Aging of Gaseous Detectors: assembly materials and procedures

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Abstract

Aging of gaseous detectors is known as the degradation of their performance under the exposure to ionizing radiation. It is a complex phenomenon that depends on many parameters. Among others, aging depends on the gas mixture and may be enhanced by the presence of pollutants in the gas. The origin of the impurities is diverse and includes outgassing from assembly materials and the gas system components, and contamination of the detector during the assembly process. Systematic studies on this topic have been carried out. Methods used to ascertain the outgassing properties of materials are described and compared. Materials that might be used for assembling gaseous detectors and associated gas systems are catalogued according to their outgassing rate. Some factors affecting the aging rate in some fast gases are presented. Finally, a set of recommendations to build and operate gaseous detectors in high luminosity experiments is given.

1. Aging of gaseous detectors

Gaseous detectors have been used for many decades in modern high energy physics experiments for particle detection and tracking. Soon after their development, it has been common to find problems associated with their long-term exposure to radiation, limiting their useful time. The observed phenomenology included the appearance of local and permanent damages detected as self-sustained discharges, excessive currents, gradual loss of energy resolution and decrease and non-uniformity of the gas gain. These observations led to the association of the problem to the presence of layers on the electrodes, possibly induced by pollution released by materials used in the gas system or chamber construction, or impurities in the gas itself. A branch of Chemistry called Plasma Chemistry studies processes with certain qualitative analogies to those that take place in the plasma surrounding the anodic wire in a gaseous detector, which might be considered as a dc plasma at 1 atmosphere. Plasma is a mixture, initially overall neutral, of positive and negative ions, neutral species, and chemically active free radicals; radicals can recombine back to the origin molecules or new ones. Polymerization is thus the process by which some monomer radicals associate in subsequent chain reactions to form a very large molecule, frequently of high molecular weight. Created

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polymers are solid, highly branched and cross-linked, have excellent adhesion to surfaces, are resistant to most chemicals and insoluble in most solvents. Deposits observed in aged chambers seem to have similar properties. During operation of a gaseous detector, formed molecules will be removed by the gas flow if they are light enough, or be deposited or react with electrode materials inducing typical aging processes. The chemistry of the process has not been deeply studied, thus a rigorous explanation of why certain chambers age and others do not cannot be yet discussed with certainty. In addition, information gathered form experiments, as distinct from controlled tests in laboratory, is sometimes contradictory and renders extrapolation to other cases difficult. The approach to the aging problem is still in most cases purely experimental. A summary of principal results until 1986 may be found in the Proceedings of the first Workshop on Radiation Damage to Wire Chambers [1]. Since then, aging has been extensively studied and even more in the last decade in view of the imminent high luminosity experiments [2, 3, 4, 5]. Observations are difficult to compare and/or extrapolate between one another. This work compiles existing data and systematic observations with the aim of determining a set of operating conditions, such as gas choice, purity and cleanliness of the system, detector assembly materials and procedures, additives and level of impurities under which gaseous detectors do not age up to reasonable levels of radiation.

2. Contributions to the aging process

The mechanisms leading to aging of gaseous detectors can be summarized as follows:

- Polymer formation in the avalanche plasma from the cloud of ions and radicals of the gas filling. This is the case of hydrocarbon molecules used in detectors exposed to large particle fluxes. Pollutant molecules may trigger or accelerate the polymerization process for a given gas mixture.
- Direct deposition on the surface of electrodes and insulators of pollutants, which are transported with the gas flow and deposited thanks to electrostatic forces. Their origin is diverse: i) outgassed vapours from organic materials. ii) Some reactive gases can be incompatible with chamber materials and plumbing. Dymethyl ether is a sample case. iii) Materials might also follow structural changes induced by the effect of ionizing radiation; new outgassed pollutants may promote polymerization.
- Some initially neutral gases become reactive because of the species created around the wire in the avalanche process. The created species are reactive enough to remove concurrently layers of some materials, mechanically damaging the detectors and polluting the filling gas. Tetra fluoride radicals are capable, for example, of removing thin layers of deposits on coated wires. This capability might on the other hand turn into a serious problem when the active species attack assembly materials.
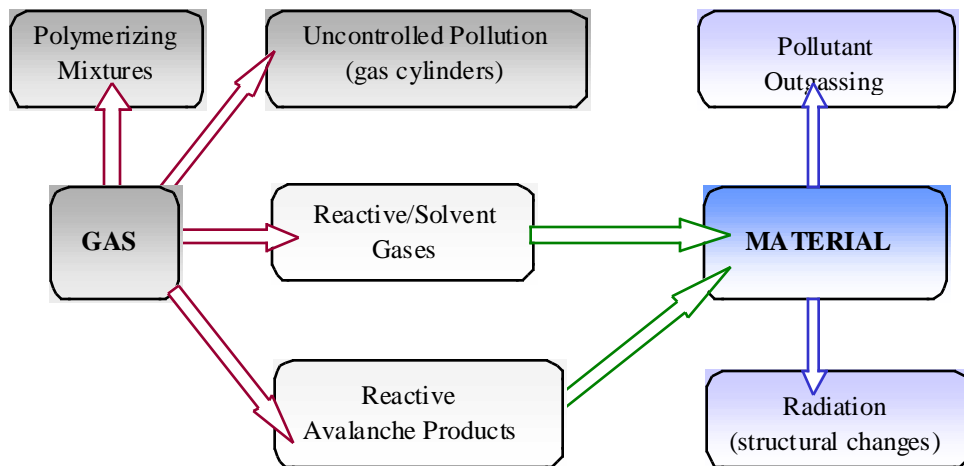
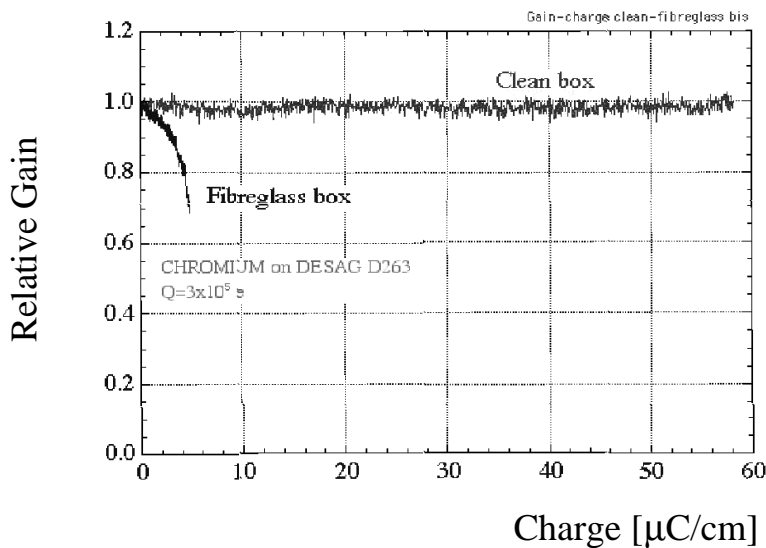Fig. 1 Contribution of materials and gas to the aging processes.

Fig. 2 Aging rate measured for two identical MSGC plates (Cr strips on DESAG 263) assembled with different materials. Very rapid aging is measured for the plate assembled with conventional MWPC materials, such as fibreglass, Araldite 106 epoxy and rubber O-rings.

