Water Vapour Removal from Gaseous Samples Used for Analytical Purposes. A Review

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WATER VAPOUR REMOVAL FROM GASEOUS SAMPLES USED FOR ANALYTICAL PURPOSES. A REVIEW

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Four different techniques, usually applied for removal of water from gas streams, are described in detail. These techniques include chemical drying using desiccants, drying with adsorbents, removal of water by cryotrapping and by permeation through membrane tubes. Their advantages and disadvantages, especially with respect to efficiency and feasibility, are discussed.

Keywords: Humidity; water removal; desiccants; adsorbents; cryogenic trapping; permeation drying

INTRODUCTION

Water is frequently an undesirable component in gas streams that should be submitted to chemical analysis, and its quantitative removal is not apparently an easy task. Taking into account the moisture content and the specific requirements in relation to a desired removal degree, the following drying requirements may be considered:

- drying of air streams before sampling of volatile analytes,
- drying of atmospheric air samples before their chromatographic analysis, particularly before the analysis of Volatile Organic Compounds (VOCs),
- drying of purging stream gases, after isolation of volatile analytes from liquid samples (mainly from aqueous samples).

The necessity of water removal from different samples before their introduction into a chromatographic column is due to the several technical and analytical

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problems that its presence may cause[1]. The problems may arise when the sample contains more than 1 mg of water[2]. To stress the problem, it can be considered that in 1 dm^3 of air, with a relative humidity of 50% at 25 °C, there are 10 mg of water.

The presence of water in gas streams that should be analyzed may cause negative effects that disturb the final results of the analysis. The following effects may be observed:

● losses of the analytes by condensation of water on the walls of the sampling vessels and devices connected to measuring instruments,

● decrease of the effectiveness of some devices used for the isolation and pre-concentration of analytes, e.g. :

   – by co-adsorption of water on the sorbent used for sampling, especially in case of hydrophilic sorbents

   – by forming ice in cryotraps, that may increase the flow resistance and even block the sampling system[3].

The main problems caused by the presence of water in samples introduced into the chromatographic column are as follows:

● variation of retention times as a result of stationary phase polarity changes due to the water thin layer formed on its surface[2,4–6],

● variation of peak area of the compounds that have retention similar to water[2,4–7],

● flame extinguishing in flame ionization detector[8], or worsening the operation of other chromatographic detection systems[2,4],

● shortening the life time of chromatographic columns.

● plugging of capillary columns by ice formation in case of the cryofocusing enrichment technique.

The procedures applied for gas stream drying can be divided into four groups[9],

● drying using desiccants,

● drying with adsorbents,

● drying by cryocondensation,

● drying by permeation.

Obviously, the drying process, besides removing the largest amount of water present in the sample, should not affect its composition.

DRYING USING DESICCANTS

The most popular drying agents (desiccants) are: anhydrous magnesium perchlorate[10-15], potassium carbonate[7,11,12,16-22], magnesium carbonate[11], anhydrous calcium chloride[16], and supported lithium chloride (Chromosorb WAW)[23].

The use of sodium carbonate, phosphorus pentaoxide (*Sicapent*[24]), P_2O_5 on vermiculite base (*Aquasorb*[25]) anhydrous calcium sulphate (*Drierite*[26]) and sodium hydroxide on a silicate base (*Ascarite*[5,27]) have also been mentioned in the literature.

The compatibility of a particular desiccant with the analytes present in the sample should be considered before its application. The desiccant should not cause contamination nor lead to the loss of compounds. Matuska et al.[28] found quantitative recoveries for $C_2 - C_{10}$ hydrocarbons with magnesium perchlorate but Doskey[29] reported losses of long chain olefins and $C_1 -$ to $C_3 -$ substituted benzenes. Good recoveries were found for both aliphatic and aromatic hydrocarbons using potassium carbonate, although, significant losses were observed for heavier aromatic compouds. Futhermore, this desiccant may create excessive back pressure by caking after prolonged use. Recently, extensive studies on the effect of different desiccant on the analytical data for non-methane hydrocarbon concentrations in ambient air samples have been performed[12]. It was found that there was no significant difference in the content of $C_2 - C_9$ aliphatic hydrocarbons (both saturated and unsaturated) in air samples treated with supported magnesium perchlorate, ascarite or potassium carbonate-sodium hydroxide. In case of aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes) the best results were obtained when air samples were dried with $Mg(ClO_4)_2$. Data obtained for heavier aliphatic hydrocarbons ($>C_6$) were not sufficient to draw a definite conclusions.

In some cases, the desiccant trap may work at elevated temperature in order to assure a quantitative passage of analytes through it. Sometimes, the trap is heated to 80–90 °C in order to recover quantitatively the analytes from the gas stream flowing through the drier.

