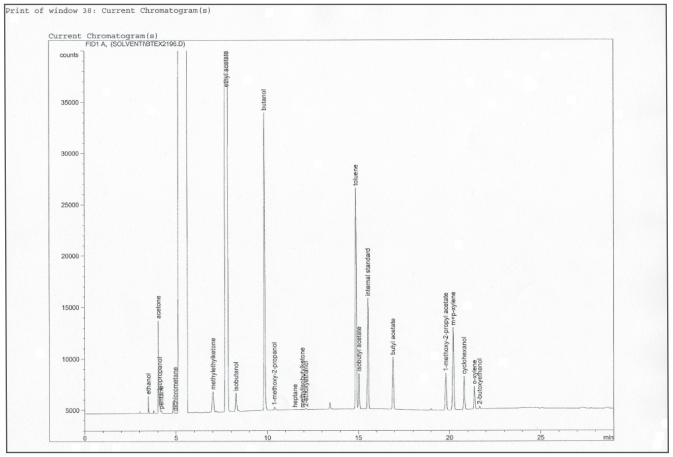
Capillary gas chromatography with FID detection outdoor environment samples: 100% dimethylpolysiloxane column 0.2 mm·50 m, film thickness 0.5 µm; split injection of 2 µl; split ratio 25:1; nitrogen carrier gas at constant pressure of 20 psi; injector temperature 240°C; oven initial temperature 35 °C for 5 minutes, 5°C·min^{-1} up to 90 °C, maintain for 3 minutes, 10 °C·min^{-1} up to 220 °C, final isotherm for 5 minutes.

workplace samples: 100% dimethylpolysiloxane column 0.2 mm·50 m, film 0.5 µm; split injection of 3 µl, split ratio 100:1; carrier N2 at constant pressure of 20 psi; injector temperature 240°C; oven initial temperature 50 °C for 5 minutes, 5 °C·min^{-1} up to 80°C, 15°C·min^{-1} up to 135 °C, 20 °C·min^{-1} up to 220 °C, final isotherm 10 minutes. Total time: 29 minutes.

The retention times for several compounds analyzed under the described conditions are listed in the table on next page.



Chromatogram of a real urban outdoor sample



FID chromatogram of a real workplace sample

USER TIP

If you perform several analyses, a barcode reader will greatly improve productivity in your laboratory and will also minimize the possibility of errors in the copying of sample labels.

Please contact us to help you in the implementation of the reader.

What make the code 130 cartridge incomparable?

	Retention time (minutes)
methanol	4.834
ethanol	5.340
acetone	5.712
isopropanol	5.835
pentane	6.121
methyl acetate	6.346
dichloromethane	6.405
2-methylpentane	7.559
methylethylketone	7.719
3-methylpentane	7.941
ethyl acetate	8.331
n-hexane	8.402
isobutanol	8.763
methylcyclopentane	9.350
1,1,1-trichloroethane	9.636
butanol	9.956
isopropyl acetate	9.978
benzene	10.203
1-methoxy-2-propanol	10.424
cyclohexane	10.580
1,2-dichloropropane	11.285
trichloroethylene	11.625
isooctane	11.667
2-ethoxyethanol	11.831
propyl acetate	11.868
n-heptane	12.068
1-ethoxy-2-propanol	12.775
methylcyclohexane	12.912
methylisobutylketone	13.258
isobutyl acetate	14.005
toluene	14.055
butyl acetate	15.279
n-octane	15.435
tetrachloroethylene	15.601
diaceton alcohol	15.915
1-methoxy-2-propyl acetate	16.609
ethylbenzene	16.997
m+p-xylene	17.241
cyclohexanone	17.436
cyclohexanol	17.436
styrene	17.716
o-xylene	17.832
2-buthoxyethanol	17.880
n-nonane	18.186
-pinene	19.129
n-decane	20.334
n-undecane	22.142

The container

The container is realised by stainless steel cloth AISI 316 with 100 mesh opening. It is electric welded with no supply of foreign materials. It has tolerance of ±0.05 mm diameter and of ±0.1 mm length.

The contents

The cartridge is packed with vegetal activated charcoal with a very large adsorbing surface. Its exceptionally low blank is obtained by conditioning it in a nitrogen stream fluidised bed at 450 °C for 16 hours.

The fluidised bed technique does not only guarantee the thorough purification of adsorbing material but also performs an accurate selection of its granulometry, by ventilation separations of the fraction under 50 mesh and over 35 mesh.

The production

The cartridge is filled up with charcoal by a very complex automated appara tus that was designed and realised in our laboratory. It avoids any contamination of the adsorbing material during the delicate process of cartridge production and ensures a very accurate dosing of the material itself, providing a variability of less than 2% of the weight of the activated charcoal among the cartridges.

The quality controls

Each cartridge batch undergoes statistical quality control of the blank level. If amounts higher than 20 ng of each of the BTEX compounds are found, the entire lot is discarded.

Sampling rate measurements

The sampling rate is measured in a standard atmosphere chamber unique in Italy and one of the few found all over Europe.

It allows the dynamic generation of high flows of controlled concentration gas mixtures from 1 $\mu g \cdot m^{-3}$ to 1,000 $mg \cdot m^{-3}$ (dynamic range from 1 to 106) of each investigated compound alone or mixed with others. The chamber allows temperature control from -20 to 60 °C, relative humidity control from 5% to 100% and air speed variation from 0.1 to 10 $m \cdot s^{-1}$.

All of the gas flows are measured as mass flows and have therefore the properties of primary standards. All of the operating parameters (gas flows, temperature, relative humidity, ...) are recorded and the records are available along with the certification documents.

Volatile organic compounds (VOCs) - thermally desorbed

What you need

yellow diffusive body code C-RAD1202

Supporting plate code C-RAD121

Vertical adapter code C-RAD122

(optional) chemiadsorbing cartridge code C-RAD145

Principle

Code C-RAD145 is a stainless steel net cylinder, with 3x8 µm mesh opening and 4.8 mm diameter, packed with 350

± 10 mg of graphitised charcoal (Carbograph 4), particle size is 35-50 mesh.

Volatile organic compounds are trapped by adsorption and recovered by thermal desorption, analysis is performed by capillary gas chromatography and FID or MS detection.

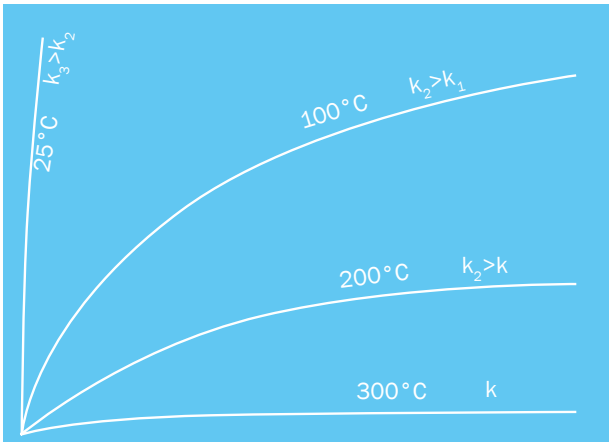
General considerations

Thermal desorption is an easy-to-use technique, but it implies some precautions and is of less general use than chemical desorption.

The recovery of adsorbed compounds is based onto the different shape of adsorption isotherms at different temperatures. Since quantitative desorption of trapped molecules should ideally be accomplished at moderate temperatures, only weak adsorbing media are employed, with active adsorbing surface between 10 and 50 times smaller than that of activated charcoal.

Use of thermal desorption requires therefore an accurate preliminary investigation about the adsorbed compound - adsorbing medium pair. Stronger adsorbents are suitable for very volatile compounds, but will yield only partial desorption of heavier compounds.

Anyway, backdiffusion is always lying in wait: due to the adsorbing medium weakness heavier compounds will eventually displace the more volatile ones. Once you have made an accurate choice of the adsorbing material, therefore, you should bear in mind that a real atmosphere is composed by a variety of compounds apart from those you are analyzing at unpredictable concentrations. As a consequence, sampling times can not be as long as those allowed by activated charcoal, otherwise lighter compounds will be lost. With the purpose of allowing reasonable sampling times (up to two weeks) the sampling rate has been dramatically reduced by changing the diffusive body from the white type (code C-RAD120) to the yellow one (code C-RAD1202).



Concentration in gaseous phase (C)

When in contact with a solid adsorbing medium, a gaseous compound will be adsorbed following the Freundlich isotherm, that is to say the adsorbed mass will be $x/m=kC^{1/n}$, where x is the mass of gaseous compound adsorbed by the mass m of the solid adsorbent and C is the concentration of the gaseous compound at the equilibrium in the gas phase. K and n depend on temperature and on the adsorbate - adsorbing medium pair. K increases with decreasing temperature and n is the closer to 1 the stronger the adsorbent.

At low temperatures, x/m depends almost linearly on the concentration in air (see the curve at 25 °C): this allows diffusive sampling. At high temperatures, the adsorbent mass is very low whatever the concentration in the gas phase: this allows the recovery of adsorbed compounds by heating (see the curve at 300 °C).

To ensure the best possible recovery yields, k and n have to be small. This, however, will compromise sampling efficiency. In other words, compounds strongly adsorbed at room temperature will be only partially recovered by thermal desorption. On the other hand, compounds that are easily desorbed by heating will be sampled at room temperature with low efficiency.

Smaller average pore size and thicker diffusive membrane make the diffusive path longer and, as a consequence, sampling rates are reduced to less than one third compared to those obtained with white diffusive bodies.

Some compounds, moreover, are thermally unstable. Thermal degradation of such compounds will cause an underestimation of their concentration or the appearance of ghost peaks.

Thermal desorption is nevertheless an outstanding analytical technique because it is easy to perform, it does not require the use of toxic solvents as carbon disulfide, it ensures very low limits of detection, is suited to mass spectrometric detection and allows the recovery of the adsorbing cartridges. Basing on our experience, we have chosen Carbograph 4 as the best compromise between sampling efficiency and recovery yields for a wide range of organic compounds.

Sampling rates

Sampling rate values at 298 K (25 °C) and 1013 hPa are listed in table on page 36. All of the values shown have been experimentally measured. Exposure tests have been performed up to the levels shown (in $\mu g \cdot m^{-3} \cdot min$) and sampling rates are guaranteed to be linear up to the limit values and for overall concentration of volatile organic compounds in air not exceeding 2,000 $\mu g \cdot m^{-3}$.

Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{1.5}$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. This produces a variation of ± 5% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 $m \cdot s^{-1}$.

Do not expose directly radiello to rain: even if small amounts of water are adsorbed by Carbograph 4, they can nevertheless interfere with analysis.

Calculations

The listed sampling rate values take already into account the recovery yields of adsorbed compounds. The average concentration over the sampling period is therefore calculated from sampled mass of analyte and exposure time without introducing any other corrective factor, apart from temperature variations of Q.

Average concentration C in $\mu g \cdot m^{-3}$ over the whole exposure time is calculated according to the following expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ \mathbf{1{,}000{,}000}$$

where:

m = mass of analyte in µg

t = exposure time in minutes

Exposure

Workplace environment

The use of light adsorbing media is not recommended in the workplace environment.

Other indoor sampling experiments and outdoor campaigns

Thermal desorption is exceptionally suited for long exposure times at low concentrations, as in outdoor campaigns and some indoor environments (e.g. homes, schools, etc.), particularly if the subsequent analysis is performed by HRGC-MS.

The recommended exposure times range from 8 hours to the upper limits shown in the table below. It is advisable to reduce sampling time if the estimated overall VOCs concentration is higher than 2,000 $\mu g \cdot m^{-3}$.

Sampling rate values at 25°C (298 K)					
	sampling rate ml·min^{-1}	exposure time upper limit	linear up to µg·m^{-3}·min	uncertainty 2σ %	limit of detection[1] µg·m^{-3}
benzene	27.8	7	410,000	8.3	0.05
benzene	26.8	14	410,0002	7.5	0.05
butyl acetate	24.5	14	580,000	12.4	0.05
2-butoxyethanol	19.4	14	550,000	9.7	0.1
cyclohexane	27.6	7	470,000	14.7	0.1
n-decane	22.3	14	450,000	22.4	0.1
1,4-dichlorobenzene	22.0	14	650,000	9.5	0.1
dimethyl disulfide	23.7	7	500,000	9.1	0.04
n-heptane	25.3	14	420,000	7.6	0.05
n-hexane	25.5	7	420,000	10.9	0.05
ethylbenzene	25.7	14	550,000	9.1	0.01
ethyl-tert-butyl ether (ETBE)	30.0	7	600,000	-	0.1
2-ethyl-1-hexanol	14.3	14	550,000	17.4	0.07
2-ethoxyethanol	26.0	14	570,000	7.7	0.05
2-ethoxyethyl acetate	20.9	14	600,000	8.0	0.05
isopropyl acetate	25.8	7	540,000	9.6	0.1
limonene	12.8	14	550,000	24.8	0.2
methyl-tert-butyl ether (MTBE)	30.0	7	600,000	-	0.2
2-methoxyethanol	4.0	7	1,000,000	--	1.0
2-metoxyethyl acetate	21.0	7	1,000,000	--	0.1
1-methoxy-2-propanol	26.6	7	600,000	11.6	0.2
n-nonane	21.0	14	440,000	11.8	0.07
n-octane	24.1	14	440,000	13.4	0.07
-pinene	6.4	14	550,000	29.5	0.2
styrene	27.1	14	550,000	24.0	0.01
tetrachloroethylene	25.4	7	1,000,000	8.9	0.02
toluene	30.0	14	550,000	8.3	0.01
1,1,1-trichloroethane	20.0	7	300,000	13.0	0.1
trichloroethylene	27.1	7	800,000	9.5	0.02
1,2,4-trimethylbenzene	21.9	14	550,000	9.6	0.05
n-undecane	12.0	14	520,000	32.7	0.05
m-xylene	26.6	14	550,000	11.3	0.01
o-xylene	24.6	14	550,000	9.1	0.01
p-xylene	26.6	14	550,000	11.3	0.01

[1]after 7 days exposure and with MS detection; analytical conditions as described in the Analysis paragraph

[2]for overall VOCs concentrations not exceeding 500 µg·m^{-3}

Storage

The cartridges are thermally conditioned in a high temperature stove with an inert atmosphere, with an oxygen content lower than 10 ppm. The duration of the adsorbent capacity of graphitized carbon is virtually unlimited and has been tested six months after production. Cartridges should be stored in a clean and solvent-free environment, in the refrigerator or at room temperature. The expiry date and the lot number are printed on the transparent plastic bag, whose integrity acts as a guarantee seal.

Analysis

The methods proposed here have been elaborated with a two-stage thermal desorber coupled to gas chromatograph and mass spectrometer.

A method for BTEX and one for VOC are proposed here. The first refers to samples from urban air monitoring where research is usually limited to benzene, toluene, ethylbenzene and xylene isomers. The second is more suitable for indoor investigations, allowing the quantification of all the compounds listed in the table above and the more gene ral qualitative research, which also includes analytes with medium polarity.

Desorption

The thermal desorber is equipped with 1/4” stainless steel. or inert coated sample tubes, they have to be hollow and free: discard the stainless steel gauze disk which is fitted to the groove and discard also the springs if present.

Code C-RAD145 cartridge has been dimensioned to fit the diameter of thermal desorption tubes. Its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length.

Once capped, the thermal desorber steel tube has to be positioned in the tray with the grooves on the bottom.

The described conditions have been optimized for seven days exposures to typical concentrations of urban atmospheres and indoor environments. Shorter exposure times or considerably higher concentrations would require different settings of split flows.

BTEX – detector FID

Temperatures and timing

- Tube Desorption: 290°C for 10minutes
- Trap Low: -10°C
- Trap Desorption: 290°C for 1 minute
- Flow path Temp.: 200°C
- Tube desorption flow: 100°C
- Outlet flow: 50 mL/min.

Usually, the cartridge enters into the thermal desorption tube by simple pouring. If it does not occur, use a pushing tool to press the cartridge till the nick on the tube.

Instrumental analysis

Column

capillary column (100% dimethylpolysiloxane), length 50 m, 0.2 mm i.d. film thickness 0.5 µm;

Temperatures

GC oven: 36 °C for 1 minute, 6 °C·min^{-1} up to 110 °C, maintain for 1 minute, 20 °C·min^{-1} up to 250 °C, final isotherm 5 minutes.

COV – detector MSD

Temperatures and timing

- Tube Desorption: 290 °C for 10minutes
- Trap Low:-10 °C
- Trap Desorption: 290 °C for 1 minute
- Flow path Temp.: 200 °C
- Tube Desorption Flow: 100 °C
- Outlet Flow:50ml/min.

Instrumental analysis

Column

Capillary column, length 60 m, d.i. 0.25 mm, film thickness 0.25µm;

Temperatures

GC oven: 45 °C for 10 minute, 5 °C·min^{-1} up to 115 °C, 10 °C·min^{-1} up to 175 °C, 30 °C·min^{-1} up to 295 °C, final isotherm 6 minutes.

Flows

Carrier gas: helium at 1.0 ml·min^{-1}

On next page we display two total ion current chromatograms from an outdoor urban site and an indoor sampling respectively.

In the first case, the benzene peak corresponds to an average concentration of 2.2 µg·m^{-3} ; in the second the concentration of 1,4-dichlorobenzene was 14 µg·m^{-3}.

USER TIP

If you perform several analyses, a barcode reader greatly improve productivity in your lab and will also minimize the possibility of errors in the copying of sample labels.

Please contact us to help you in the implementation of the reader.

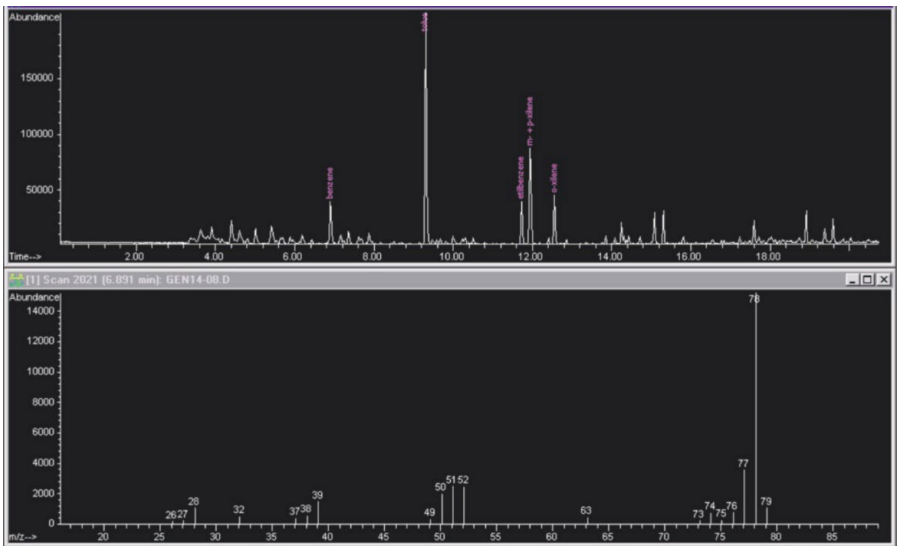
USER TIP

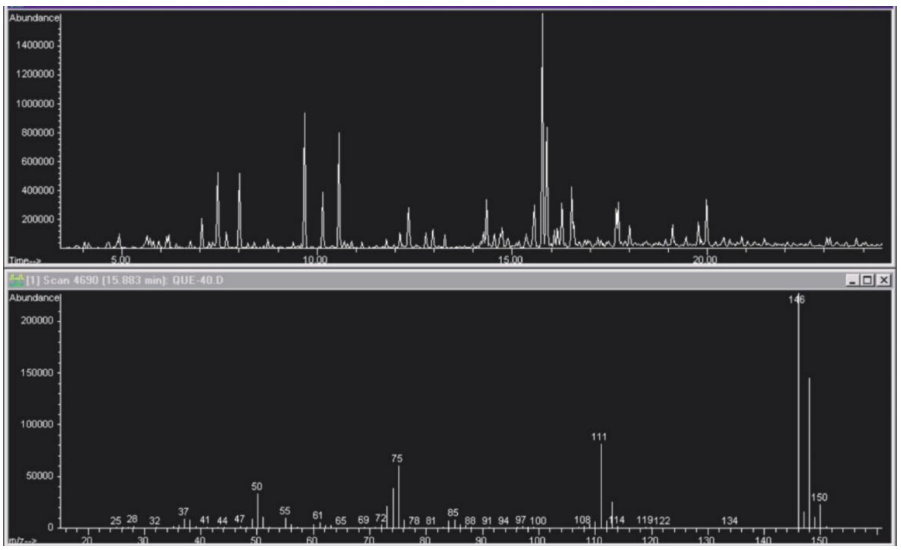
For a very accurate BTEX calibration we offer the preloaded cartridges code C-RAD407

Calibration

Calibration curves are obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed through Markes Calibration Solution Loading Rig™ (C-CSLR) (for more information on routine calibration of TD method, download Application Notes 007 and 075).

