ENVINT DEN08/18 DENUDER SYSTEM

Preface

Envint DEN08/18 denuder system is a compact, simple to operate and inexpensive system which allows sampling of ambient atmosphere of gas phase species and particulate matter avoiding interferences, sampling artefacts and allowing samples to be analysed and evaluated in terms of air quality.

Diffusion denuder tubes offers the possibility to sample directly gas phase species thanks to their diffusional properties. If the denuder walls are coated with a perfect sink for the selected species, molecules are irreversibly adsorbed on the walls, while particulate, thank to much higher diffusion coefficient, proceed unaffected through the denuder and can be collected on filters. A proper pump provides sampling of the system in ambient air. The denuder technique is a well-recognised method for the collection of atmospheric pollutants and showed good results in many applications. Therefore, the system DEN08/18 has been designed in order to overcame difficulties and technical problems inherent the filed use of denuder based technique. This goal has been reached through the optimisation of the three subsystems of DEN08/18:

a) The denuder Tubes
b) The filter pack
c) The sampling module

The Denuder Tubes

They are the main elements in the sampling train enabling the separation of gas-phase components and particulate matter. As depicted in the figure below, let us suppose to have a cylindrical denuder with inner walls coated with a substance able to adsorb irreversibly a certain type of gas molecule. While travelling through the tube, gas molecules are completed deployed thanks to their high diffusion coefficient. Particulate matter, characterised by a diffusion coefficient orders of magnitude lower, will proceed unaffected in the tube and can be recovered at the end by means of proper filter media. In this way a complete and efficient separation between gas molecule and particles can be achieved, leading to atmospheric samples unaffected by sampling artefact. After sampling, gas molecules adsorbed on the walls are removed by extraction with water or other suitable solvent. Particulate matter is collected on filters and analysed according to a variety of analytical methods.

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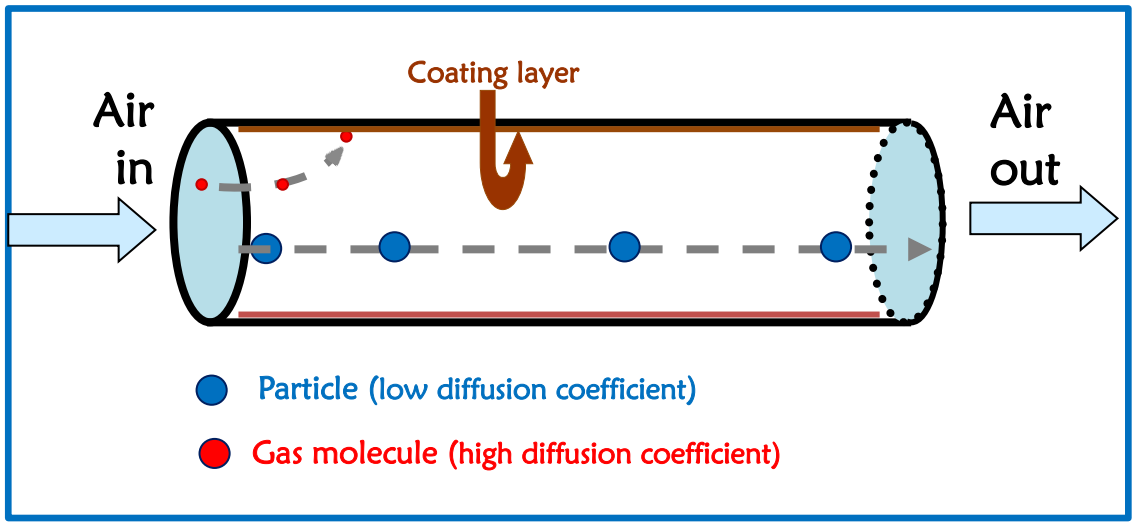

Denuder tubes have long been used in atmospheric chemistry studies for a variety of gas species. Unfortunately, the collection efficiency of the basic cylindrical design is inherently low, thus new types of denuders of higher efficiency have been developed. Among those, annular denuders have been found to be the best option for sampling atmospheric species.