The probability of all these mechanisms to occur depends on a large number of factors. Gas flow, gas gain, the geometry and electric field configuration, presence of additives and others play an important role. The contribution of materials and gas pollution to trigger aging processes is shown schematically in Fig. 1. The importance of materials selection is manifested in Figs. 2 and 3. Fig. 2 [6] shows the dramatic effect of the choice of materials used to assemble Micro Strip Gas Chambers (MSGC). The rate of aging increases orders of magnitude simply by using some organic elements in the assembly, a conventional choice for

low rate multiwire proportional chambers. Fig. 3 [4] shows different aging rates measured with the same MSGC connected to two different gas systems: the ultra clean system is assembled and equipped with components following ultra high vacuum standards (VCR connections, welded electropolish stainless steel piping, long metallic exhaust pipe, etc) and the minimal quantity of possibly polluting components (one Viton and one Kalrez joints in the electronic mass flowmeters); the second gas system is assembled with the minimal possible sources of pollution, but standard metal valves and few rubber O-rings and sealants.
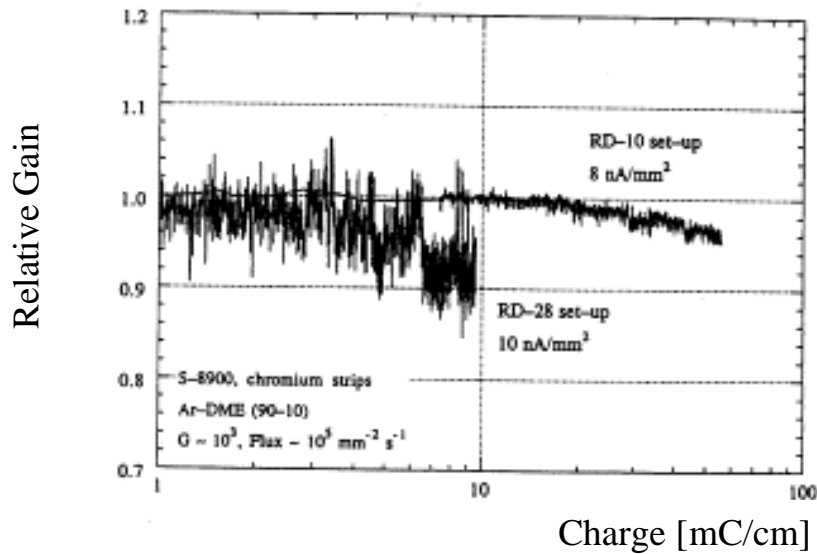

Fig. 3 Gain dependence on charge measured with the same MSGC operated in a ultra clean gas system and a clean system containing few rubber O-rings, valves with Teflon joints and few spots sealed with Torr-Seal.

A systematic search aimed to find possible pollutants in the standard set-up identified few ppm of $C_2Cl_4F_2$ released at each manoeuvring of the metal valves as capable of significantly accelerating the aging rate of the MSGC [7]. The source of pollution could be the Teflon joint, some lubricant or any residual cleaning product used during the assembly of the valve. Once the source of pollution was identified, all valves were removed from the gas mixer and cleaned just by baking them at around 100 °C for few hours. Further aging tests carried out in this set-up confirmed the excellent degree of cleanliness.

By suitably choosing the operating conditions, gaseous detectors work satisfactorily up to collected charges equivalent to many years running in high luminosity experiments. We will show that an adequate choice of materials for detectors and gas systems and assembly procedures seems mandatory to minimize aging effects.

3. Outgassing tests

The use of new materials with attractive mechanical, electrical and radiation resistance properties is conditioned by their outgassing properties when in contact with a given mixture. We describe in this section some methods used to determine the rate of outgassing of some assembly materials and parts for gas systems.

3.1. Gas analysis

A method to determine the outgassing properties of certain material is the analysis of a gas sample that is in contact with the material. A basic test consists of flushing clean gas through a box where the material under investigation has been introduced and analyzing the gas as it flows out. The surface of each individual sample and the gas flow should be kept constant to allow comparative studies. The material can be heated up in order to increase the rate of possible outgassing, so that relative large amounts of pollutants can be produced in a few days, thus increasing the sensitivity of the measurements (unfortunately the scaling factor is unknown). Still impurity detection has the intrinsic limitations of the analysis station: i) the incapacity to detect substances below some given quantity, and ii) the inability to separate, thus identify, certain compounds. Another drawback is that even if outgassing is detected, the particular pollutant might not be harmful for the gaseous detector operated at high rate.

Data presented here has been obtained analyzing the gas composition and possible pollutants using a Gas Chromatograph[1] (GC) and two associated detectors: a Mass Spectrometer[2] (MS) and an Electron Capture Device[3] (ECD). The GC is simply an oven with a capillary column capable of separating gas substances depending on their interaction properties with the column. A signal appears for each separated compound at some retention time, defined by the column and temperature profile. In the MS detector a 70 eV electron source ionizes and fragments molecules. A quadrupole mass filter sorts the resulting ions according to their mass over charge (M/Z) ratio. Signal appears as ion abundance as function of retention time in the column or M/Z ratio. As a result identification of each molecular compound is possible, having detection sensitivity up to the ppm level. The ECD is the second detector connected to the GC. Its operation is based on the fact that at normal temperature and pressure some gases behave as perfect insulators. Consequently, the presence of very few charged species (electronegative molecules such as halogens and halocarbons –freons-) can be readily observed by amplification in an electric field. There is no information other than signal amplitude versus retention time, and a specific calibration has to be made for each compound to attain pollutant identification. Its advantage is the extreme detection sensitivity, better than ppb.

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[1] Hewlett Packard 5890 Series II
[2] Hewlett Packard Mass Selective Device 5971 A
[3] Hewlett Packard G1223 A

3.2. Gas analysis and aging test

A positive result obtained with the method described in the previous section should be considered as necessary although not sufficient for a material to be used for assembling a detector. The definite test should consist of an aging test. Comparable from a qualitative point of view is the answer obtained monitoring the gas gain of a clean, validated gaseous detector, which is connected downstream the outgassing box where the material under test is introduced, and strongly irradiated. This test allows correlating the presence of impurities in the gas with aging effects in the detector. In this case the response is more extensive than the simple gas analysis, but unfortunately the irradiation conditions (high dose rates) makes it difficult to extrapolate the results to the final running conditions and lifetime scale of the experiments. Thus existing data obtained either from systematic outgassing studies or experience gained with detectors has only a pre-selective character when designing new detectors.

3.3. TML and CVCM tests

A quick method to search for low outgassing materials was developed by NASA in the early 60s. The method consists of testing micro-quantities by condensing the volatile products to determine the amount of volatile condensable materials. This method gives a much faster answer than the detailed analysis of gas samples, where specific quantitative and qualitative calibrations have to be done to determine each detected pollutant and its concentration. In the so-called TML and CVCM tests a number of samples can be tested at one time. Each sample is placed into an aluminium foil boat. Following a 24-hour pre-conditioning at 25 °C, 50% relative humidity and standard atmospheric pressure to ensure that the samples receive common preliminary treatment, the individual samples are weighed. The samples are then loaded into individual compartments in a solid copper bar that can be heated. A cover, requiring that all volatile materials escape only through a small diameter exit port, closes each compartment. The sample is heated to 125° C by conduction and radiation for 24 hours. This causes the volatile materials to be driven off. A significant portion of the escaping volatiles collects on a disk if the condensation temperature is 25° C or above. The mass loss of the sample is determined from the weights before and after the 125° C exposure, and the percentage loss is calculated to provide the Total Mass Loss (TML). In a similar manner, the difference between the weight of a clean collector and of the collector having condensed materials will provide the mass of condensables. This mass of condensables is calculated as a percentage of the starting mass of the sample, and stated as CVCM. Materials having TML and CVCM equal to or lower than 1.0% and 0.1% respectively are considered as low outgassing.

The outcome of such test is limited, as the resulting information does not identify pollutants, even it does not indicate their nature. However the existing list of low outgassing materials catalogued with this method is enormous and its outcome compatible with the more exhaustive tests carried out by irradiating counters. The accessible NASA database [8] contains more than 1600 entries for adhesives, 500 entries for rubbers and elastomers, 800

entries for potting compounds, etc. It can help pre-selecting assembly materials before doing more time-consuming tests.

4. Outgassing rate of some assembly materials

4.1. Room temperature curing epoxy compounds

Epoxy compounds that polymerize at room temperature are very attractive because they permit to assemble detectors having materials with very different expansion coefficients. Table 1 shows the list of epoxy compounds curing at room temperature and labelled as low outgassing.

Epoxy	Outgas	Effect in Detector	Used by
STYCAST 1266 (A+B)	NO	NO	CERN/GDD
STYCAST 1266 (A+Catalyst 9)	NO	NO	HERA-B/OTR
HEXCEL EPO 93L	NO	NO	Out of production
ECCOBOND 285	NO	NO	HERA-B/ITR
ARALDITE AW103 (Hardener HY 991)	NO	NO	CERN/GDD ATLAS/TRT
TRABOND 2115	NO	NO	ATLAS/TRT

Table 1 Low outgassing epoxy compounds curing at room temperature. Both gas analysis and aging test have been carried out to characterize these glues.