Inject slowly 1 µl of each calibration solution under nitrogen flow (40 ml·min^{-1}) and let the system purge for 2 minutes. Analyze the cartridge as you would do with a sample. We suggest you to prepare a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 8, 4, 2, 1, 0.04, 0.02 and 0.01 µg·µl^{-1} of each compound.





TIC chromatograms of an outdoor urban sampling (left) and of indoor air (below). Mass spectra of benzene and of 1,4-dichlorobenzene are shown on bottom of each picture, at concentrations of 2.2 and 14 $\mu g \cdot m^{-3}$ respectively. Despite the low concentration values, the signal-to-noise ratio is very high in both cases. As a consequence, very reliable mass spectral identification is possible by comparison with mass spectral data libraries with no need of further processing.

Cartridge recovery

The cartridges can be reconditioned using the thermal desorber in "tube conditioning" mode, heating them to 350 °C for at least 20 minutes in an inert gas flow (helium or nitrogen at a flow of 50 ÷ 100 $ml \cdot min^{-1}$). Or using Markes TC-20 multitube conditioning and dry purge unit.

Nitrogen and sulfur dioxides (NO_2 and SO_2)

What you need

blue diffusive body code C-RAD1201

Supporting plate code C-RAD121

Vertical adapter code C-RAD122

Chemiadsorbing cartridge code C-RAD166

Principle

The cartridge code C-RAD166 is made of microporous polyethylene coated with triethanolamine (TEA). Nitrogen (NO_2) and sulfur (SO_2) dioxide is chemisorbed onto TEA as nitrite and sulphite or sulphate ions respectively. Nitrite is quantified by visible spectrophotometry while sulphite and sulphate are analysed by ion chromatography (NO_2 and SO_2 can be analysed together by ion chromatography).

Sampling is selective for gaseous molecules: any airborne nitrite, sulphite or suplhate will not cross the diffusive membrane.

Sampling rates

NO_2

The sampling rate value Q_{298} at 298 K (25 °C) and 1013 hPa is ***0.141 ± 0.007 ng·ppb^{-1}·min^{-1}***.

SO_2

The sampling rate value Q_{298} at 298 K (25 °C) and 1013 hPa is ***0.466 ± 0.022 ng·ppb^{-1}·min^{-1}***.

Effect of temperature, humidity and wind speed

Sampling rate of NO_2 varies from the value at 298 K on the effect of temperature (in Kelvin) following the equation:

$$Q_K = Q_{298} \cdot \left(\frac{K}{298} \right)^{7.0}$$

where ***Q2*** is the sampling rate at the temperature K ranging from 263 to 313 K (from -10 to 40 °C) and Q_{298} is the reference value at 298 K.

Sampling rate for SO_2 does not vary with temperature between 263 and 313 K (from -10 to 40 °C).

Sampling rate is invariant with humidity in the range 15 - 90% and with wind speed between 0.1 and 10 m·s^{-1} for both gases.

Calculations

NO_2

The concentration C_{NO2} is calculated according to the equation:

$$C_{NO2} = \frac{m_{NO2}}{Q_K \cdot t}$$

where m_{NO2} is nitrite mass in ***ng*** found on the cartridge, ***t*** is exposure time in ***minutes*** and Q_K is the sampling rate value at the temperature ***K*** in Kelvin.

SO_2

Convert the sulphite found onto the cartridge into sulphate by multiplying its mass by 1.2, then sum the obtained value to the sulphate found in the cartridge. The concentration in ppb is calculated according to the equation:

$$C_{SO2} = \frac{m_{SO4}}{0.466 \cdot t}$$

where m_{SO4} is the overall sulphate mass in ng found in the cartridge (sulphate itself and sulphite converted into sulphate) and t is exposure time in minutes.

USER TIP
It is advisable to measure the sampling temperature by the thermometer code C-RAD126.

Exposure

Exposure up to 15 days is feasible but if relative humidity is higher than 70% for the entire sampling duration it is not advisable to sample for more than 7 days. Due to the fact that TEA is very hygroscopic in fact, even if water does not actually interfere with sampling or analysis, the excess water adsorbed by the cartridge could cause some loss of adsorbing medium by percolation.

WARNING: NO_2 results may differ from those produced by automatic chemiluminescent instrumentation due to exponential variation of the sampling rate of radiello with temperature. This phenomenon is characteristic of all NO_2 samplers that use TEA as an absorbent medium. The reason is not yet completely clear, but it is assumed that it depends in part on the balance in the air between the species NO_2 and N_2O_4, whose ratio is strongly linked to temperature: the TEA captures only the species NO_2.

Limit of quantitation and uncertainty

Sampling rate of NO_2 and SO_2 is linear ranging from 10,000 to 5,000,000 ppb·min. Limit of quantitation after 7 days exposure is 1 ppb for both gases. The uncertainty at 2σ is 11.9% for NO_2 and 9.2% for SO_2.

Storage

The cartridges are stable for at least 12 months before and 4 months after the sampling, if kept in the dark at 4 °C. Expiry date is printed on the plastic bag.

Do not expose all of the cartridges belonging to the same lot, keep at least two of them as blanks.

Analysis

Add 5 ml of water in the plastic tube with the cartridge and stir vigorously by a vortexer for 1 minute. Do the same with two-three unexposed cartridges.

Colorimetric determination of nitrite ion

Nitrogen dioxide is quantitatively converted to nitrite ion. Prepare the following reactives:

- sulphanilamide: dissolve 10 g of sulphanilamide in 100 ml concentrated HCl and dilute to 1,000 ml with water
- NEDA: dissolve 250 mg of N-(1-naphthyl)ethylendiamine dihydrochloride in 250 ml of water (discard the solution when it turns brown).

Transfer 0.5 ml (or a different volume, see the table below) of the cartridge extraction solution to a plastic or glass 10 ml tube along with 5 ml of sulphanilamide reactive. Cap tightly, stir and wait for 5 minutes. Add 1 ml of NEDA reactive, stir and wait for 10 minutes. Do the same with unexposed cartridges.

Measure the absorbance of samples at 537 nm using water to zero the spectrophotometer, then subtract the blank value from unexposed cartridges. Prepare the calibration standards in the same way from sodium nitrite solutions of concentration ranging from 0.1 to 20 $mg \cdot l^{-1}$ expressed as NO_2-.

When nitrite ion concentration is higher than 20 $\mu g \cdot ml^{-1}$ (corresponding to 7 days of exposure to 70 ppb) the absorbance value is no longer comprised in the

calibration curve. To analyse the samples, draw smaller amounts of the extraction solution as shown in the table. In order to maintain the overall volume unaltered, add the listed volume of water.

average expected concentration for 7 days exposure in ppb	sample volume ml	water volume to be added ml
up to 70	0.5	0
from 70 to 150	0.25	0.25
higher than 150	0.1	0.4

Determination of the sulphite and sulphate ions

Though SO_2 is converted into sulphite and sulphate ions with variable ratios, the sum of the two ion equivalents is linear with exposure to SO_2. To obtain calibration curves, prepare solutions containing both ions at concentrations ranging from 5 to 50 $mg \cdot l^{-1}$. Perform the ion chromatography analysis of the standard solutions and the extraction solutions from radiello cartridges in the same way according to your usual laboratory practice.

Ozone (O_3)

What you need

blue diffusive body code C-RAD1201

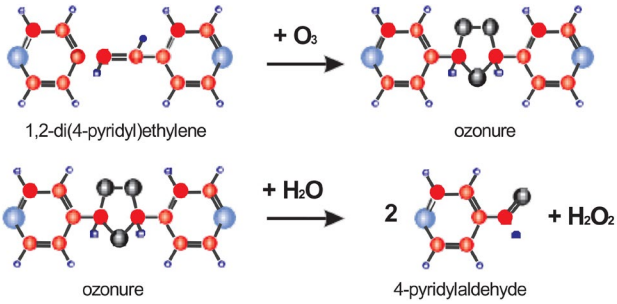
Supporting plate code C-RAD121

Vertical adapter code C-RAD122

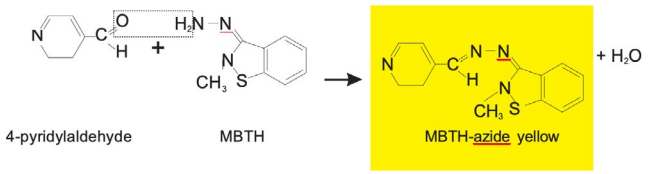
Optional chemiadsorbing cartridge code C-RAD172

Principle

The adsorbing cartridge is formed by a micropore polyethylene tube filled with silica gel coated with 4,4'-dipyridy- lethylene and closed, at one end, by a PTFE cap. Upon exposure, acid-catalysed ozonolysis of 4,4'-dipyridylethy- lene leads to 4-pyridylaldehyde. Silica gel ensures the presence of water, necessary to complete ozonolysis reactions.



In the laboratory, 4-pyridylaldheyde is condensed with 3-methyl-2-benzothiazolinone hydrazone (MTBH) to yield the corresponding azide, yellow coloured.



The absorbance of the solution is measured at 430 nm. Production of 4-pyridylaldehyde is a specific reaction of ozone; neither nitrogen oxides nor organic compounds, if present, do interfere.

Sampling rate

The sampling rate value Q_{298} at 298 K (25 °C) and 1013 hPa is ***24.6 ml·min^{-1}***. Sampling is linear in the exposure range from 10,000 to 4,000,000 µg·m^{-3}·min^{-1}.

Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{1.5}$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. Sampling rate is not influenced by humidity or wind speed.

Calculations

The average concentration over the whole exposure time is calculated according to the equation

$$C\ [\mu g \cdot m^{-3}] = \frac{\mathbf{m}\ [\mu g]}{\mathbf{24.6\ t}\ [\text{min}]}\ \mathbf{1{,}000{,}000}$$

where ***m*** is ozone mass in µg sampled by radiello and ***t*** is exposure time in minutes.

Exposure

Introduce the cartridge in the diffusive body and make sure that the PTFE cap is positioned at the same end of the screw.

In outdoor environments, where typical ozone concentrations range from 2 to 400 $\mu g \cdot m^{-3}$, we suggest exposure time from 24 hours to 14 days. The ideal range is from 3 to 7 days.

In workplace environments it is advisable to sample over the entire 8 hours shift.

Limit of detection and uncertainty

The limit of detection is 2 µg·m-3 for 7 days exposures. The cartridge is saturated after 14 days exposure at 400 µg·m-3. The uncertainty at 2σ is 14.5% over the whole sampling rate linearity range.

Storage

The cartridges need only protection from direct sunlight: keep them in a drawer or a cupboard at room temperature. In these conditions, the blank level does not exceed 0.015 absorbance units for up to six months.

Expiry date is printed onto the plastic bag wrapping each cartridge.

Generally, an increase of blank level does not imply that the cartridge must be discarded. The only consequence is a corresponding increase of the analytical limit of quantification.

After exposure the samples have to be stored in the dark as before, along with three unused cartridges to be analysed as blanks. Analyse them within a week.

Analysis

Reactives and materials

- 3-methyl-2-benzothiazolinone hydrazone hydrocloride (MBTH): dissolve 5 g per litre in water and add 5 ml of concentrated sulfuric acid; this solution is to be freshly prepared.
- 4-pyridylaldehyde
- micropore filter membrane 0.45 µm

User tip
For a simple and accurate filtration make use of the filtration kit code C-RAD174.

Procedure

Draw the cartridge out from the plastic tube, discard the PTFE cap and pour the silica gel into the tube. Add 5 ml of MBTH solution, recap the tube and stir vigorously. Let the tube stand for at least one hour to react, stirring from time to time. Filter through the micropore filter (if you make use of the code C-RAD174, act as follows: fit the filter to the syringe, transfer the solution

from the tube to the syringe and filter it into a second tube or directly into the spectrophotometer measure cell).

Measure absorbance at 430 nm using water to zero the spectrophotometer. The yellow colour is stable for several days if the solution is kept well capped in its tube.

Treat in the same manner three unused cartridges of the same lot and subtract the average blank value from the absorbance values of the samples.

IMPORTANT:
If the absorbance value is higher than the calibration curve upper limit dilute the sample with the MBTH solution: never use water to dilute! Water alters the pH of the solution with unpredictable variations in the linearity of absorbance values vs concentration.

Calibration

Dissolve 100 µl (112.2 mg at 20° C) of 4-pyridylaldehyde in 1 litre of water and dilute this solution (e.g. 1:2, 1:5, 1:10) to obtain calibration solutions. Transfer 0.5 ml of each calibration solution in a plastic tube together with 4.5 ml of MTBH solution. Stir and let stand for one hour, then read the absorbance at 430 nm (filtration is not needed). Plot the cali-bration curve for ozone mass vs measured absorbance, taking into account that:

1 µg of 4-pyridylaldehyde = 0.224 µg of ozone.

Hydrogen sulfide (H_2S)

What you need

white diffusive body code C-RAD120

Supporting plate code C-RAD121

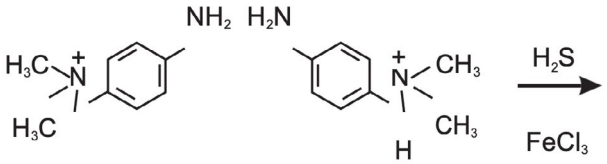
Vertical adapter code C-RAD122

(optional) Chemisorbing cartridge code C-RAD170

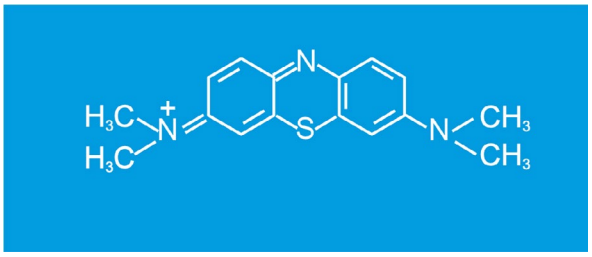
Principle

The cartridge code C-RAD170 is made of microporous polyethylene and impregnated with zinc acetate. Hydrogen sulphide is chemisorbed by zinc acetate and transformed into stable zinc sulfide.

The sulfide is recovered by extraction with water. In contact with an oxidizing agent as ferric chloride in a strongly acid solution it reacts with the N,N-dimethyl-p-phenylendiammonium ion to yield methylene blue.



N,N-dimethyl-p-phenylendiammonium



Methylene blue is quantified by visible spectrometry.

Sampling rates

The sampling rate value Q_{298} at 298 K (25 °C) and 1013 hPa is ***0.096 ± 0.005 ng·ppb^{-1}·min^{-1}***.

Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = 0.096\left(\frac{K}{298}\right)^{3.8}$$

where Q_K is the sampling rate at the temperature K ranging from 268 to 313 K (from -5 to 40 °C).

Sampling rate is invariant with humidity in the range 10 - 90% and with wind speed between 0.1 and 10 m·s^{-1}.

Calculations

Once Q_K at the sampling temperature has been calculated, the concentration ***C*** is obtained according to the equation:

$$C = \frac{m}{Q_K.t} \; 1{,}000$$

where ***m*** is the mass of sulfide ion in ***µg*** found onto the cartridge and ***t*** is exposure time in minutes.

Exposure

Exposure duration may vary from 1 hour to 15 days. Sampling is linear from 2,000 to 50,000,000 ppb·min of H_2S.

Limit of detection and uncertainty

The limit of detection is 30 ppb for 1 hour exposure or 1 ppb for 24 hour exposure. The uncertainty at 2σ is 8.7% over the whole exposure range.

Storage

The cartridges are stable at least for 12 months before and 6 months after exposure. Do not expose all of the cartridges of the same lot: keep at least two of them as blanks.

Analysis

Reactives and materials

- sulfuric acid: slowly add 25 ml of concentrated sulfuric acid to 10 ml water and let the solution cool;
- amine: dissolve 6.75 g of N,N-dimethyl-p-phenylendiammonium oxalate in the sulfuric acid solution. Dilute this solution to 1 litre with sulfuric acid - water 1:1 v/v. Kept in a dark bottle and well capped, this solution is stable for at least four weeks. CAUTION: this solution is very poisonous.
- ferric chloride: dissolve 100 g of ferric chloride hexahydrate ($FeCl3{\cdot}6H_2O$) in 40 ml of water.
- ferric chloride-amine: mix 10 ml of ferric chloride solution with 50 ml of amine solution. This solution has to be freshly prepared;
- sulfuric acid for dilution: slowly dissolve 40 ml of concentrated sulfuric acid in 900 ml of water, let the solution cool and make up to 1,000 ml.

Procedure

Add 10 ml of water to the plastic tube containing the cartridge, recap and stir vigorously, preferably by a VORTEX stirrer.

Add 0.5 ml of ferric chloride - amine solution, recap **immediately** and stir. The tube must be capped immediately in order to avoid that the developed hydrogen sulfide can escape from the tube before reacting.

Wait for 30 minutes and measure absorbance at 665 nm using water to zero the spectrophotometer. The colour is stable for several weeks.

Do the same with two or three unexposed cartridges of the same lot and obtain the average blank value, then subtract it to the samples.

Calibration

Calibration curves may be prepared by sodium sulfide standard solutions, which have to be titrated just before use. As diluted sodium sulfide solutions are very unstable (the sulfide content can diminish as much as the 10% in an hour) it is strongly recommended to make use of the calibration solution code C-RAD171, following the instructions included.

USER TIP
Code C-RAD171 calibration solution relieves you from the task of preparation and titration of the sodium sulfide solutions.

IMPORTANT:
Absorbance is linear up to 1,200 absorbance units, corresponding to an exposure value of about 80,000 ppb·min. If higher absorbance values are obtained, dilute the samples with the sulfuric acid for dilution.

Be careful to apply the same dilution ratio to the samples and the blanks.

NEVER USE WATER TO DILUTE

Ammonia (NH_3)

What you need

blue diffusive body code C-RAD1201

Supporting plate code C-RAD121

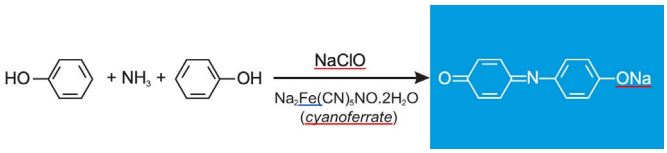
Vertical adapter code C-RAD122

(optional) Chemisorbing cartridge code C-RAD168

Principle

The cartridge code C-RAD168 is made of microporous polyethylene and impregnated with phosphoric acid. Ammonia is adsorbed as ammonium ion. Airborne ammonium salts dispersed as particulate matter do not cross the diffusive membrane of radiello.

Ammonium ion is quantified by visible spectrometry as indophenol: at basic buffered pH ammonium ion reacts with phenol and sodium hypochlorite, with pentacyanonitrosylferrate catalysis (in the following cyanoferrate), to form indophenol. The reaction product is intensely coloured in blue, and its absorbance measured at 635 nm.



indophenol

Sampling rate

The sampling rate value Q_{298} at 298 K (25 °C) and 1013 hPa is ***235 ml·min^{-1}***.

Effect of temperature, humidity and wind speed

The effect of temperature on sampling rate is negligible (<0.1%/ °C) in the range from 275 ÷ 312 K (2 ÷ 39 °C). Sampling rate is invariant with humidity in the range 10 - 90% and with wind speed between 0.1 and 10 m·s^{-1}.