Table I shows the efficiency of the typical chemical desiccants.

As the drying effectiveness may change during the drying process, the drying agent should posses a good drying potential and capacity. A desiccant has a good drying potential when is able to reduce effectively the water vapour pressure of the effluent and has a good capacity of drying when is able to retain a large amount of water with a constant intensity of drying. Substances such as P_2O_5, $CaCl_2$, $MgSO_4$ or Na_2SO_4 fulfil the requirements in relation to the intensity and capacity of drying. For example, the application of potassium carbonate and cal-

cium chloride was found to remove 80 to 90% of water vapour from air almost saturated with water vapour[16]. Both desiccants exhibited a similar behavior, a drawback of $CaCl_2$ was that it required a more frequent reconditioning and induced more important charge losses in the analytical system. Furthermore, the losses of monoterpenes did not exceeded 10% and were independent of gas humidity. Calcium sulphate exhibits high intensity of drying but has low capacity.

TABLE I The level of residual humidity after gas drying using the most popular desiccants

Desiccant	Residual humidity calculated for dry air at standard conditions [mg/m³]	Absorption capacity in relation to water (% of compound mass)
P_2O_5	<0.02	~ 100
KOH (melted)	2	no data
$Mg(ClO_4)_2$ anhydrous (Anhydron)	2	48
$CaSO_4$ anhydrous	5	6.6
$CaCl_2$ (melted)	340	
$CaCl_2$ (granulated)	1,500	90

Table II shows the drying capacity of different drying agents.

TABLE II Drying capacity of different drying agents (at 20 °C)

Drying agent	Water vapour pressure over drying agent [mm Hg]
P_2O_5	0.00002
$Mg(ClO_4)_2$ anhydrous (Anhydron)	0.0005
$Mg(ClO_4)_2 \times 3H_2O$ (Dehydryt)	0.002
KOH (melted)	0.002
Al_2O_3	0.003
$CaSO_4$ anhydrous (Anhydryt)	0.004
H_2SO_4 concentrated	0.01
silica gel	0.01
CaO	0.2
$CaCl_2$	0.2
$CuSO_4$	1.3

The major inconvenience of this type of drying is an increase in the flow resistance through the drier during its use (saturation with water). In some cases, the sorbent can be regenerated, e.g. a bed of LiCl can be regenerated by heating to 120°C and passing a purging gas[23]. Inert gases can be dried by passing them through scrubber filled with concentrated sulphuric acid.

DRYING USING ADSORBENTS

Silica gel and aluminium oxide are the most frequently applied for this purpose. Particularly suitable is silica gel impregnated with cobalt salts. The colour of cobalt salt indicates the degree of saturation of silica with water vapours (blue – dry, pink - saturated with water). Silica can be regenerated by heating in an oven at 120 °C.

Zeolites (molecular sieves) are synthetic sodium or calcium silicates, depending on structure denoted by A or X symbols. Zeolites have weak basic properties and are resistant to high temperature (500–600 °C).

Presently, about 40 natural zeolites are known and about 20 molecular sorbents are produced synthetically. The molecular sorbents unlike other popular sorbents such as silica gel or activated carbon have very uniform pore sizes. This property is applied mainly for separation and fractionation processes. In Table III the basic properties and the application areas of molecular sieves are given.

TABLE III Properties and applications of zeolites

Zeolite type	Diameter of channels [nm]	Types of adsorbed compounds	Range of applicability in drying
3A	0.38	H_2O, NH_3	Drying of hydrogen, air, noble gase, methanol, ethanol
4A	0.4	H_2O, NH_3, H_2S, SO_2, CO_2, light alkanes, alcoholes, higher alkanes	Drying of acetone, ethers, benzene, ethylacetate, pirydine, DMSO, DMF
5A	0.5	above compounds and ethyline oxide, ethyloamine, alcoholes, higher n-alkanes	THF
10X	0.9	above compounds and iso-alkanes, benzenes, naftalene, simple heterocyclic compounds, chloroalkanes	
13X	1.0	above compounds and more complex aromatic compounds	Drying of phosphoric acid, hexamethylotriamide

Table IV presents the surface area of some adsorbents currently used for drying.

TABLE IV Specific area of selected adsorbents

Adsorbent	Specific surface area $[m^2/g]$
Bentonite	150
Aluminium oxide	200 – 250
Wide-pore silica gel	400 – 530
Narrow-pore silica gel	550 – 700
Molecular sorbent (zeolite)	700 – 1100
Activated carbon	700 – 1200

All adsorbents have a specific adsorption capacity. Therefore, after a work cycle they should be regenerated. The important advantage of molecular sorbents is the possibility of their multiple regeneration (over 2000 cycles) without changes of their adsorption properties.