As for subsequent tables, it is shown if any outgassing has been detected with the analysis station described in Section 3.1, and the effect of the outgassed pollutants, if any, in the monitored gain of a strongly irradiated gaseous detector. For materials considered as low outgassing the gas analysis should not reveal the presence of pollutants in the gas; the gas gain of the irradiated counter stays constant (measured with about 1% accuracy) up to accumulated doses above 0.5 C/cm of wire. The TML and CVCM values classify all the tested epoxies as low outgassing except Stycast 1266 and Araldite 103. However, these two-epoxy compounds have been thoroughly tested and validated irradiating counters. All components shown in the table are presently employed by different experiments. Stycast 1266 (parts A and B) has been widely used to assemble MSGCs. It has good moisture resistance, electrical properties and good adhesion to metal, glass and plastics. Yet its long curing time (>16 hours) forced the

Outer Gaseous Tracker of the Hera-B experiment [9] to try a new hardener suggested by the producer: catalyst 9 mixed with Stycast part A. The new combination decreases the curing time by a factor 3 while keeping excellent outgassing properties. The inner tracker of Hera-B, a set of hundred detectors based on the MSGC and GEM technology [10] makes use of Eccobond 285 in the assembly steps where room temperature curing is mandatory. Araldite AW 103 mixed with HY 991 hardener is presently used as sealing glue for the straws of the Transition Radiation Tracker (TRT) of ATLAS [11] and for construction of the triple-GEM stations of the COMPASS experiment [12]. Tra-Bond 2115 is used in specific parts of the TRT assembly, where its excellent capillary effect helps the construction procedure.

Source	Epoxy	Outgas	Effect in Detector
CERN/GDD ATLAS/TRT	**ARALDITE AW 106** **Hardener HV 935 U**	YES	YES
CERN/GDD	**DURALCO 4525**	YES	YES
CERN/GDD	**DURALCO 4461**	YES	YES
CERN/GDD	**HEXCEL A40**	YES	-
CERN/GDD	**TECHNICOLL 8862** **Hardener 8263**	YES	-
CERN/GDD	**NORLAND NEA 155**	YES	-
CERN/GDD	**EPOTEK E905**	YES	-
CERN/GDD	**NORLAND NEA 123**	YES	-

Table 2 List of epoxy compounds curing at room temperature for which the GC detects some pollutants at the ppm level. For some epoxy compounds, an aging test of a validated gaseous detector has been carried out. Permanent gas gain variations have been detected.

Table 2 lists the low temperature curing epoxy compounds for which the gas analysis station detects some pollutants at the ppm level. For some of them an aging test of a validated detector has been additionally carried out [13]. In such cases, permanent gas gain variations have been detected. A sample case is Araldite AW106 (and hardener HV 935 U). This epoxy, cured at room or higher temperatures, has been commonly used for gaseous detector assembly due to the excellent mechanical, electrical and radiation resistance properties. Aging tests and several gas analyses have been performed to ascertain its possible effect on aging. During the aging test the gas gain of the irradiated counter, connected downstream the box containing the sample, decreases when the Araldite AW106 is heated up to speed up the rate of pollutants outgassing (Fig. 4). Removing the sample from the gas stream slightly recovers the gain but it never reaches the original value. The counter response remains degraded even after flowing

clean gas for several days, indicating a permanent damage. Fig 5 shows the M/Z spectrum of the analyzed gas flowing out of the heated box containing the Araldite 106 [14]. The outgassing is present at low temperatures but increases significantly if the sample is heated. Pollutants such as butane, hexane, trimethyl pentane and trimethyl butane are detected and identified with the MS detector. The values for TML and CVCM are 3.26% and 0.02% respectively [15], classifying this epoxy as non-low outgassing according to NASA standards.

4.2. High temperature curing epoxy compounds

Some epoxies curing at temperatures above 50 ^{o}C have been tested and they are listed in Table 3. For some epoxies it is possible to find that detection of outgassed compounds does not imply a bad effect in the response of an irradiated counter. This for instance the case of Epotecny E505. This epoxy has been extensively used in the construction of MSGCs, which

Source	Epoxy	Curing T (^{o}C)	Outgas	Effect in detector	Global result
CERN/GDD	EPOTECNY E505 SIT	50	YES	NO	OK
HERA-B/ITR	EPOTEK H72	65	YES*	NO	OK*
CERN/GDD	AMICON 125	85	NO	-	OK
CERN/GDD	POLYIMIDE DUPONT 2545	65	NO	-	OK
ATLAS/TRT	RUTAPOX L20	60	NO	-	OK
CERN/GDD	ARALDITE AW 106	70	YES		BAD
CERN/GDD	LOCTITE 330		YES	YES	BAD
CERN/GDD	EPOTECNY 503	65	YES (Silicone)		BAD
CERN/GDD	NORLAND UVS 91	50	YES	-	BAD

Table 3 List of investigated epoxy compounds curing at temperatures above 50 ^{o}C.
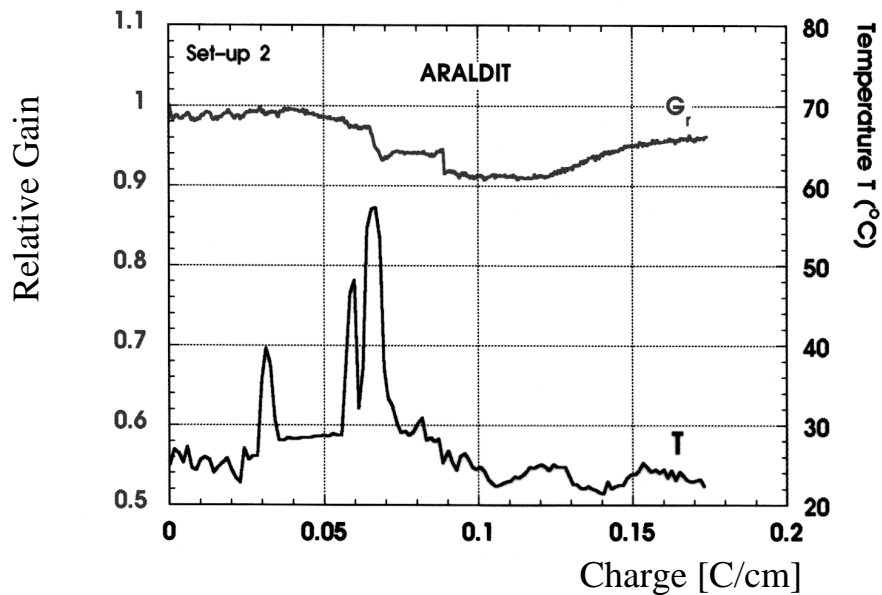
Figure 4 Normalized gas gain as a function of accumulated charge when the operating gas, Ar-DME (90-10), is in contact with Araldite 106 (and hardener HV 935 U) samples. The temperature of the sample along the test is also shown.
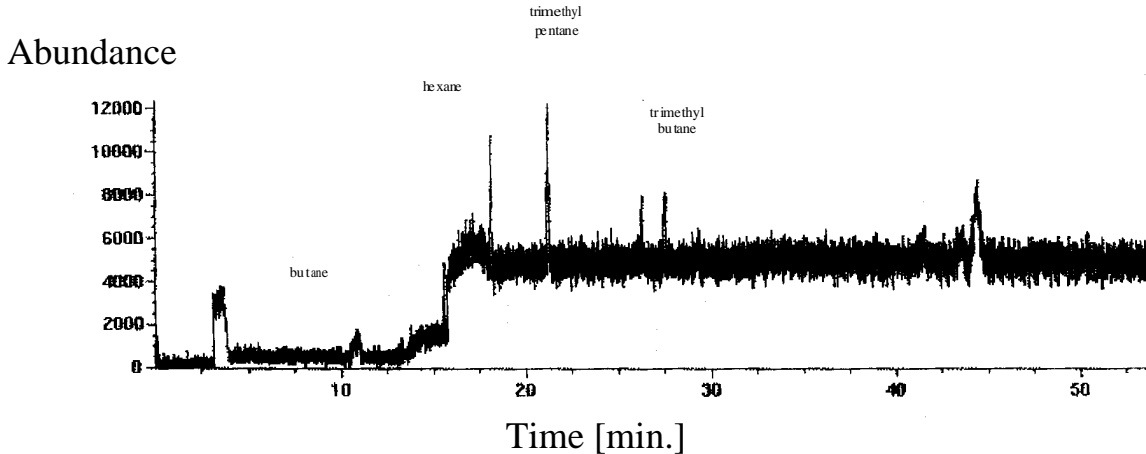