Calculations

The concentration ***C*** in µg·m^{-3} is obtained according to the equation:

$$C = 0.944 \left(\frac{m}{235 \cdot t} \right) 1{,}000{,}000$$

where ***m*** is the mass of ammonium ion in ***µg*** found onto the cartridge and t is exposure time in ***minutes***. 0.944 is the numerical factor necessary to convert ammonium ion into ammonia (see Analysis)

Exposure

Introduce the cartridge in the diffusive body and make sure that the PTFE cap is positioned at the same end of the screw.

Ammonia is sampled linearly in the range from 2,000 - 20,000,000 $\mu g \cdot m^{-3} \cdot min$. Exposure time is allowed to range from 1 hour to 14 days.

IMPORTANT:
Do not touch the microporous portion of the cartridge with your fingers: sweat contains ammonium ions.

Limit of detection and uncertainty

The limit of detection is 1 µg·m-3 for 24 hour exposure. The uncertainty at 2σ is 6.5% over the whole allowed exposure range.

Storage

The cartridges are stable at least for 12 months before and after exposure if kept at room temperature in an ammonia-free environment. Do not expose all of the cartridges of the same lot: keep at least two of them as blanks.

Analysis

Materials

- plastic or glass tube, volume 12 ml, with cap
- micropipette with variable volume from 0.1 to 1.0 ml
- 5 ml glass pipet

Reactives

- buffer solution (pH 10.6): dissolve 1.1 g of NaOH and 3.04 g of NaHCO3 in one litre of water
- phenol: dissolve 10 g of phenol in 100 ml of ethanol
- cyanoferrate: dissolve 0.5 g of sodium pentacyanonitrosylferrate dihydrate ($Na2Fe(CN)5NO{\cdot}2H_2O$) in 100 ml of water and add a few drops of 10% NaOH. Keep this solution in a dark bottle and prepare it freshly.
- oxidising solution: sodium hypochlorite with 1% of active chlorine in 0.2 M NaOH. Keep cool in a dark bottle.

Ammonium ion quantification

Open radiello tube and cautiously discard the cartridge PTFE cap (it may have been contaminated with handling). Help yourself with a pair of pliers.

Add 10 ml of deionised water to the cartridge in its tube (make sure that no trace of ammonium ion is found in the water you use). Recap the tube and stir vigorously by a VORTEX stirrer for at least 15 seconds.

Transfer 1 ml of the solution into another tube along with 0.4 ml of phenol, 0.4 ml of cyanoferrate, 5 ml of buffer solution and 1 ml of oxidising solution.

Wait for 1 hour and then measure the absorbance of the solution at 635 nm using water to zero the spectrophotometer.

Do the same with two unexposed cartridges and subtract their absorbance value to the samples. Generally, the blank value does not exceed 0.040 absorbance units.

For exposure value higher than 500,000 $\mu g \cdot m^{-3} \cdot min$ the absorbance value is no longer linear: dilute a known fraction of the coloured solution with the buffer.

Calibration curves are conveniently prepared with ammonium chloride solutions in the range from 0.5 to 10 $mg \cdot l^{-1}$ as ammonium ion.

IMPORTANT:
If sample is too concentrated (absorbance no longer linear) **DO NOT DILUTE WITH WATER:** the pH value is critical in the determination of the colour intensity.

Hydrochloric acid (HCl)

What you need

white diffusive body code C-RAD120

Supporting plate code C-RAD121

Vertical adapter code C-RAD122

(optional) Chemiadsorbing cartridge code C-RAD169

Principle

Code C-RAD169 cartridge is made of stainless steel net loaded with silica gel (0.1 to 0.4 mm particle size). Gaseous hydrochloric acid is adsorbed by silica gel and subsequently extracted with water to be quantified by ion chromatography as chloride ion.

Sampling is selective for the gaseous molecules: any airborne chloride salt will not cross the diffusive membrane of radiello.

Sampling rate

The sampling rate value (Q_{298}) at 25 °C (298 K) and 1013 hPa is ***103 cm3·min^{-1}***

Effect of temperature, humidity and wind speed

Sampling rate varies from the value at 298 K (25 °C) on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = 103 \left(\frac{K}{298} \right)^{1.5}$$

where Q_K is the sampling rate at temperature K and Q_{298} is the sampling rate value at the reference temperature of 298 K. This yields a ± 5% variation of Q for a 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15 - 90% for short exposure time (see Exposure) and with wind speed between 0.1 and 10 m·s^{-1}.

Calculations

Let m be the mass of chloride ion in µg found onto the cartridge and t the exposure time in minutes, the environmental concentration C of hydrochloric acid in µg·m^{-3} is obtained according to the equation:

$$C = \left(\frac{1.028m}{Q_K t} \right) 1{,}000{,}000$$

where Q_K is the sampling rate at temperature K (in Kelvin) and 1.028 is the ratio between molecular masses of HCl and Cl-(see Analysis).

Exposure

Hydrochloric acid is sampled linearly in the range from 20,000 ÷ 20,000,000 µg·m-3·min.

Workplace environment

In workplace environment we recommend exposure time from 15 minutes to 8 hours: the ceiling values can be measured.

Outdoor environment

We recommend exposure time from 2 hours to 2 days. Exposure time as long as 7 days is allowed if average relative humidity does not exceed 50%, taking into account the water absorbing properties of silica gel.

We also recommend to protect radiello from rain by the mountable shelter code C-RAD196.

Limit of detection and uncertainty

The limit of detection is 10 µg·m-3 for 24 hour exposure. The uncertainty at 2σ is 3.5% over the whole allowed exposure range.

Interferences

Gaseous chlorine is adsorbed by silica gel and is revealed as 0.02 ng of chloride ion for 1 µg·m-3·min of chlorine.

Storage

Kept in a clean environment free from gaseous hydrochloric acid, the cartridges code C-RAD169 are stable for at least 24 months before and after sampling.

If more than six months have passed since you received the cartridges, before environmental sampling campaigns, it is advisable to analyse some cartridges to check for contamination from the background. Discard the cartridges if they contain more than 5 µg of chloride ion.

Analysis

Add 2 ml of deionised water to the cartridge in its tube (make sure that no trace of chloride ion is found in the water you use). Recap the tube and stir vigorously by a VORTEX stirrer for 1-2 minutes. Analyse the solution by ion chromatography. Subtract the blank value obtained from two unexposed cartridges.

Prepare the calibration solutions with sodium or potassium chloride concentrations ranging from 0.5 to 25 mg/litre as Cl-.

Hydrofluoric acid (HF)

What you need

Blue diffusive body code C-RAD1201

Supporting plate code C-RAD121

Vertical adapter code C-RAD122

(optional) Chemisorbing cartridge code C-RAD166

Principle

The cartridge code C-RAD166 is made of microporous polyethylene coated with triethanolamine (TEA). Gaseous hydrofluoric acid is adsorbed by TEA and subsequently extracted with water to be quantified by ion chromatography or by ion selective electrode as fluoride ion.

Sampling is selective for the gaseous molecules: any airborne fluoride salt will not cross the diffusive membrane of radiello.

Sampling rate

The sampling rate at 25 °C and 1013 hPa is ***187 $cm^3 \cdot min^{-1}$***.

Effect of temperature, humidity and wind speed

Sampling rate is invariant with humidity in the range 10 - 90% for short exposure time (see Exposure) and with wind speed between 0.1 and 10 $m \cdot s^{-1}$. The effect of temperature is under investigation.

Calculations

Let ***m*** be the mass of fluoride ion in µg found onto the cartridge and t the exposure time in minutes, the environ- mental concentration ***C*** of HF in $\mu g \cdot m^{-3}$ is obtained according to the equation:

$$C = \frac{1.053\ m}{187t}\ 1{,}000{,}000$$

where 1.053 is the ratio between molecular masses of HF and F^-(see Analysis).

Exposure

Hydrofluoric acid is sampled linearly in the range from 10,000 to 50,000,000 $\mu g \cdot m^{-3} \cdot min$.

Workplace environment

In workplace environments we recommend exposure time from 15 minutes to 8 hours: the ceiling values can be measured.

Outdoor environment

We recommend exposure time from 2 hours to 14 days.Protect radiello from rain by the mountable shelter code C-RAD196.

Limit of detection and uncertainty

The limit of detection is 7 µg·m-3 for 24 hour exposure. The uncertainty at 2σ is 4.5% over the whole exposure range.

Storage

Kept in a dark place at 4 °C, the cartridges stay unaltered for at least 12 months before exposure and 4 months after sampling. Expiry date is printed on the plastic bag wrapping each cartridge.

If more than six months have passed since you received the cartridges, before environmental sampling campaigns, it is advisable to analyse some cartridges to measure any contamination from the background. Discard the cartridges if they contain more than 2 µg of fluoride ion.

Keep at least two unexposed cartridges for each lot and analyse them as blanks.

Analysis

Ion chromatography

Add 5 ml of the eluent solution to the radiello tube. Stir vigorously by a VORTEX stirrer for 1-2 minutes. Let the tube stand for 10 minutes, then stir manually and inject the solution in the ion chromatographic apparatus without further treatment.

Analyse 1-2 unexposed cartridges and subtract the average blank value to the samples.

Ion Selective Electrode

Prepare an ionic strength buffer as follows. Dissolve 57 ml of acetic acid in 500 ml water and add 50 g of sodium chloride and 0.3 g of sodium citrate. When complete solubilisation has been achieved, adjust the pH value to 5.0-5.5 (ideal value is 5.3) by adding drops of 10 M sodium hydroxide. Make up to 1 litre with water.

Add 5 ml water to radiello tube and stir vigorously by a vortexer for 1-2 minutes, then let stand for 10 minutes.

Introduce a magnetic stirring bar in a 20 ml beaker, add 10 ml of ionic strength buffer and 1 ml of the extraction solution of the cartridge. Start the magnetic stirrer and make the potentiometric measurement by an ion selective electrode for fluorides. In the described analytical conditions, the electrode response should be linear in the range from 1 to 1,000 $mg \cdot l^{-1}$ of F^- with slope close to 59.0 ± 0.5 (if potential is expressed in mV).

Analyse 1-2 unexposed cartridges and subtract the average blank value to the samples.

IMPORTANT:
Always use water with fluoride content lower than 0.5 $mg \cdot l^{-1}$.