Generally, the regeneration of drying agents is performed by thermal desorption at elevated temperatures and bed purging with inert gas. The regeneration (activation) of molecular sieves is conducted at 300–320 °C.

The drying with adsorbent is frequently used for preparation of "zero gas", when all components including water vapours are removed from the gas stream[27].

Like in the case of hygroscopic salts, the drying with adsorbents should not affect the sample composition, especially by irreversible adsorption of analytes together with water. This may occur with very polar and heavy compouds. In such case, a slow and temperature-controlled, heating of adsorbent trap is applied to release analytes adsorbed simultaneously with water[25,30].

DRYING BY CRYOCONDENSATION

Water removal by cryocondensention is performed by passing the gas stream through a cooled trap (-80 °C). This ensures the decreasing of water vapour up to 1 mg/m^3, not affecting the content of volatile organic compounds.

The composition of cryogens and freezing mixtures used for cooling traps are given in Table V. Table VI presents the dependence of water vapour pressure on temperature.

TABLE V Substances and cooling mixtures

Mixture components	Cooling temperature [°C]
ethanol-dry ice	to −72
chloroform-dry ice	to −77
ethyl ether-dry ice	to −77
liquid SO_2-dry ice	to −82
liquid NH_3	-34
liquid O_2	-180
liquid air	-190
liquid N_2	-196

TABLE VI Dependence of partial pressure of water vapour on temperature

Temperature [°C]	Partial pressure of water vapour [mm Hg]
+20	17.5
0	4.6
-20	0.77
-70	0.002
-100	0.00001

In environmental analysis, the drying is also performed by physical condensation of water in especially designed condensers[2,26,31–33] at ambient or moderate subambient temperatures (−10 °C) on glass beads prior to sample elution onto GC column.

Drying efficiency mainly depends on the trap geometry and temperature, as well on the flow rate of the gaseous stream through the cooling trap.

PERMEATION DRYING

The basic element of such procedure is a tube made of Nafion (DuPont)®, a copolymer of tetrafluoroethylene (by polymerisation of which teflon is obtained

– PTFE) and perfluoro-poly[trifluorometylo(oxapropylo)]-sulphonic acid. The specific composition of such polymer containing ionic (sulphonic) moieties in a hydrophobic matrice, enables the transport of water molecules along the ionic fragments according to a concentration gradient.

The membranes with selective water permeability were first used for drying gas streams before the analysis of SO_2 or chlorohydrocarbons[2,34,35]. Nafion is able to absorb up to 13 water molecules for each sulphonic acid group, that represents 22% by weight of water. Despite the fact that the membrane permeation process is a slow diffusive process, the adsorption of water by hydration of sulphonic groups is very fast, providing a really efficient process.

When a gas stream containing water flows along a Nafion tube, water diffuses through the tubing to external surface and evaporates. Other sample components do not behave in this way. Only some polar organic compounds (ketones, amines, alcohols, acids, DMSO) and ammonia can be partly lost due to absorption and permeation. Therefore, such process is highly selective and prevents contamination of the sample and losses of analytes.

The driving force of water movement through a Nafion membrane is the difference in water partial pressures on both sides of the wall. The drying process of a gas flowing through a permeation tube takes place continuously when the water vapours are constantly removed from the external side of the tube (e.g. by purging the tube externally or placing it in a drying bed).

The permeation process of gas drying proceeds so fast that residence time $ca.$ 1s is enough to achieve high degree of gas drying. Because the water, absorbed by the polymer cannot be removed completely the drying process is stopped when the gradient of water does not exist. Using this method it is possible to dry gases up to the water concentration of about 100 mg/m^3, that corresponds to a dew point of –45 °C. The application of permeation driers has been described in many papers[36–49].

The drying process can be conducted in static[3] or dynamic[40] mode. Figure 1 shows the construction of a drier working in a static way[35], which may be especially useful in field conditions.

The dried gas is passed through the tube with the flow of 50–100 cm^3/min at ambient temperature. Under such conditions the water vapours diffuse through the tube wall and are absorbed by the container packing. It was found that such a drier was able to dry air, with relative humidity of 20–80 %, up to a dew point of –30 °C working continuously for seven days. Of course, the effective time of working depends on ambient temperature, air humidity and on the type and amount of drying agent in the container.