Figure 5 M/Z spectrum of the gas analyzed as it comes out of the box containing the Araldite 106 sample heated up to 60 °C. Several compounds are detected being their quantity some tenths of ppm.

have successfully followed numerous, successful, long-term aging tests. Epotek H72, used for the assembly of MSGC+GEM detectors presently running in Hera-B, slightly pollutes the operating gas in the firsts hours of contact with it. Though the irradiated counter shows very stable behaviour under irradiation, indicating that the detected pollutant might be volatile and it is easily removed from the system thanks to the gas flow.

4.3. Other adhesives

Table 4 shows the conductive epoxies that have been tested. All of them have not induced detectable gas pollution. During aging tests performed with the final detectors no aging effect could be correlated with the use of these conductive epoxies. Table 5 shows the outgassing rate of adhesive tapes.

Some sealing materials might contaminate the interior of an otherwise clean and contamination-free detector. Table 6 lists the results observed when testing some sealants for detectors and gas systems. Varian Torr seal is often used as leak sealer in ultra high vacuum applications due to the known low outgassing rate. Even if some outgassing is detected one should note that this components are usually employed in very small quantities to fix small gas leaks. This would explain why for instance the pollution outgassed from DOW CORNING R4-3117 RTV does not affect the response of the irradiated detector where few leaks have been potted with few milligrams of this sealant [16]. Besides, as we shall see in section 4.6, silicone-containing compounds should be generally avoided for the construction of high rate gaseous detectors.

Source	Epoxy	Outgas	Effect in Detector	Global Result
CERN/GDD	**TRADUCT 2922**	NO		OK
HERA-B/OTR	**SILBER LEITKLEBER 3025 (A+B)**	NO	NO	OK
ATLAS/TRT	**TRABOND 2902**	NO	NO	OK

Table 4. Outgassing tests of conductive epoxies.

Source	Name	Outgas
HERA-B/OTR	**SCOTCH 467 MP**	YES
HERA-B/OTR	**TESAFIX 4388**	YES

Table 5 Gas analyses of adhesive tapes.

Source	Material	Type	Outgas	Effect in Detector	Global Result
CERN/GDD	**VARIAN Torr-Seal**	Solvent-free epoxy resin	NO	NO	**OK**
CERN/GDD	**RHODORSIL CAF4**	Caoutchouc Silicone RTV	NO	NO in very small quantities	**OK ?**
CERN/GDD	**DOW CORNING R4-3117 RTV**	Silicone based	YES	NO in very small quantities	**OK ?**
HERA-B/OTR	**LOCTITE 5220**	Polyurethane-based	YES	-	**BAD**

Table 6 Outgassing tests carried out for some sealants used for fixing small gas leaks in chambers and gas systems.

Source	Material	Type	Outgas	Effect in Detector	Global Result
CERN/GDD	**STESALIT 4411W**	Fibreglass	YES	NO	**OK**
CERN/GDD	**VECTRA 150**	Liquid Crystal Polymer	YES	NO	**OK**
CERN/GDD	**PEEK Crystalline**	Polyeteherether ketone	NO	NO	**OK**
ATLAS/TRT	**ULTEM**	Polyetherimide	NO	-	**OK**
ATLAS/TRT	**C-Fiber**	C-fibre	NO	-	**OK**
ATLAS/TRT	**POLYCARBONATE**	C-fibre	NO	-	**OK**
HERA-B/ITR	**FIBROLUX G10**	Fibreglass	YES	-	**BAD**
HERA-B/ITR	**HGW 2372 EP-GF**	Fibreglass	YES	YES	**BAD**
CERN/GDD	**RYTON**	Polysulphur phenylene	YES	YES	**BAD**
CERN/GDD	**PEEK Amorphous**	Polyetherether ketone	YES	-	**BAD**

Table 7 Rigid materials tested for outgassing.

4.4. Rigid assembly materials

The selection of rigid materials for use in detector assembly is a very important part of the design. Not only must the material be capable of being fabricated into required components but it must stand up to the environmental conditions. For high rate detectors, low pollutant outgassing should be considered as one of the deciding factors. Table 7 lists the rigid materials that have been tested. Gas pollution to the ppm level is detected for standard fibreglass materials. A replacement candidate is Stesalit 4411W (epoxy without filler glass fibre mat). It has good machining, excellent mechanical and electrical properties and proved low outgassing properties [13]. Rigid materials such as ULTEM, Polycarbonate, VECTRA and Ryton have the advantage that can be moulded into assembly pieces. Ryton has shown large rate of gas pollution accompanied by a dramatic effect on the gas gain of an irradiated counter [13]. VECTRA is a low outgassing plastic of smetic (or liquid crystal) structure with interesting properties [14]; for example, two Vectra pieces can be welded with a heating plate providing after polymerisation homogenous leek proof connections. PEEK is a new high performance thermoplastic with excellent radiation resistance, resilient to most chemicals and relatively inexpensive. Amorphous PEEK (type Victrex) shows some degree of outgassing as well as mechanical changes and discoloration if tested with DME. However, if the material is thermally annealed to produce crystalline PEEK, this plastic seems to be an excellent choice.
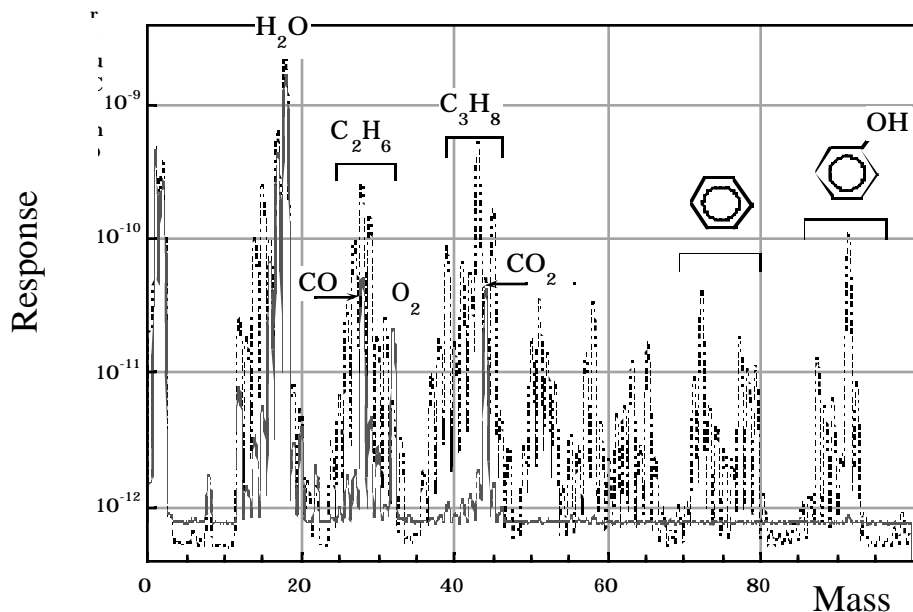

Figure 6 Response of an ion analyzer for two samples of Nuvovern LW, a two-component Polyurethane [15]. The sample showing heavy outgassing has been processed using the component hardener few days after the recommended expiration date.

One should take into account that high-temperature and pressure-moulded plastics are not free of surface contaminating materials. If they are not moulded with exactly the right process

conditions some outgassing can be expected. This can occur even if the mechanical properties meet specification requirements. Other source is the mould release agent. Many of then are silicone-based.