Anaesthetic gases and vapours N_2O, isoflurane, ethrane, halothane, sevorane and desflurane

What you need

Sampling kit code C-RAD125

Containing 20 single packages each composed of:

Permeative body (code C-RAD1203)

1 supporting plate (code C-RAD121)

1 vertical adapter (code C-RAD122)

1 adsorbing cartridge (code C-RAD132)

the listed components are contained in a closed aluminum envelope, which is wrapped by a thermowelded paper-polyethylene bag.

The whole is sterilized by γ-rays.

The single components are also available non-sterilized in 20 pieces per package.

Principle

Code C-RAD132 cartridge is made of stainless steel net loaded with a mixture of molecular sieve and activated charcoal 35-50 mesh.

Nitrous oxide and halogenated anesthetic gases permeate the silicone membrane and are sampled by the molecular sieve and by activated charcoal respectively.

The sampled compounds are displaced by a water-methanol mixture and are quantified by capillary gas chromatography and a headspace sampler.

N_2O, isoflurane, ethrane and halothane are detected by the Electron Capture Detector (ECD) and by Mass Spectrometric Detector (MSD) with good sensitivity; sevorane and desflurane cannot be quantified by ECD detection and have to be analyzed by mass spectrometry.

Sampling rates

Sampling rate values at 25 °C (298 K) and 1013 hPa are listed in the table on the right.

Effect of temperature, humidity and wind speed

Sampling rate varies from the values at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation:

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{1.5}$$

where Q_K is the sampling rate at temperature K and Q_{298} is the sampling rate value at reference temperature of 298 K. This yields a ± 5% variation of Q for a 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 10 ÷ 90% for exposure time not exceeding 8 hours and with wind speed between 0.1 and 10 $m \cdot s^{-1}$.

	sampling rate ($ml \cdot min^{-1}$)
N_2O	1.01
isoflurane	2.25
ethrane	3.39
halothane	4.93
sevorane	0.92
desflurane	1.20

Calculations

Concentration in air is obtained by the following equation:

$$C = \frac{m}{Q_K \cdot t} \; 1{,}000$$

where:

C = concentration in $mg \cdot m^{-3}$

m = mass of analyte found on the cartridge in µg

Q_K = sampling rate in $ml \cdot min^{-1}$

t = exposure time in minutes

Exposure

Sampling rate is constant for exposure time up to 8 hours at relative humidity up to 80% with N_2O concentration up to 500 ppm and overall halogenated anesthetic compounds concentration up to 100 ppm.

Limit of detection and uncertainty

The cartridges are conditioned to ensure a chromatographic blank level lower than one third of the sampled mass of each anesthetic upon exposure to one tenth of its limit value for half an hour time.

If a thoroughly conditioned ECD is employed, 4 hours of exposure ensure the following analytical sensitivities: 0.5 ppm of N_2O, 0.002 ppm of isoflurane, 0.01 ppm of ethrane and 0.002 ppm of halothane. Sevorane and desflurane are not detected by ECD. Acquiring by mass spectrometry in SIM mode (Single Ion Monitoring), detection limits close to the ECD performances can be achieved for N_2O, isoflurane, ethrane and halothane. For sevorane and desflurane, 1 hour exposure allows to detect 0.1 and 0.2 ppm respectively.

Storage

The sampling kit code C-RAD125 is sterilized by gamma rays. Use of the sampler makes it no longer sterile. With the exception of the adsorbing cartridge, the sampler is re-usable. If kept in a dry place free from chemical contamination, the cartridges are stable for at least 12 months.

After the sampling, the samples are stable for 30 days if stored in a dry place, away from chemical contaminations and at temperatures ranging from 4 to 8 °C.

IMPORTANT:
DO NOT STERILIZE THE SAMPLER BY AUTOCLAVING. Autoclaving treatment permanently damages the silicone permeative membrane.

Analysis

Materials needed for the analysis

- 20 ml headspace glass vials with open-top aluminum crimp caps and rubber/PTFE septa
- water/methanol mixture 60/40 v/v (gradient grade methanol for HPLC, grade III laboratory water)
- usual laboratory glassware

Materials needed for the calibration curve

- pure N_2O in a gas cylinder
- halogenated anaesthetic compounds
- gastight syringe (volume 500 µl) and other syringes (volume 100 and 10 µl)
- 1 liter glass bottle with threaded neck, equipped with open-top screw cap and rubber/PTFE septum (the volume of the bottle must be precisely measured and the bottle must be rinsed with dry nitrogen before use)
- magnetic stirrer with large magnetic stirring bar (about 30-40 mm long)
- usual laboratory glassware

Elution of samples

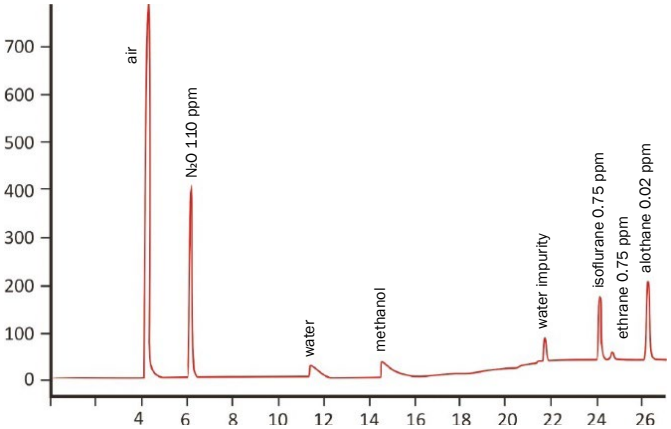
Introduce 10 ml of water/methanol mixture in a headspace vial by a volumetric pipette. Add the radiello cartridge and cap immediately. Stir and let equilibrate, place the vial in the headspace bath and let equilibrate for one hour at 45 °C.

Instrumental analysis
ECD detection (sevorane and desflurane are not detected)

- Sample volume: 1 ml
- gas chromatographic column: polystyrene-divinylbenzene PLOT, 30 m long, 0.32 mm inner diameter, 20 µm film thickness (allows quantification of nitrous oxide and other anaesthetic gases in one chromatographic run)
- carrier gas: N2 at 1.0 atm
- split ratio: 10/1
- GC oven: 40° C for 2 min, 10° C·min^{-1} up to 150° C, 6° C·min^{-1} up to 200° C, final isotherm for 5 minutes
- injector temperature: 150° C
- detector temperature: 300° C

In the described analytical conditions chromatograms like to the one in the figure are obtained. In the example shown, exposure time was 4 hours at the concentration values indicated and with relative humidity of 70%.

ECD Analysis



Concentration in gaseous phase (C)

MS detection

The instrumental conditions are as described above, with the exception of the carrier gas (helium has to be used instead) and the make-up gas, which is not employed. Acquire by SIM (Single Ion Monitoring) focusing the detector on the following signals (the base peak is underlined):

N₂O: 44; ***desflurane***: 51, 149; ***isoflurane*** and ***ethrane***: 51, 67, 1 7; ***halothane***: 1 7, 198, 179; ***sevorane***: 33, 131, 181

If high concentrations of CO_2 interfere (it gives a strong signal at m/z 44), N_2O can be quantified basing on the signal at m/z 30. On page 55 a typical GC-MS chromatogram (as total ion current) is displayed. It can be observed that, as an effect of the vacuum applied on the detector end of the column, retention times are shorter with respect to those obtained with ECD detection.

Calibration

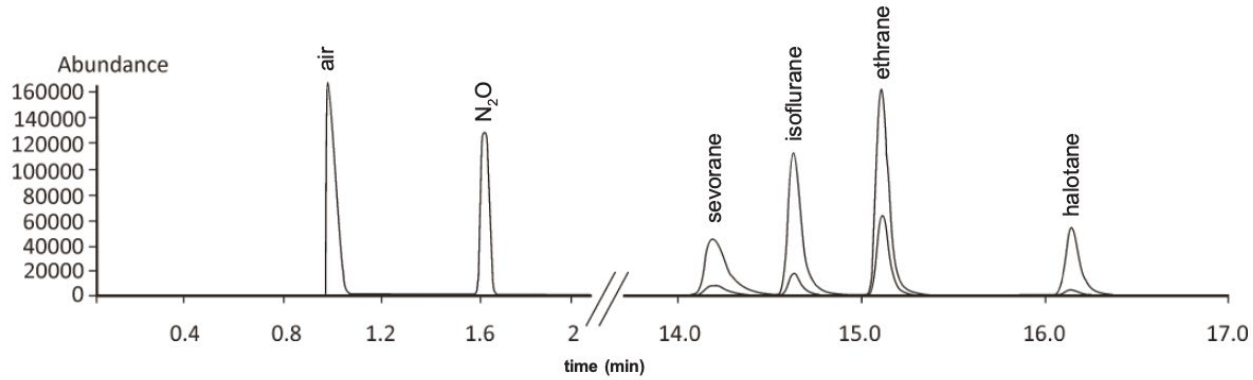
Calibration curves for N_2O and halogenated anaesthetics can be prepared simultaneously.

Draw pure N_2O in a gas sampling bulb. Transfer 20 ml of pure N_2O in the 1 litre bottle through the septum by a gastight syringe. Switch on the magnetic stirrer and let the mixture equilibrate for 30 minutes.

Standard solutions of the halogenated compounds must be prepared in water/methanol 60/40 v/v in order to contain from 0.05 to 3.0 mg·l^{-1} of each compound; five calibration levels are recommended.

For each level pipet 10 ml of calibration solution in an empty vial, add a blank code C-RAD132 cartridge and cap immediately.