Annular denuder is made by using two cylinders in which air passes through the annular space. It can be shown that the efficiency of this design can be expressed by the so-called Gormley-Kennedy equation:

$$\frac{C}{C0} = \alpha \exp(-\beta \frac{\pi DL(d1+d2)}{4F(d2-d1)})$$

Where α and β are constants, *C0* is the gas concentration at the entrance of the denuder, *C* is the concentration at the exit. *D* is the diffusion coefficient of the gas species, *L* is the geometrical length of the denuder, *F* the operating flow rate, *d1* is the diameter of the inner tube, while *d2* the diameter of the outer tube. Clearly *(d2-d1)* is the size of the annular space. By decreasing *d2-d1*, a very high efficiency can be achieved even for denuders having a relatively small length. At the same time, by reducing *(d2-d1),*the denuder can be operated at high low rate, increasing the amount of gas molecules collected on the annular surface and pushing the sensitivity of the sampling method at very low concentrations.

A denuder tube is therefore fully characterised by the following operating parameters:

- Annular diameters *d2* and *d1*
- Operative flow rate *F*
- Length *L*

The annular diameter *(d2-d1)* should be as small as possible. However, it should maintain along the tube a constant geometrical pattern. The operative flow rate is a function of the sensitivity of the analytical method and it may require relatively high or low flow rate, or sampling step extending for a higher or lower time. Based upon a consolidated scientific experience, ENVINT is now proposing the

denuders listed below. which are able to cover the most common applications in atmospheric sampling

Denuder Type	Length (mm)	d2 (mm)	d1	Flow rate (L/min)
LW_DN1522	150±1	17,2±0,2	15±0,05	1-7
LW_DN2022	205±1	17,2±0,2	15±0,05	1-9
LW_DN1242	120±1	40±0,3	31,6±0,1	3-15
LW_DN1842	180±1	40±0,3	31,6±0,1	3-20

However, since most applications do not require high sampling flow rates, the first two models are those who are recommended for the system ENVINT DEN 08/18. The following figure shows the model LW_DN1522.

The filter pack

As said before, a complete sampling line should be able to sample gas species and particulate matter, so it should include one or more denuders and a series of filters in which particulate matter is collected. Next figure shows the sampling train with the details of the filter pack equipped with two filter holders (F1 and F2). The present design of the filter pack allows the use of 35 mm diameter filters. This choice is the best compromise between small size, low cost and sufficient analytical performances. Upon request, the filter pack may be procured for standard 47mm filters.

In sampling operation, air is travelling from the bottom to top and passes through the elements described in the box.

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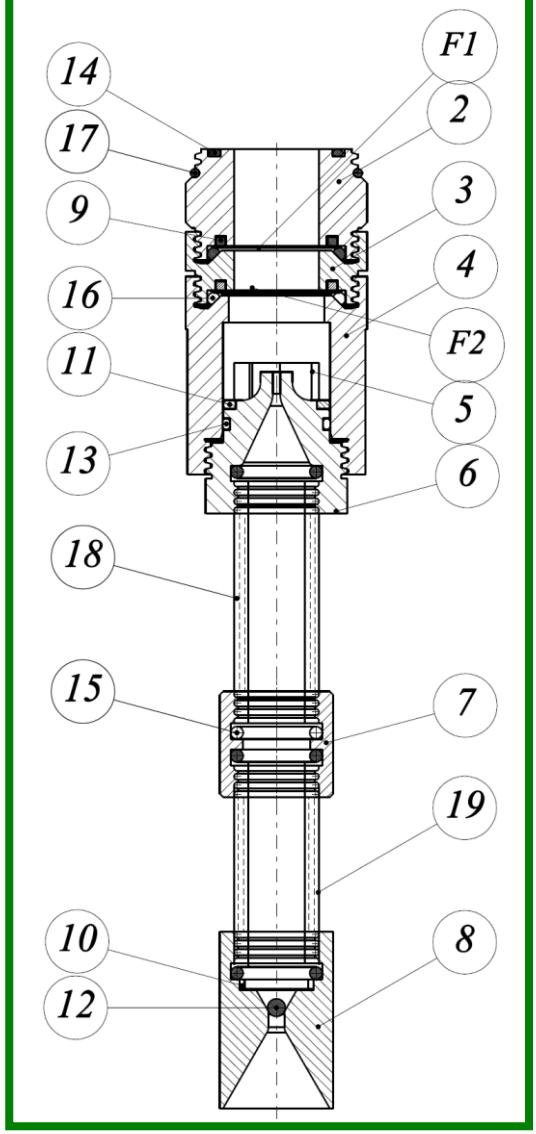