4.5. Accidental contamination

A source of contamination usually underestimated turns up from the incorrect processing of materials by incorrect weighing, mixing or use of an insufficient or incorrect cure cycle. Fig. 6 [15] shows the response of an ion analyzer for two samples of Nuvovern LW, a two-component Polyurethane. Both samples have been processed under identical conditions; for one of them the hardener was used few days after the recommended expiration date. The spectrum shows for both samples outgassed volatile components such as oxygen, water, CO and CO_2, probably adsorbed by the polyurethane during the mixing process. The sample improperly processed shows in addition some hydrocarbons of high molecular weight and heavy aromatic components typical of components that have not properly cured.

An adhesive will outgas more while it is being cured than after it is cured. Glue curing under clean gas flow will help removing reaction products released during room temperature.

4.6. Silicon contamination

Silicone has been systematically found coating aged chambers, although in many cases the origin of the pollutant has not been clearly identified. Probably the pollutant was part of the assembly materials or components in the gas system. Possible sources are silicone rubber sealants, potting and encapsulation compounds, silicone adhesives, silicone vacuum grease used to lubricate O-rings, mould-release agents, polluted gas cylinders, detergent residues (sodium metasilicate), glass and related products such as glass fibres used for reinforcing resins, silicone oil commonly used in bubblers and diffusion pumps. Fig. 7 shows the unambiguous effect of a silicone bubbler placed downstream an irradiated MSGC, as compared to the response of the same detector connected to a long, clean exhaust line.
Silicone can polymerize both with hydrocarbons and oxygen to form rather heavy polymers, thus not easily removable by the gas flow. It should be taken into account that silicone has a high natural affinity for most materials and the tendency to migrate. It is relatively inert chemically and unaffected by most solvents, therefore among the most difficult surface contaminants to remove. It has recently been found that silicone can be etched away by F-species created in the gas avalanche [17] and spread out in the system, thus triggering polymerization processes.

5. Detector assembly procedures

Contaminates during assembly can make the best-designed detector to fail. As a general rule, the assembly area must be isolated from other manufacturing areas, and usually
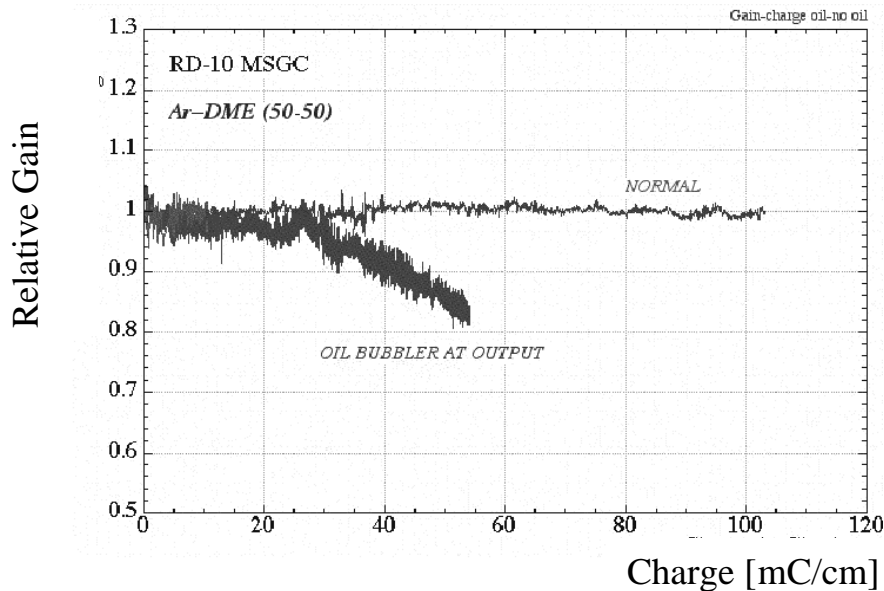
Figure 7 Lifetime of a MSGC irradiated in a clean gas system in Ar-DME (90-10) and the unambiguous effect
of a silicon bubbler placed downstream the counter.

following clean room standards. Some equipment should be avoided or protected. Examples of contamination are tools with lubricated shafts, soldering or brazing equipment that requires heating of volatile fluxes, motors and vacuum pipes with outgassing oils. Another important source of contamination is the personnel. The people in the production should know the reason why something must be done in a certain manner, hence careful and exhaustive training is needed. Examples of contamination are street clothing; hair, make-up, fingernail and fingerprints are source of oil and particulates and many creams and cosmetics contain silicones. Proper education will greatly decrease problems in the manufacturing.

The assembly process has to be well specified and stable. It should be rechecked periodically and only include proved improvements result of a careful observation of the process. A good assembly process includes procedures about cleanliness of assembly components and its verification. Tracing capability is also an important feature, especially when building very large systems.

6. Gas system components

Components used to build gas systems have to be selected with care to avoid unexpected pollution of an initially clean gas mixture. The components choice should include the selection of materials which are low outgassing and chemically compatible with the gas mixture. These

principles should be used to assemble, not only the final gas mixer, but also any system supplying gas during the assembly process and testing of detectors in the laboratory.
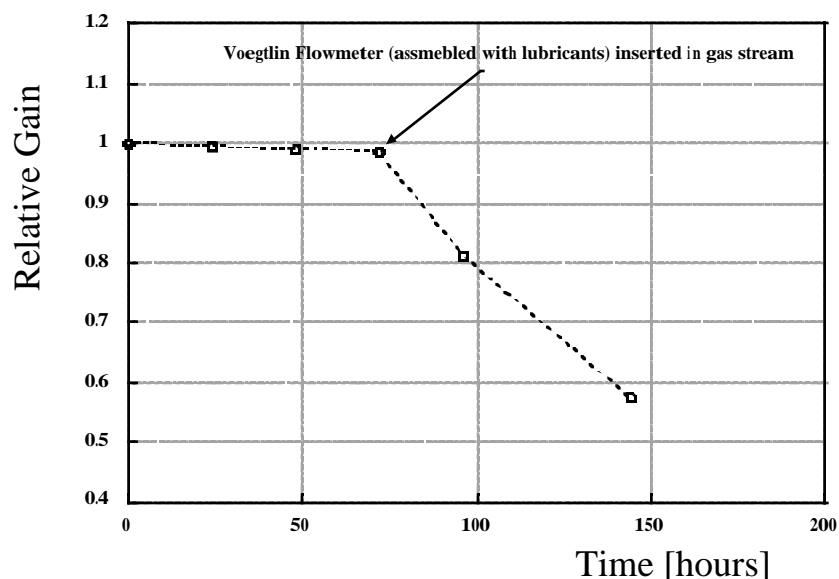

Figure 8 Effect of pollutants released by a standard flowmeter assembled with lubricated joints and needle valve on the gain of a ATLAS/TRT straw tube.

Fig. 8 shows the response of an irradiated ATLAS/TRT straw tube operated in a clean gas system supplying Ar-CF_4-CO_2 [63-10-27]. When a standard flowmeter, constructed with a lubricated valve and few greasy Viton O-rings, is inserted in the gas stream after about 70 hours of continuous irradiation the gain of the straw falls very fast due to immediate polymerization processes triggered by released pollutants. A procedure to clean the flowmeter [18] consists of disassembling and cleaning all parts in a series of ultrasonic baths[4] of isopropyl alcohol, followed by a clean distilled water bath. A new alcohol volume is used for each bath. The parts are then heated to 70 ^{o}C before the flowmeter is remounted. Fig. 9 shows the normalized gas gain of three straws irradiated under the same conditions as shown in Fig. 8, but with the cleaned flowmeter in the gas system. This practice should be used if any doubt would exist about the cleanliness of other parts of the system, such as pipe connectors. Other complex components, such as valves and cylinder pressure regulators are also potential polluting sources. Components used for ultra high purity applications are usually assembled

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[4] The ultrasonic bath should be performed following some basic rules: the components to clean are placed in a small volume of solvent in a beaker made out of glass or stainless steel, with a flat bottom. The beaker is suspended in water, that acts as a sonic coupling medium. Fluid levels in the tank and container should be more or less matched, and the volume of parts to be cleaned should be limited to less than about 25% of the fluid volume. For complex parts, several changes of orientation may be required for careful cleaning. Cleaned items should be removed from solutions while the unit is still operating, to provide a thorough rinsing action.

following strict cleanliness requirements. However, still a careful selection of joints has to be made in term of gas compatibility and outgassing. Table 8 shows the results of some tests carried out for some commonly used O-rings. Viton, one of the most common materials, has shown some outgassing at the ppm level. Though it has been satisfactorily used in very clean gas systems.