MSD Analysis



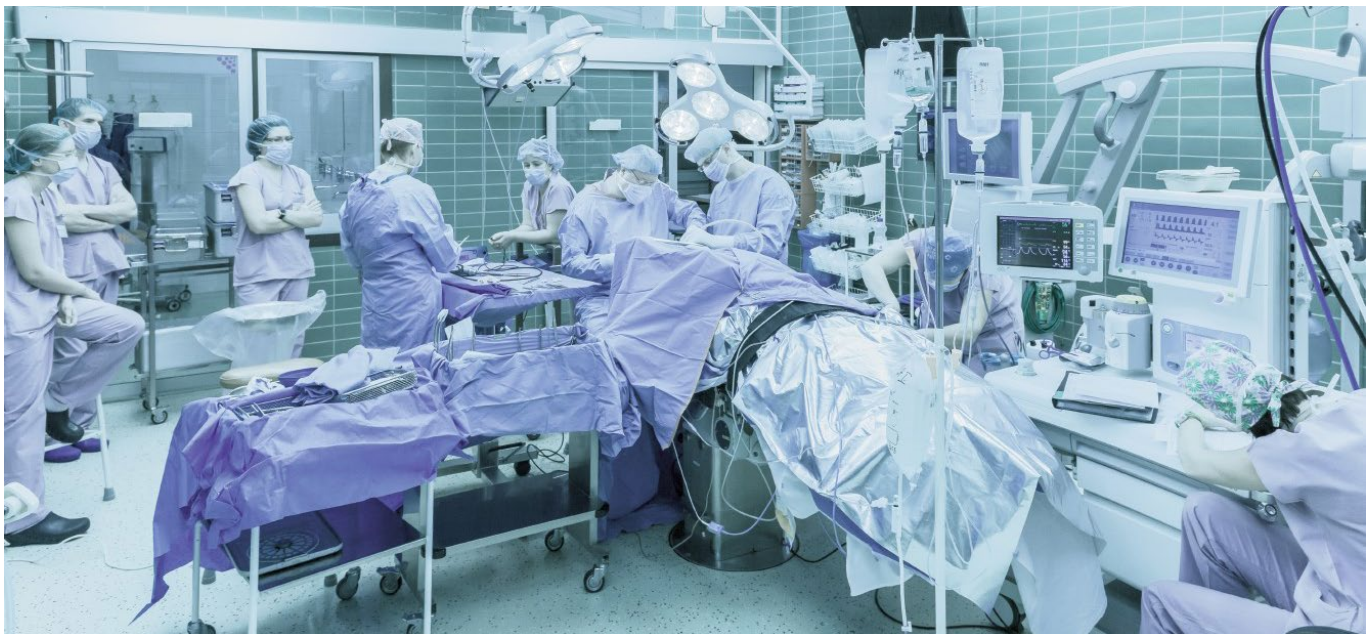
Add also a precisely measured volume of diluted N_2O drawn from the bottle by a gastight syringe (usually added volume ranges from 50 to 1,000 µl), stir and let equilibrate at 45 °C for 1 hour.

The values above generally comprise the usual conditions of operating theatres. The analyst may choose different values if needed, but equivalent exposure values should not exceed 400,000 $mg \cdot m^{-3} \cdot min$ for nitrous oxide and 50,000 $mg \cdot m^{-3} \cdot min$ for each of the halogenated compounds.

Pay attention: the ECD and/or MSD response may not be linear. If this should be the case, use a second order calibration curve.

Useful data

name	chemical formula	molecular weight	1 $mg \cdot m^{-3}$ at 25°C = ppm
nitrous oxide	N_2O	44.0	0.556
sevorane	$CH_2F\text{-}O\text{-}CH(CF_3)_2$	200.0	0.123
desflurane	$CF_3\text{-}CHF\text{-}O\text{-}CHF_2$	168.0	0.146
forane	$CHF_2\text{-}O\text{-}CHCl\text{-}CF_3$	184.5	0.133
ethrane	$CHF_2\text{-}O\text{-}CF_2\text{-}CHClF$	184.5	0.133
halothane	$CF_3\text{-}CHBrCl$	197.4	0.124



Phenol, methylphenols and dimethylphenols (thermally desorbed)

What you need

white diffusive body code C-RAD120

Supporting plate code C-RAD121

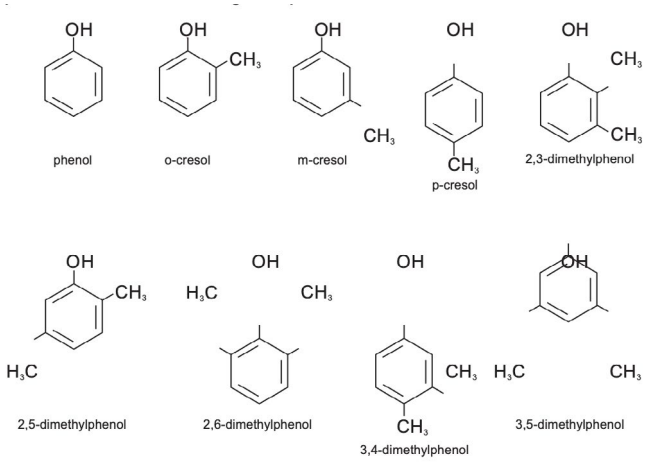
Vertical adapter code C-RAD122

(optional) chemisorbing cartridge code C-RAD147

Principle

Code C-RAD147 cartridge is a stainless steel net cylinder with 100 mesh opening and 4.8 mm diameter, packed with 250 ± 10 mg of Tenax-TA, particle size 20-35 mesh. Phenols are trapped by adsorption and recovered by thermal desorption, analysis is performed by capillary gas chromatography and MS detection.

The method has been optimized for the following compounds:



Sampling rates

Sampling rate values (in ml·min^{-1}) at 298 K (25 °C) and 1013 hPa are listed in the table on the right. All of the values shown have been experimentally measured.

Effect of temperature, humidity and wind speed

Sampling rates varies from the value at 298 K on the effect of temperature (in Kelvin) as expressed by the following equation

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^{1.5}$$

Where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. This produces a variation of ±5% for 10 °C variation (upwards or downwards) from 25 °C.

Sampling rate is invariant with humidity in the range 15 ÷ 90% and with wind speed between 0.1 and 10 m·s^{-1}.

	sampling rate ml·min^{-1}	limit of detection1 µg·m^{-3}	uncertainty at 2σ %
phenol	38	0.3	24.1
o-chresol	45	0.4	17.5
m-chresol	48	0.4	8.0
p-chresol	48	0.4	8.0
2,3-dimethylphenol	53	0.4	26.0
2,5-dimethylphenol	51	0.3	25.2
2,6-dimethylphenol	46	0.4	7.6
3,4-dimethylphenol	60	0.4	22.1
3,5-dimethylphenol	61	0.4	22.2

[1]*after 24 hours exposure and with MS detection; analytical conditions as described in the Analysis paragraph.*

Calculations

The listed sampling rate values take already into account the recovery yields of adsorbed compounds. The average concentration over the sampling period is therefore calculated from sampled mass of analyte and exposure time without introducing any other corrective factor, apart from temperature variations of Q.

Average concentration C in $\mu g \cdot m^{-3}$ over the whole exposure time is calculated according to the following expression:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ \mathbf{1{,}000{,}000}$$

where:

m = mass of analyte in µg

t = exposure time in minutes

Exposure

Workplace environment

Exposure time can range from 2 to 8 hours.

Other indoor sampling experiments and outdoor campaigns

The recommended exposure times range from 8 hours to 7 days.

Storage

The duration of Tenax adsorbent capacity is virtually unlimited. If kept in a cool place not contaminated by phenols, white and adsorbent capacity remain unchanged for at least twenty-four months. The expiry date and the lot number are printed on the transparent plastic casing, whose integrity acts as a guarantee seal.

After exposure the cartridges, well capped and kept in a cool and solvent-free place, maintain their content unaltered for at least three months.

Analysis

The analytical method hereafter described have been set up by a two-stage thermal desorber and mass spectrometer detector.

Desorption

The thermal desorber is equipped with 1/4” stainless steel or inert coated. sample tubes, they have to be hollow and free: discard the stainless steel gauze disk which is fitted to the groove and discard also the springs if present.

Code C-RAD147 cartridge has been dimensioned to fit the diameter of thermal desorption tubes. Its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length.

Once capped, the thermal desorber steel tube has to be positioned in the carousel with the grooves on the bottom.

The desorption conditions described below have been developed to obtain the best results from cartridges exposed for seven days to the usual concentrations of urban and indoor pollution. Shorter exposure times or much higher concentrations than usual may make it necessary to readjust the splits.

Temperatures and timing

- Tube desorption: 290°C for 10 minutes
- Trap low: -10°C
- Trap desorption: 290°C for 1 minute
- Flow path temp.: 200°C
- Tube desorption flow: 100°C
- Outlet flow:50 mL/min.

Instrumental analysis

Column

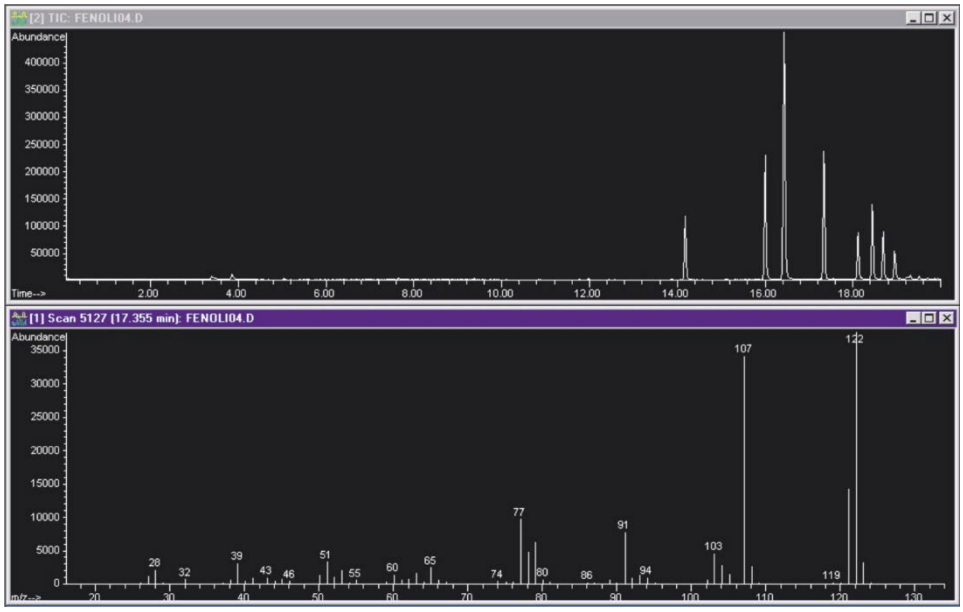
capillary column, length 60 m, internal diameter 0.25 mm, film thickness 0.25 µm; the column is directly fitted to the six-port valve of thermal desorber apparatus

Temperatures

- GC oven: 40 °C for 5 minutes, 5 °C·min^{-1} up to 115°C, 10 °C·min^{-1} up to 165 °C, 30 °C·min^{-1} up to 285 °C, final isotherm 3 minutes
- GC–MS interface: 260 °C

Flows

- helium carrier gas: 1.6 ml·min^{-1}



In the figure above a typical chromatogram (as total ion current) is shown.