8 – Teflon ball valve to avoid diffusion of pollutants inside the tube when they are not sampling. During sampling the ball **12** is pushed up and air is allowed to enter the sampling train.

18, 19 Denuder tubes (in this case two tubes) connected via element **7.** The number of tubes may be from one to three according to the specific application,

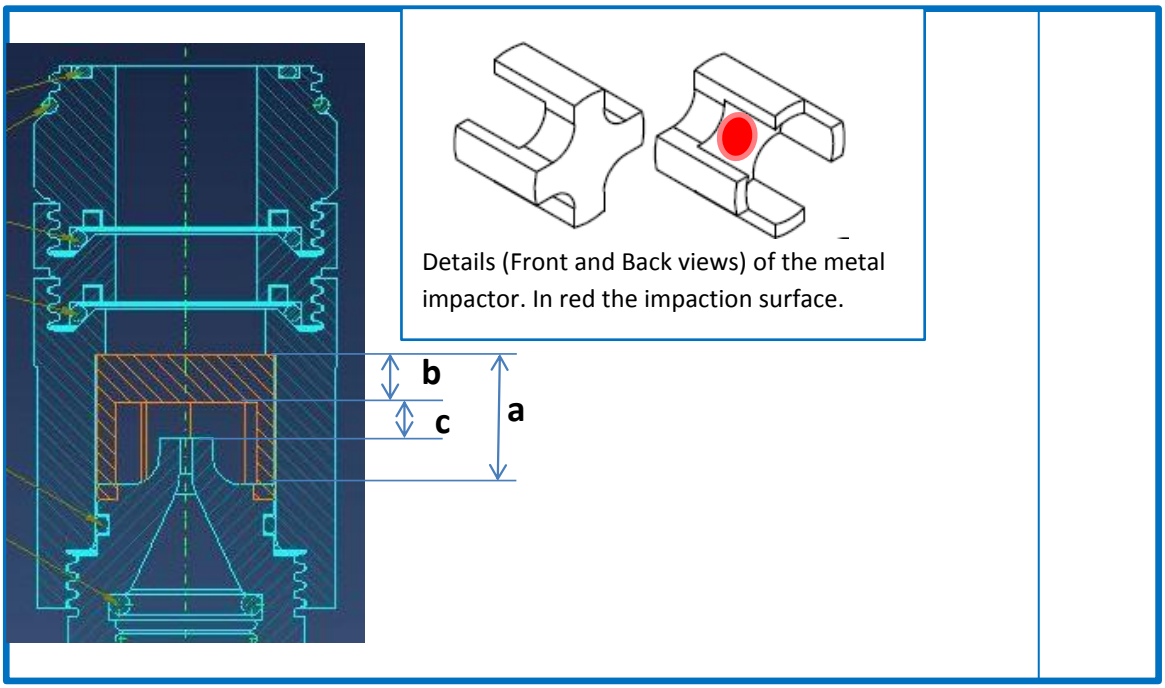
5 Impactor for the selection of particle size. This is an high precision impactor which select the desired size range of particulate matter according to operating flow rate. For instance, the impactor may select the size range PM10 or PM2,5.