Material	Type	Outgas	Effect in Detector	Global Result
KALREZ	Fluoropolymer	NO	NO	OK
VITON	Fluorinated copolymer	YES	YES	BAD
EPDM	Copolymer ethylene propylene	YES	-	BAD
PVDF	Fluorinated polyvinyldene	YES	-	BAD

Table 8 Results of tests carried out for some commonly used O-rings.

Material	Type	Outgas	Effect in Detector	Global Result
PP	Polypropylene	NO	NO	OK
RILSAN NYLON	Polyamide	Water	NO	OK*
PEEK Crystalline	Polyetherether ketone	NO	NO	OK
PEEK Amorphous	Polyetherether ketone	YES	-	BAD
PEE		YES	-	BAD
PUR	Polyurethane	YES	-	BAD

Table 9 Outgassing properties of some plastic piping.

Plastic piping is often used because of its insulating properties, elasticity, low density and price as compared with the reliable, electropolished, stainless steel pipes. In order to obtain the desired physical characteristics, these complex materials are frequently modified chemically or with additives. As a result, they are often made more susceptible to outgassing. Table 9 shows the list of some plastic pipes that have been tested. Generally plastics should be kept to

a minimum due to their high gas permeability. At test laboratories, nylon piping can be used for instance as a clean and simple way of adding small concentration of water to the gas mixture, due to the natural outgassing of water from or diffusion through the tube walls.
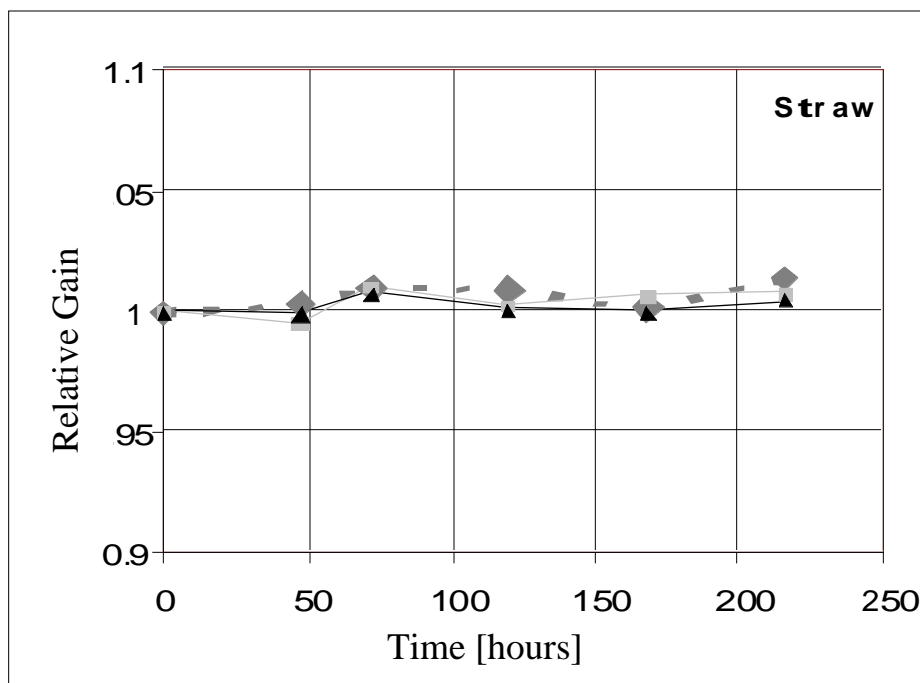

Figure 9 Response of three ATLAS/TRT straw tubes irradiated in a validated clean gas system, which is modified to insert a Voegtlin flowmeter after it has been disassembled and thoroughly cleaned in a series of ultrasonic baths to remove lubricants.

A major problem when selecting clean gas components is the difficulty to find complete specifications and product descriptions; usually they do not contain enough information. Even more, once an adequate product has been found and successfully tested following a strict validation process that includes long-term aging tests of counters, it is difficult to trust the cleanliness conditions for larger quantities. The golden rule to obtain a reliable gas system seems to be the definition of the cleanliness requirements by understanding precisely the effect of particular pollutants in the detector, to avoid pollution during the assembly process, and to flush gas through the open system as much and as soon as possible to clean up possible pollutants.

7. Some factors affecting aging rate in some gases

The operational parameters of gaseous detectors such as gas gain, discharge probability, signal characteristics and others have been optimized for different gas mixtures. Nowadays there is still some controversy about the choice of the optimal gas mixture, first because the

selection depends on the particular experiment, and second, for high rate experiments the aging of the detector has to be kept to a minimum. Few gases have proved to be stable under such harsh conditions. We shall see the factors that might degrade the detector response for few of the commonly used gases.

7.1. Hydrocarbon mixtures

The use of hydrocarbons as quenching gas in proportional counters has been a rather popular choice because it gives an excellent energy resolution and small variations in gain. These advantages counteract its known tendency to polymerize [19, 20] and the fact that it has been often found that this gas does not provide very long lifetimes. However, as aging of gaseous detectors depends on a large number of parameters, several tests with Ar-CH$_4$ 90-10 have been done varying material of the electrodes of the counter, gas purity and radiation
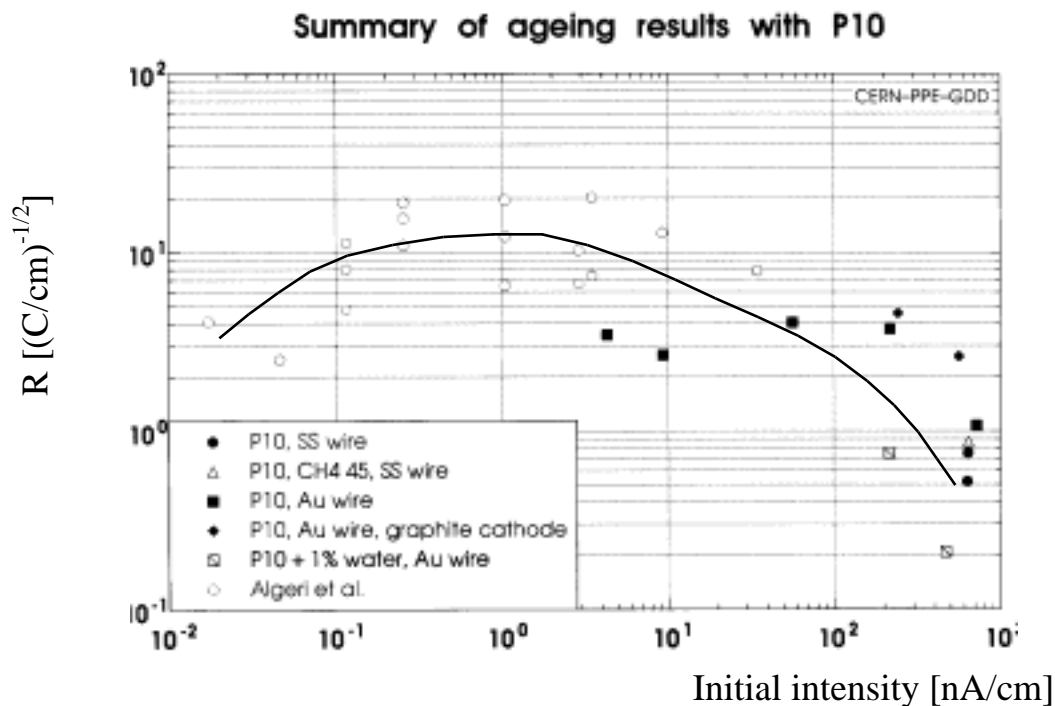

Figure 10 Aging rate characterized by the R' value in (C/cm)$^{-1/2}$ against the initial current in nA/cm of wire drawn. All counters have operated in P10 varying some conditions.

dose, in order to discern which parameters play an important role in the aging process [21]. This study serves as a sample case as probably the observations apply to any hydrocarbon-based mixture. Fig. 10 shows, for the totality of tests with this mixture, the level of aging

characterized by the R' value in $(C/cm)^{-1/2}$ [9], against the initial current in nA/cm of wire drawn in the counter, mainly defined by the product of gain by particle rate. R' is defined as

$$G_r = a \ e^{(-R' \sqrt{Q})}$$

being G_r the gas gain relative to the initial one and Q the accumulated charge expressed in C/cm. The R' value does not depend on the particular dose accumulated in the aging run.