Calibration

Calibration curves are obtained by gas-phase injection of methanol solutions of the target compounds onto blank cartridges. Injections are performed using Markes Calibration Solution Loading Rig (C-CSLR) (for more information on routine calibration of TD method, download Application Notes 007 and 075). through a GC injector, where a short piece of wide-bore (0.53 mm i.d.) deactivated uncoated column is installed. The other end bears a Swagelock reducing connection (1/16”-1/4”).

The 1/4” Swagelock nut has to be equipped with a PTFE ferrule instead of the original steel one (use PTFE ferrules that come along with the thermal desorber caps).

Introduce a blank code C-RAD147 cartridge in a Markes empty tube and connect the tube to the C-CSLR and fit the tube to the Swagelock nut. Keep the injector at 170 °C but do not heat the oven. Inject slowly 1 µl of each calibration solution under nitrogen flow (40 ml·min^{-1}) and let the system purge for 2 minutes. Analyse the cartridge as you would do with a sample. We suggest you to prepare a complete set of calibration solutions by subsequent dilutions such as they contain, for example, 4, 2, 1, 0.05, 0.025 and 0.01 µg·µl^{-1} of each compound.

Cartridge recovery

The cartridges can be reconditioned using the thermal desorber in tube conditioning mode, heating them at 280

° C for at least 20 minutes in an inert gas flow (helium or nitrogen at a flow of 50 ÷ 100 ml·min^{-1}) or using Markes TC-20

To prepare the calibration standards fit a 1/16”-1/4” Swagelock reducing connection to the GC injector by a short piece of wide-bore deactivated uncoated column.

1,3-butadiene and isoprene

What you need

yellow diffusive body code C-RAD1202

Supporting plate code C-RAD121

Vertical adapter code C-RAD122

(optional) chemiadsorbing cartridge code C-RAD141

Principle

Cartridge code C-RAD141 is a 4.8 mm diameter stainless steel mesh tube with a mesh size of 3x8 µm, filled with approximately 480 mg of graphite carbon (Carbopack X) 40/60 mesh.

1,3-butadiene and isoprene are trapped by adsorption, recovered by thermal desorption and analysed by capillary gas chromatography with MS detector.

Sampling rates

Sampling rate values were measured experimentally at 20°C (273 K) and 1013 hPa in a dynamic controlled atmosphere chamber.

The sampling rate for 1,3-butadiene in the workplace is ***30.5 ± 0.3*** ml·min^{-1} (nominal value at a concentration between 114 and 226 µg·m^{-3} for 8-hour exposures). For the longer term (7 days) sampling the value is ***4.7*** ml·min^{-1} [Strandberg et al. (1), (2)].

For isoprene the sampling rate is ***41.2 ± 4.9*** ml·min^{-1} (in the range 2 ÷ 6,680 µg·m^{-3} for exposures of 30 to 480 min).

Effect of temperature, humidity and wind speed

Both temperature and relative humidity affect the sampling rate of 1,3-butadiene. If the temperature drops to 5 °C, the bias is +12.9% at 20% RH or -2.4% at 80% RH, compared to 20 °C and 50% RH. Avoid sampling at temperatures close to 40 °C, as the sampling rate shows a significant decrease.

The effect of temperature and relative humidity on the isoprene sampling rate is lower: at low temperature and humidity (5°C, 21% RH) the sampling rate is 10% higher, while at high temperature and humidity (41°C, 77% RH) there is a 23% decrease.

Do not expose the sampler directly to rain. Always use the weather box code C-RAD196 for outdoor sampling to prevent water from entering the membrane and wetting the absorbent.

Calculations

The average concentration C over the exposure time interval is calculated from the mass of the analyte found on the cartridge (corrected for the blank, if measurable) and from the exposure time, using the sampling rate values above, as follows:

$$C\ [\mu g \cdot m^{-3}] = \frac{m\ [\mu g]}{Q_K\ [ml \cdot min^{-1}] \cdot t\ [min]}\ \mathbf{1{,}000{,}000}$$

where:

m = mass of analyte in µg

t = exposure time in minutes

(1) Strandberg et al. Atmos. Environ., 2006. 39(22), 4101-4110.

(2) Strandberg et al. Atmos. Environ., 2006. 40(40), 7686-7695.

Limit of detection

The blank response, the limit of detection (LOD) and the limit of quantification (LOQ) depend on the instrumentation and the analytical conditions.

Under the analytical conditions specified below, the blank value is not detectable, i.e. it is less than 0.5 ng for both compounds.

The LOQ for 8-hour workplace exposure is 0.1 $\mu g \cdot m^{-3}$. For a 7-day exposure to ambient air, the LOQ is 0.03 $\mu g \cdot m^{-3}$; see also Strandberg et al. (2).

Measurements uncertainty

The following table shows the values of uncertainty in 1,3-butadiene measurements in the workplace, evaluated with two different approaches. Uncertainties were first determined under laboratory conditions, following the methods of the ISO GUM (Guide to Expression of Uncertainty in Measurement, International Organization for Standardization) and ISO 5725

(Accuracy (trueness and precision) of measurement methods and results General principles and definitions) standards. In this case, the uncertainty takes into account all the contributions involved in the whole measurement process (time, T, RH on the sampling rate, uncertainty of the measured mass and so on), contributions which were determined according to EN 838. Subsequently, the uncertainty was determined by a field comparison with OSHA 56 (as a reference method), according to ISO 13752.

Uncertainty of measurement for an 8-hour sampling of 1,3-butadiene in working environment

Relative combined expanded uncertainty (2·uc)	200 $\mu g \cdot m^{-3}$	442 $\mu g \cdot m^{-3}$ (0.1 TLV)	2210 $\mu g \cdot m^{-3}$ (0.5 TLV)	4420 $\mu g \cdot m^{-3}$ (TLV-TWA ACGIH)
Laboratory tests at 20 °C, 50% RH (EN 838, calculations by ISO GUM)	48.4%			
Field comparison (ISO 13752)	37%	25%	11.1%	7.9%

Storage

After exposure, the samples, well capped in their glass tubes, have to be stored in the freezer, because 1,3-butadiene and isoprene are reactive compounds. Laboratory tests according to EN 838 showed for both compounds a loss of analyte of 7-8% after 14-day storage. The samples shall therefore be analysed within 14 days from the end of exposure, in order to ensure the maximum loss of analyte remain within 10%.

Analysis

The method proposed here was developed with a two-stage thermal desorber coupled to a gas chromatograph and mass spectrometer.

Desorption

The 1/4 "stainless steel tubes supplied with the thermal desorber must be empty and free: remove the stainless steel disk placed inside it in correspondence with the circular incision and, if present, also the springs.

The code C-RAD141 cartridge has been sized so that its outer diameter fits to the inner diameter of the thermal desorber tube. Moreover, its length is such that, when the cartridge is introduced into the tube and is stopped by the groove, it is positioned exactly centrally with respect to the tube length.

Once capped, the thermal desorber steel tube has to be positioned in the tray.

Temperatures and timing

- Tube desorption: 350°C for 10 minutes
- Trap low :-10°C
- Trap desorption: 290°C for 1 minute
- Flow path temp.: 200°C
- Tube desorption flow: 100°C
- Outlet flow:50mL/min.

Instrumental analysis

Column

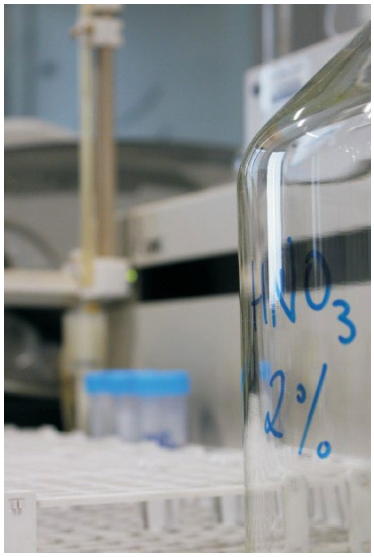
J&W GS-GASPRO, length 60 m, i.d. 0.32 mm; the column is directly fitted to the six-port valve of thermal desorber apparatus.

Temperatures

- GC oven: 80 °C for 1 minute, 25 °C·min^{-1} up to 175 °C, maintain for 8 minutes, 25 °C·min^{-1} up to 250 °C, final isotherm 11.2 minutes
- Interface GC-MS: 290 °C
- Ionic source: 230 °C, quadrupole 150 °C

Flows

- Carrier gas: helium at 1.8 ml·min^{-1}



Calibration

The calibration curve is performed by injecting known aliquots of a certified gaseous mixture of 1,3-butadiene in nitrogen onto virgin cartridges. The operation is carried out the injector of a gas chromatograph whose output is connected with a short piece (10 cm) of a deactivated capillary column (0.25 mm id) connected to a Swagelock reducer 1/16 "-1/4" .

Instead of the 1/4 ”steel ferrule of the reducer use a PTFE ferrule.

Introduce a cartridge in the thermal desorber tube and insert the tube in the Swagelock reducer, keeping the injector at 50 °C and the oven cold. Inject different volumes of the gas mixture under a flow of nitrogen of 30 ml·min^{-1}, leaving the gas flowing for 2 minutes.

It is recommended to use a mixture of 1,000 ppm of 1,3-butadiene in nitrogen and to inject aliquots of 20, 40, 60, 80 and 100 µl of mixture (with a 100 µl gas-tight syringe) or 100 aliquots , 200, 300, 400 and 500 µl of mixture (with a 500 µl gas-tight syringe) according to the desired calibration range.

Cartridges conditioning

The cartridges can be reconditioned using the thermal desorber in "tube conditioning" mode, heating them to 350°C for at least 20 minutes in an inert gas flow (helium or nitrogen at a flow of 50 ÷ 100 ml·min^{-1}) or using Markes TC-20 (multi-tube conditioning and dry purge unit)

Index by code

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