F2 First filter to collect particulate matter from the denuder lines. This filter collects all particles according to size classification of impactor 5. Eventually, a back-up filter may be also accommodated on this filter holder

F1 Second filter for the collection of gases released by F2. Those gases are of acidic or alkaline nature and can be collected on properly impregnated filters.

In details, element 8 is the input line. It is shaped in order to ensure a high collection efficiency for particulate matter of size larger than 15 µm and is followed by a Teflon ball valve. The denuder line has been designed to be used with the sampler ENVINT GAS 08/16. The instrument, as it will be shown later on, is a dual pump sampling system able to accommodate up to 8 different sampling lines. Sampling is programmed by tablet according to time and date and events. This means that the denuder lines installed on the sampler could be inactive for a long period of time (days). During this time, the active surfaces of the denuder tubes may adsorb reactive gases from the ambient atmosphere by diffusion leading to errors in the measurement of ambient concentration of the relevant species.. The Teflon ball prevents this kind of contamination. During the sampling step, the ball is raised up by the air stream and air is allowed to pass through the sampling line. After sampling,

the ball close the input again, back diffusion is prevented and the sampling line can be removed anytime by the operators without problems.
After the transit in the denuder tubes, air is accelerated in the element 6 and forced to the impactor surface 5. The details of the impactor is shown in the following figure.



Details (Front and Back views) of the metal impactor. In red the impaction surface.

The filter pack is machined to a fixed value of the distance **a**. The thickness **b** of the impaction element, evidenced in gold colour in the figure, defines the distance **c** between the accelerating nozzle and the impaction surface. By knowing the inlet flow rate or by changing **b** only, it is possible to modulate the cut size of the impactor. This means that the user could use the same filter pack to accommodate impactors having different cut-size by simply modulating **b**.
Since inertial impactors may release particulate impacted on the surface, this Filter Pack is such that, in this case, particles will fall down and will not affect the sample collected on the filters. Rebounding of particulate can be avoided by adding a very thin layer of grease on the impaction surface. Use fingers to remove excess grease leaving just a thin layer on the impaction surface. Any vacuum grease will work properly. After sampling, the impactor can be cleaned by a cotton swab or a soft tissue dipped in acetone.
After the impaction, particulate matter is collected on the first filter. Filters are looking down toward the sampled airstream. After the first filter, a second filter can be accommodated. After filtering, the air, free of reactive gases (collected on denuders) and free of particulate (collected on filters) is forced to the sampling pump (GAS08/16 or other pumping system). Since the Filter Pack uses 35 mm filters operating in the flow range 2-7 L/min, the expected pressure drop is not very high and any sampler can be conveniently used.

The denuder filter pack system, as said before, has been developed for a complete, simple and inexpensive use in air pollution monitoring requiring evaluation of reactive gas phase species and particulate matter, Although the operational use of the system is relatively simple, great care should be exercised in the preparation of the denuder-filter pack since the risk of possible contamination is always present. In this chapter, some information about the operational use of the system is given.
Next pictures show an assembled and disassembled sampling line.

The assembled DEN08 sampling line

DEN08 disassembled sampling line

As shown before, it consists of:

- Inlet Teflon ball valve

- Denuders in series coupled with the connector, the
- Filter pack which fits to ENVINT GAS08/16 or any other pumping system through a hose connector.

Filter pack ready to be sampled by means of an external pump

To assemble the sampling line, the operator should have the denuders already coated and the filter pack assembled. Cleaning and coating procedures for the denuders have been given before, in this subchapter handling and preparation of filter pack is given. Picture below shows the details of parts relevant to the filter pack.