The drying process can be also conducted continuously in a dynamic system[50–54]. Figure 2 presents schematically the construction of such a drier. In
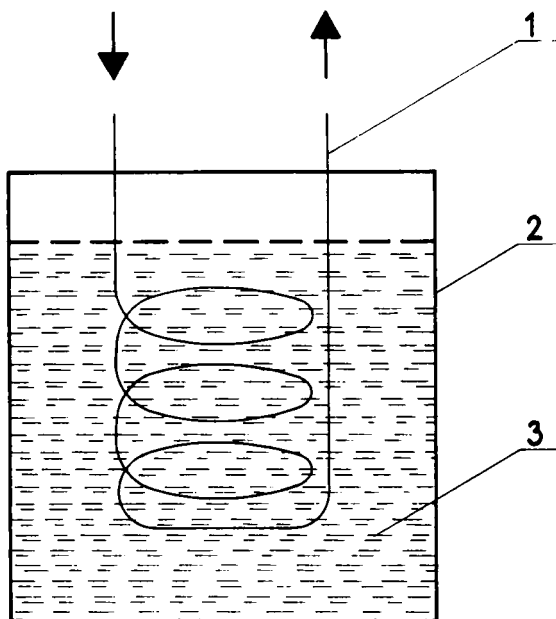
FIGURE 1 Scheme of a drier operated in static system: 1 – Nafion permeation tube (100 cm), 2 – drier housing, 3 – drier packing (molecular sieve or desiccant)

that case, the water from the external side of the permeation tube is removed by a stream of dry gas. A different construction of a drier operated in a dynamic mode is shown in Figure 3.

The transport intensity of water from dried gas is proportional to the difference of partial pressure of water vapour on both sides of tube. The transport will take place when both streams have the same pressures but different humidity, as well as during the same humidity but with different pressures.

The permeation method of water removal may be treated as a specific type of a denuder technique, which is frequently applied for preconcentration of different kinds of analytes from gaseous streams[55].

CONCLUSIONS

In spite of the availability of many different drying techniques it is difficult to indicate a universal solution. Traps filled with hygroscopic salts and sorbents usually are efficient in retaining water but in some cases their use is limited
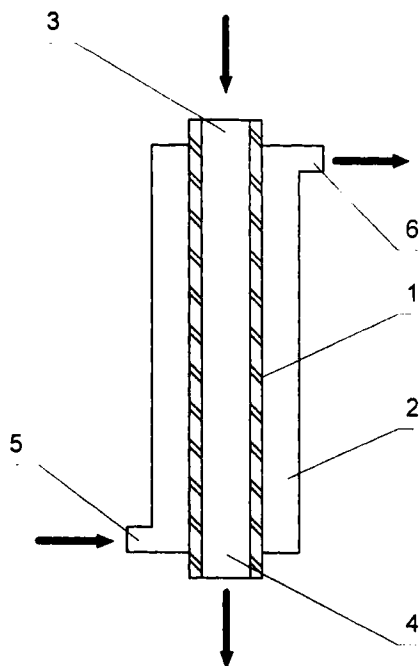
FIGURE 2 Scheme of a drier operated in dynamic system: 1 – permeation tube, 2 – mantle, 3 – inlet of wet gas, 4 – exit of wet gas, 5 – exit of purging gas, 6- inlet of purging gas
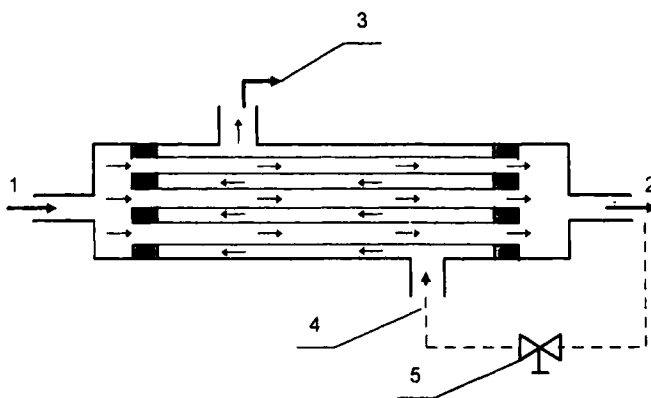

FIGURE 3 Construction of permeation drier operated in dynamic system: 1 – inlet of gas for drying (wet, with high pressure), 2 – exit of dried gas (with high pressure), 3 – exit of purging gas (containing humidity, with low pressure), 4 – inlet of purging gas (dry, with low pressure), 5 – decompression valve

because of the possible loss of specific compounds (especially high boiling and polar compounds). Cold traps are also very effective but they require the proper maintainance of the cold bath. Membrane-type driers such as Nafion are highly recommended because they provide a clean and efficient drying. A comparison of different techniques are presented in Table VII.

TABLE VII Comparison of different techniques of gas drying

Drying technique	Comparison criterion		
	necessity of inspection of drying device	necessity of periodical service of drying device	necessity of filtration of dried gas
drying with desiccants	yes	yes (packing change)	yes (after drying)
drying with adsorbents	yes	yes (regeneration)	yes (after drying)
condensation (>0 °C)	no	no	no
cryocondensation	yes	yes (removing of ice plugs)	no
permeation drying	no	no	yes (before drying)

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