Several conclusions might be extracted from Fig. 10:

- Independently of the materials of the electrodes and, more importantly, of the purity of methane, the rate of aging for P10 does not vary considerably for a given set of initial conditions. This would suggest that the methane itself polymerizes in the avalanche plasma and produces deposit layers on the wire surface.
- The rate of aging normalized per unit of charge and length is not constant, but depends on the charge collection rate during the aging test. In plasma chemistry is known that radiation-induced polymerization is a function of the square root of the dose [1]. At large irradiation rates, the density of ions and radicals will be lower due to space-charge effects. This weakens the field and the avalanche extends over larger regions; the rate of polymerization would decrease, and in turn, so would the concentration of deposits on the wire. This tendency permits to suppose that in real experiments, where the irradiation conditions are not as drastic as in the laboratory tests, a faster aging rate can be expected.
- The rate of aging improves if water (at % level) is added. This is in accordance with the generally accepted idea that oxygen containing molecules, among others, prevent to some extent the polymer chains growing. It might also be that water gives some electrical conductivity to thin insulating films deposited on the wires. However for these tests, the improvement is still limited to consider this mixture as an operative gas in high luminosity experiments.

7.2. Dimethyl ether

Dimethyl ether appeared in the 1986 Aging Workshop as a reliable quencher for gaseous detectors operated at high rates. Since then, many groups have study the aging behaviour of DME-based mixtures. Fig. 11 [21] compares the lifetime of identical irradiated counters under Ar-CH$_4$ and Ar-DME in proportions 90-10. The counter in DME accumulates a large dose without major degradation of its properties. However some gain reduction is still observed in aging tests with DME. This may be probably due to a progressively larger amount of pollutants in the gas mixture as the DME cylinder is being used. Fig. 12 shows the aging rate, expressed by the R' parameter, as function of DME used in the cylinder during the tests. Certain impurities present in the liquid DME enter in the gaseous phase through a selective process called Rayleigh distillation. For the tests shown in the figure, the pollutants detected by gas chromatography when the DME cylinder has been used around 25% are freon 11 and

12 and few hydrocarbons. Their concentration stays anyhow at the ppm level. The triangle point corresponds to the addition of water to the gas mixture that seems to prevent the aging process. The solution is simple but might not be applicable to all kind of detectors; water concentration should probably be adjusted for the running conditions of each particular detector.
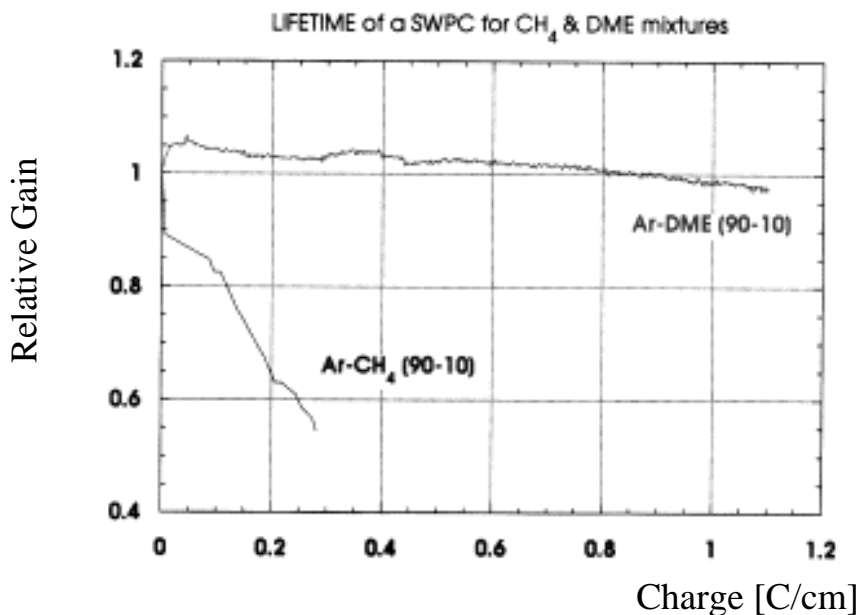

Figure 11 Comparison of the response of a clean single wire proportional counter irradiated in Ar-DME and Ar-CH$_4$.

Material	Swell (%)
LDPE (foil)	- 0.6
VECTRA	0.0
PEEK Crystalline (pipe)	+ 0.3
KALREZ (joint)	+ 1.6
PE	+ 1.8
Kel-F (joint)	+ 4.0
PCTFE (joint)	+ 4.0
PVDF (joint)	+ 5.0
Kapton (foil)	+ 5.4
PEEK (Amorphous (pipe)	+8.7

Table 10. Effect of the exposure of some conventional materials used in detectors or gas systems to 2 hours of liquid DME.

DME has proved to work for high rate detectors. Yet it has a very high sensitivity to traces of pollutants at ppb level, which are difficult to control. In addition, being a rather reactive gas, time-consuming studies have to be performed to check the resistance of DME to some common materials used in chambers. For instance, and as it is shown in Table 10, the immersion for 2 hours of conventional detector assembly materials in liquid DME shows some degradation, measured in this case as percentage of swelling. Even if a laborious laboratory work is done to find a set of adequate assembly materials, it remains to be verified if these clean conditions can be maintained in complex systems. DME has been widely replaced by CO_2, which seems to be less sensitive to small pollution and non-flammable, the cost being the increase of operating voltage and the larger energy of discharges, with all the consequences on chamber operation.
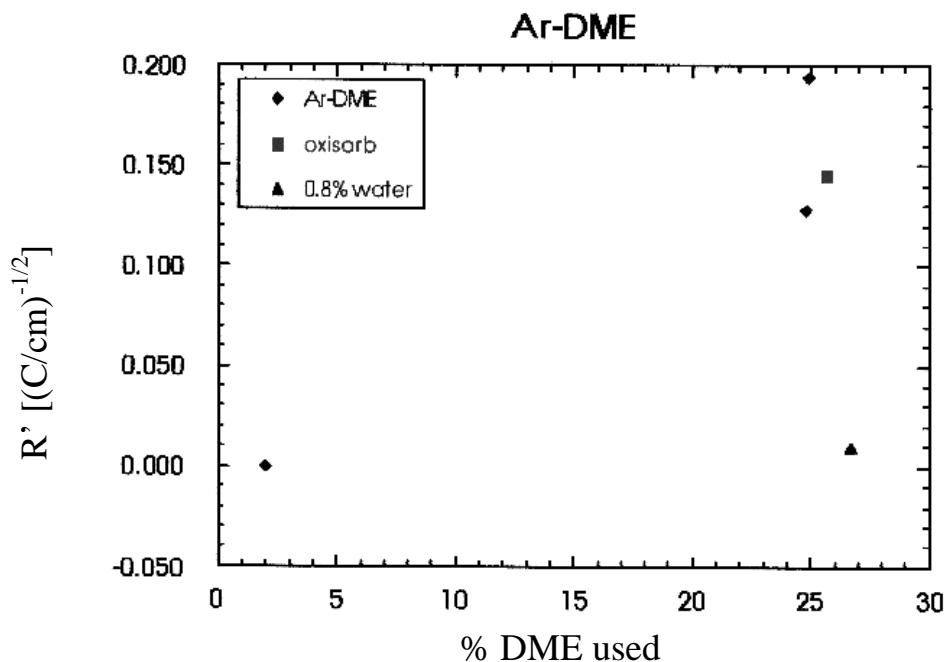

Figure 12 Aging rate for several tests carried put with Ar-DME (90-10) expressed as R' as function of the use of the DME cylinder. The triangle point corresponds to the rate of aging measured when 0.8% of water is added to the gas mixture.