Disassembled DEN08 filter pack

From the right to left, the pictures show:

1) First plug used to close the filter pack and right end
2) Accelerating nozzle
3) Metal impactor surface
4) Impactor body

5) First filter holder
6) Second filter holder
7) Second plug to close the filter pack at left end

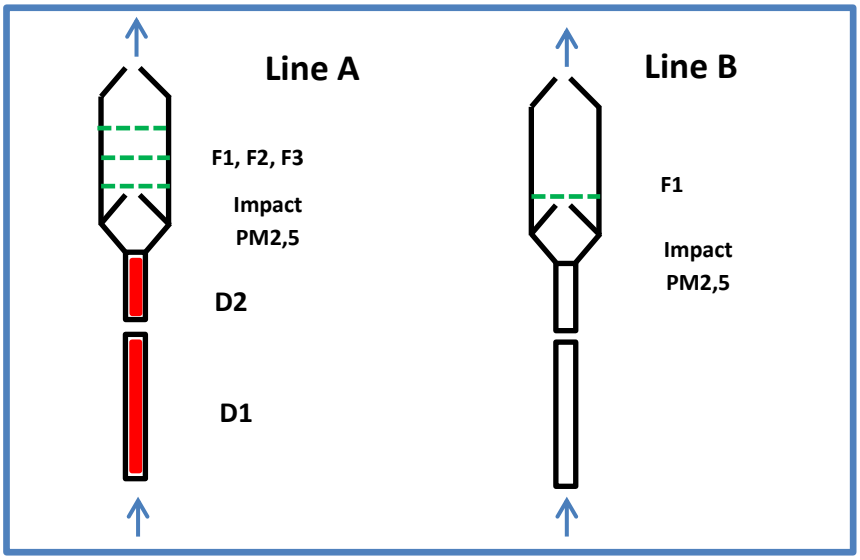
Filter pack is specifically designed to accommodate directly the denuders DN1522 and DN2022. An adapter allows also the use of the denuders DN1242 and DN1842.

Sampling module GAS08/16

The sampling train described above was developed in order to maximise its flexibility by using an appropriate sampling line. ENVINT GAS08/16 Gas/Aerosol sampler is a device specifically developed and intended for the selective sampling of gases and aerosol present in the atmospheric environment. Sampling step is completely automatic and does not need any kind of external intervention. In addition to requirements set in Art. 6 of the Directive, it can be used in air pollution monitoring, source apportionment and air pollution dispersion studies. It can sample reactive gases without any interference by particles by using annular denuders.
Basically, the instruments consists of a double independent sampling circuits operating with two sampling pumps for nominal flow rates ranging from 1 to 10 L/min. Each sampling circuit is controlling up to four sampling lines which can configured according to the scheme A and B outlined below.
Technical specifications are given below:

Type of sampler	Dual pump with denuder/filter pack sampling system
Number of sampling lines	8
Channel activation	Electro-valves
Available sampling packs (see description)	1) Denuders and filter pack with PM2,5 impactor 2) Single filter with PM2.5 Impactor
Filters	37mm diameter Quartz, Teflon, Paper
No of filter packs	- 4 filter packs type A - 4 filter pack type B - 8 filter packs of either type 1 or type 2
Impactors	PM2,5 or PM10 (other cut sizes on request)
Other sampling devices	Cartridges for VOC, impregnated filters, etc.
Sampling flow rate	1 to 10 L/min programmable by user
Accuracy and precision	1%
Volume correction	Correction at standard T and P on request
On Board sensors	Temperature, Relative Humidity, Atmospheric Pressure, Flow rate, Pump current (related to back-pressure)
External sensors	Unlimited through I^2C interface
Digital input	Up to 3 (dry contacts connection)
Programming	Tablet with Android OS (included)
Electronic Connections	Local Wi-Fi
Data output	Digital (pen drive) or output on tablet
Type of sampling	- Single or twin sampling operation

	- Sequential sampling according to programmed timing - Sampling on Events by Digital inputs
Input voltage	12VDC, Current 1A by external supply
Power fail	Automatic restart
Size	LxDxH cm 60x25x90
Weight	10 Kg (complete with filter holders)
Operating Temperature	-10 to +35°C
Operating external relative humidity	100%



- In Line A, the denuder D1 (Coated with an alkaline substance) removes acidic gases, while the denuder D2 (Coated with an acid substance) remove alkaline gas such as ammonia. Air, spoiled by reactive gases, passes through an impactor (PM10 or PM2,5) and then filtered in a first front filter F1 (Teflon filter). After the front filter, air passes through the back-up filters intended for the collection of evaporated acid species (F2) and alkaline species (F3).
- In Line B, the denuders are not coated and serve as fluido-dynamic coupling. After the impactor, air is filtered in a Quartz filter. This can be used for the gravimetric analysis as well as for the evaluation of Elemental and Organic carbon. Line B is consistent with the standard methods for the collection and gravimetric measurement of particulate matter.

GAS 08/16 can then operates as a normal 8 lines sampler or operates according to a random or sequential sampler over two types of sampling lines. Sampling line A and a sampling line B can be operated in parallel at the same time providing samples for:

- Reactive gas concentrations
- Gravimetric and EC/OC analysis
- Ionic composition of particulate matter

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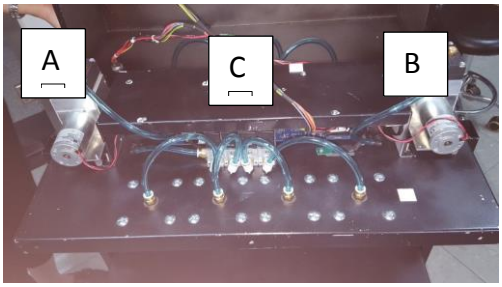
External view of the sampler GAS08/16



Internal view of the GAS08/16 with the two pumps (A and B) and the electronic circuit board (C).

Applications

In the twin configuration outlined above, GAS 08/16 may provide very important information about the composition of particulate matter, as required by several legislations. For the European case, Directive 50/2008/EC which requires the following information:

- Gravimetric Measurements of PM2,5
- National Exposure target for PM2,5
- Average exposure indicator for PM2,5
- Soluble ions (art.6) where at least the following chemical species shall be included:

Sulphate
Nitrate
Ammonium
Chloride
Sodium
Potassium
Calcium
Magnesium
Elemental Carbon
Organic Carbon

DEN08 System is providing all these information, also discriminating between evolved and non-evolved ions, thus it is coherent with the current legislation. In fact the information provided by the two sampling line operating in parallel are the following:

$[NO_3^-]$evolved =$[NO_3^-]$N	(1)
$[Cl^-]$evolved =$[Cl^-]$N	(2)
$[NH_4^+]$evolved =$[NH_4^+]$N+$[NH_4^+]$PA	(3)
$[NO_3^-]$unevolved =$[NO_3^-]$T	(4)
$[Cl^-]$unevolved =$[Cl^-]$T	(5)
$[NH_4^+]$unevolved =$[NH_4^+]$T	(6)
$[NO_3^-]$fine =$[NO_3^-]$unevolved+$[NO_3^-]$evolved	(7)
$[Cl^-]$fine =$[Cl^-]$unevolved+$[Cl^-]$evolved	(8)
$[NH_4^+]$fine =$[NH_4^+]$unevolved+$[NH_4^+]$evolved	(9)
$[SO_4^{-2}]$fine =$[SO_4^{-2}]$T	(10)
[PM_{10} or $PM_{2,5}$] Q	(11)
[EC and OC] Q	(12)
[NH_3 gas] D2	(13)
[SO_2, Acids gas] D1	(14)

where terms N, PA T D and Q stand for the back-up alkaline filter (Nylon filter), back up acid filter (phosphorous acid coated paper filter), Teflon filter, Quartz filter and Denuders respectively. i.e, 14 parameters very important for the management of air quality.
In addition, before dissolution, the front Teflon filter may be analysed by a non-destructive technique such as X-Ray Fluorescence to provide concentration data on some element such as those contained in soil, thus mainly present in the “coarse” fractions as consequence of dust resuspension.