7.3. CF$_4$

The use of CF_4, known as an aging preventing agent even for small concentrations in the mixture, has progressively been adopted for most gaseous detectors operated at high rates and needing high electron drift velocities. A balance between polymerization and etching processes is establish depending on the charge density (particle rate and gas gain), the relative concentration of gas components and may be the gas flow. The right balance permits to

achieve lifetimes above tenths of C/cm for the straw tubes of the ATLAS experiment [17]. It appears however that in gaseous detectors etching is the favoured process: CF4 dissociates in rather stable species, F and CF_X radicals. They have enough energy to break chemical bonds in polymers which are then reduced to stable, volatile products. These products are probably removed from electrodes by the gas flow. This belief led few years ago to think that using CF_4-based mixtures would allow the requirements for cleanliness in experiments to be relaxed. Presently, it has been shown that these mixtures are still sensible to pollutants, as the balance between deposition-polymerization greatly depends on the species that are added to the CF_4. Detailed studies have been performed to find wires resisting etching in CF_4 mixtures. It has been found [22] that non-golden wires react with fluorine radicals produced in the avalanche to form metal fluorides, which may promote further deposition. Gold wires are essentially inert and have therefore good aging properties. However, strong etching effects have been observed in presence of water quantities above 0.1%. The magnitude of the etching destruction depends too on the wire production technology and gold thickness [17].
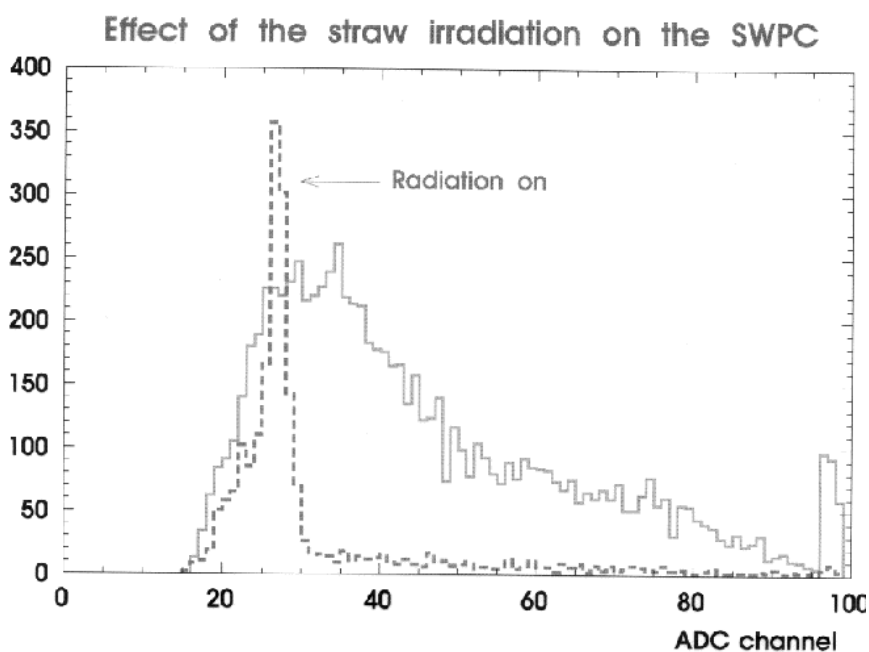

Figure 13 Pulse height measured in a single wire proportional counter (3 cm drift distance), which is gently
irradiated but connected downstream a small diameter straw tube in Xe-CF_4-CO_2 (50-30-20). When
the straw tube is strongly irradiated the large energy pulses (continuous line) are suppressed due to
the effect of electronegative species created in the avalanche.

Fig. 13 shows the pulse height measured in a single wire proportional counter, which is gently irradiated but connected downstream a 4 mm diameter straw tube flushed with Xe-CF_4-CO_2 (50-30-20). When the straw tube is strongly irradiated, the wire counter pulse height is dramatically modified. Pulses with larger amplitude are suppressed suggesting that the gas composition is modified by some relatively stable species created in the avalanche. Some

neutral but electronegative radicals reach the counter, with a drift distance between electrodes (around 30 times bigger tan in the straw) large enough to capture electrons. This dramatic effect would put under question if this gas, despite the excellent results in terms of aging, might be used for detectors operating over the long-term. Many non-metallic components of the gas system and assembly materials could be affected.

It has been also pointed out [23] that F-compounds are able to react with silicone compounds. It was suggested that CF_4 could be use to clean up traces of silicone in large systems. Presently, it is observed that this effect might be a real danger for large systems, because the silicone compounds are effectively removed but distributed ubiquitously polluting the detector and promoting heavy polymerization.

8. Conclusions and summary

The present knowledge about aging of gaseous detectors does not allow formulating a set of definite guidelines to avoid degradation of detectors under large radiation loads. Experience from experiments or laboratory, where conditions are better controlled, allow nevertheless to set some general principles that might help if not to prevent, to minimize aging effects. Such a multi-parameter process can only be understood after an efficient R&D phase has defined a set of working conditions, which are particular to each type of detector and its conditions of use. Among the parameters to identify, the following should be clearly understood: selection of the gas mixture, gas gain and gas purity, which implies a careful selection of gas system components, assembly materials and procedures. The long-term capability can then be evaluated and extrapolated to real conditions if final prototypes are tested under conditions as close as possible to the final ones, and strictly controlled. Among these parameters, it seems mandatory to irradiate large areas with a charge density as close as possible to the one expected in the final experiment. Space charge effects and discharges should be avoided as they hide or increase respectively polymerization processes.

Summarized in tables we present the outgassing results for several materials that can be used to assemble gaseous detectors and gas systems. A list of low outgassing assembly materials exists, that includes epoxy compounds, rigid materials, sealants, elastomers, etc. The effect of materials that outgas at the ppm level has to be tested for each particular case. That is the case for materials such us Viton, Teflon, Polyurethane, etc. In general, there is no good or bad material. A material is adequate or not for a very particular type of detector and conditions of use. Existing data, obtained either from systematic outgassing studies or experience gained with detectors, has only a pre-selective character that can help designing a detector before carrying out more time-consuming tests. Once the material selection appears to be adequate, the ultimate validation consists of irradiating the detector assembled with the chosen materials. It seems on the other hand rather universal that silicone compounds that easily migrate (lubricant-type) should be meticulously avoided, especially with some gas mixtures. One should note that the sources of silicone contamination are enormous and sometimes intricate to find.

Mixtures of noble gas and hydrocarbon are not trustable for long-term high rate experiments. Hydrocarbons tend to polymerize by themselves. It is only a question of time when polymers will deposit on the electrodes with enough thickness to disturb detection efficiency. It is accepted that oxygen-containing additives can improve detector lifetime in such mixtures. DME (CH_3-O-CH_3) has proven to give long lifetimes. However, a careful material selection for detector assembly and gas system components is required due to the high reactivity of this gas. Halogen contamination at ppb level shortens detector lifetime under DME. Such low pollution levels are difficult to monitor and to keep under control. CO_2 seems to be the conventional replacement as an easy-to-use mixture. CF_4-containing mixtures are very attractive in terms of aging due to the fine polymerization-deposition balance phenomena. It is expected that radical and ions issued from the avalanche process are chemically reactive, competing with any polymerization process promoted by pollutants in the gas. The competition between these two processes might slow down conventional aging effects. Unfortunately contradictory effects have been observed with CF_4 mixtures. Being a promising radiation hard mixture, detailed studies are necessary to set the conditions under which a particular detector might satisfactorily work. They need strict control of pollutants (specially water and may be oxygen) to avoid shifting the fine etching-deposition balance. F-radicals are rather active. They clean up aged wires, but also are they able to attack some materials used in the assembly. They are capable, for instance, of etching away Si-compounds that may promote strong polymerization processes. Supporting this idea, semiconductor industry uses CF_4 to etch silicone and silicon-oxide substrates. Chemical processes involved in this type of gas mixtures are very complex, and probably highly sensitive to minor impurities. This means that all possible precautions should be taken when designing detectors and associated gas systems.

Acknowledgments

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