[Element]fine =[Element]T	(15)

It is worth stressing that the described sampling line is just related to the measurement of several species of significance for inorganic secondary pollution according to the following definitions:

1) $[NO_3^-]$evolved =$[NO_3^-]$N , Nitrates found in the back up Nylon filter due to volatilisation (As Nitric Acid) of Ammonium Nitrate from the first Teflon Filter
2) $[Cl^-]$evolved =$[Cl^-]$N Chlorides found in the back up Nylon filter due to volatilisation (As Hydrogen Chloride) of Ammonium Chloride from the first Teflon Filter
3) $[NH_4^+]$evolved =$[NH_4^+]$N+$[NH_4^+]$PA sum of ammonium evolved from the first Teflon filter and found in the Nylon back-up and on the impregnated filter
4) $[NO_3^-]$unevolved =$[NO_3^-]$T Nitrates not evolved, thus found in the Teflon filter
5) $[Cl^-]$unevolved =$[Cl^-]$T Chlorides not evolved, thus found in the Teflon filter
6) $[NH_4^+]$unevolved =$[NH_4^+]$T Ammonium not evolved, thus found in the Teflon filter
7) $[NO_3^-]$fine =$[NO_3^-]$unevolved+$[NO_3^-]$evolved Total nitrates in particulate matter

8) [Cl^-]fine =[Cl^-]unevolved+[Cl^-]evolved Total Chlorides in particulate matter
9) [NH_4^+]fine =[NH_4^+]unevolved+[NH_4^+]evolved Total Ammonium in particulate matter
10) [SO_4^{-2}]fine =[SO_4^{-2}]T The fine particulate SO_4^{-2} is not volatile; therefore, its concentration is taken as that on the Teflon filter only
11) [PM_{10} or $PM_{2,5}$] Q Standard gravimetric concentration of particulate matter
12) [EC and OC] Q Standard Elemental and Organic Carbon
13) [NH_3 gas] D2 Ammonia in gas phase
14) [SO_2, Acids gas] D1 Acid gases j gas phase

However, the system can be made more simple and adapted for the measurement of selected species, For instance, by using one denuder and one Teflon filter, it is possible to measure simultaneously the concentration of sulphur dioxide in gas phase and of sulphates in particulate matter.
Some examples of additional configurations is given below

Configuration of sampling line		Measured species
Denuders	**Filter Pack**	
1 Alkaline coating (Na2CO3)	1 Nylon or 1 Teflon	SO_2(gas); SO_4 (part)
1 Acid Coating (Citric or Phosphorous Acid)	1 H_3PO_3 paper impregnated	NH3(gas); NH4+ (Part)
1 Alkaline Carbon	1 Nylon	NO2(Gas)+NO3.(part)
1 NaCl	1 Nylon	HNO3(gas)+NO3-(part)
1 NaCl + 1 Alkaline Coating	1Nylon	HNO3(gas); HNO2 (gas); NO3.(Part)
1 KI	1 Quartz	PAH without interference by Ozone
1 DPNA	1 Glass Fiber + 1 impregnated DPNA	Aldehydes in gas phase and particulate matter

Without denuders, the system behaves as a normal sampling apparatus. In this case, in order to reconstruct the same fluido-dynamic conditions, it is recommended to use at the inlet a “dummy denuder”, i.e. a denuder not coated which reconstruct at the inlet of the sampling line the flow filed developed by using real coated denuders.
Since the system is very flexible, these configurations can be mixed-up, providing the solution for most monitoring requirements.
Besides the above application, the use of ENVINT DEN08 is very valuable in the following general applications:

- Evaluation of chemical composition of particulate matter
- Mass concentration measurements of PM2,5 and PM10.

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- Sequential or conditional sampling to external inputs.
- Simultaneous measurement of PM fractions and gas/aerosol concentration by sampling time distribution.
- Urban and traffic pollution
- Indoor pollution
- Industrial pollution
- Pollution in working sites
- Environmental impact assessment
- Air pollution alerts ad emergencies
- Source apportionment studies