Plasma Chemistry in Wire Chambers

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(M.S. Thesis)

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May, 1990

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This work was supported by the Director, Office of Energy Research, Office of High Energy and Nuclear Physics, Division of High Energy Physics of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Abstract

The phenomenology of wire chamber aging is discussed and fundamentals of proportional counters are presented. Free-radical polymerization and plasma polymerization are discussed. The chemistry of wire aging is reviewed. Similarities between wire chamber plasmas (>1 atm dc-discharge) and low-pressure rf-discharge plasmas, which have been more widely studied, are suggested.

Construction and use of a system to allow study of the plasma reactions occurring in wire chambers is reported. A proportional tube irradiated by an ^{55}Fe source is used as a model wire chamber. Condensable species in the proportional tube effluent are concentrated in a cryotrap and analyzed by gas chromatography/mass spectrometry.

Several different wire chamber gases (methane, argon/methane, ethane, argon/ethane, propane, argon/isobutane) are tested and their reaction products qualitatively identified. For all gases tested except those containing methane, use of hygroscopic filters to remove trace water and oxygen contaminants from the gas resulted in an increase in the average molecular weight of the products, consistent

with results from low-pressure rf-discharge plasmas. It is suggested that because water and oxygen inhibit polymer growth in the gas phase that they may also reduce polymer deposition in proportional tubes and therefore retard wire aging processes. Mechanistic implications of the plasma reactions of hydrocarbons with oxygen are suggested. Unresolved issues in this work and proposals for further study are discussed.

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Acknowledgements

Of the many people who contributed to this project, three were central to the formation of this thesis. It has been a privilege to work with John Kadyk on a day-to-day basis; he has provided me with an outstanding first-hand scientific education. I am greatly indebted to my advisers Dennis Hess and Michael Williams for their guidance, keen insights and unwavering enthusiasm.

I gratefully acknowledge Bernard Sadoulet for his interest in this work.

It is a pleasure to thank Doug Shigley for his superb management of the many mechanical needs of this project; it could not have been completed without him.

Thanks go to Ron Jones for meeting all of my often-unreasonable demands for electronic equipment. Thanks also to Walt Johansen and Jeff Hull for valuable discussions.

Finally, I lay the blame for this work with my high school science teachers Dick Gray and Phil Perry. They got me started.

1 Wire Aging

Wire chambers are commonly used in the field of high energy physics for particle detection and tracking. In modern experiments, a very large (up to 100,000 wires), and consequently very expensive, wire chamber is normally a component of the experimental detector. The specific type of wire chamber used for an experiment depends strongly on the type of data to be collected. There are numerous types of wire chambers, and modifications and innovations are being reported continually. The theory of operation of wire chambers is not germane to this discussion, and the interested reader is referred elsewhere [1,2].

Wire chambers are radiation detectors, and so, by their nature, operate in a radiation environment. It has been repeatedly observed, however, that in the course of their normal operation, exposure to radiation results in performance degradation. There are several manifestations of this degradation; these mechanisms are collectively referred to as "aging." Aging is a matter of serious concern since it often limits the useful lifetime of a wire chamber to less than that needed for the experiment.

1.1 Background

Since the realization of the existence of wire aging problems, there have been attempts to mitigate the effects. The goal of most early studies, however, was to determine suitable operating conditions rather than to understand the exact causes of aging. Consequently, the accumulated lore of aging developed into a "cookbook" of remedies that were observed to be effective in certain instances.

Wire aging is, unfortunately, affected by a large number of variables including electrode voltages, gas pressure, gas flowrate, gas composition, radiation dose rate, and chamber geometry. Gas composition is perhaps the most difficult of these to control, because it depends on the nominal purity of the gas, previous contents of gas cylinders, plumbing and other materials of construction, possible reactions with chamber materials, air leaks, oil bubblers, etc. In view of the large number of variables, it is not surprising, therefore, that there was a certain reluctance to publish results, due to the realization that in any particular circumstance it could not easily be ascertained that the culpable variable had actually been identified and controlled. Much of the aging lore remained anecdotal and was discussed among workers in the field.

The Workshop on Radiation Damage to Wire Chambers [3] was perhaps the beginning of a concerted effort to agglomerate aging results and remedies and to think about the underlying chemistry of the problem. Subsequently, there have

been two review articles [4,5] that summarize many aging results and suggestions for improved resistance to aging. A comprehensive history of the aging problems associated with early wire chambers was provided by Sauli [6].

1.2 Proportional Counters

When a charged particle passes through a gas, it ionizes some of the gas molecules. If the gas is in an electric field, the electrons freed by this ionization will be accelerated towards the anode wire, where, by means of an electron avalanche, they can be detected. In very simplified terms, a wire chamber is a three-dimensional array of anode and cathode wires. The ionization trail left in the gas as a particle travels through it is detected and measured so that the particle track can be reconstructed from the recorded data.

The amplification of a signal by an avalanche is called gas gain. The same avalanche mechanism is responsible for gas gain in both proportional counters and wire chambers. Indeed, a proportional counter is a single-wire wire chamber. Because wire aging is a side effect of the avalanche, it will be helpful to have a basic understanding of this process. Since the resulting chemistry should be independent of the type of device in which it occurs, it is adequate to describe here only the fundamentals of proportional counters. A comprehensive description of the physics of propor-

tional counters and many practical details regarding their construction and operation are given, e.g., by Knoll [7].

The term "proportional" refers to a regime of electric field strength and gas pressure ($\sim 10^4$ - 5×10^4 V/cm for gases at atmospheric pressure) in which the curve of pulse size vs. voltage is linear. This means that the total charge ultimately collected at the anode is proportional to the charge represented by the primary ionization. Proportional counters normally operate with gains of 10^4 - 10^5 .

1.2.1 Gas Gain

Proportional counters rely on the phenomenon of the electron avalanche to amplify the charge deposited as the primary ionization within the gas to a detectable level. Due to an applied electric field, the electrons and (positive) ions drift toward the anode and cathode, respectively. While drifting, they are accelerated by the field, and so gain energy. They also undergo many collisions with neutral gas molecules. Although the ions, due to their low mobility, do not gain much energy between collisions, the electrons, being much less massive, are easily accelerated and gain significant energy between collisions. When the field is sufficiently high (on the order of 10^4 V/cm for gases at atmospheric pressure), the electrons gain enough energy between collisions to ionize other gas molecules. The electrons released by such ionizations are also accelerated by the field, and they contribute to further ionization. As the

electrons drift closer to the anode wire, where the electric field is stronger (field strength $\sim 1/r$) and the probability of ionization higher, even more electrons are released. This process is called avalanche formation; the avalanche ends when all of the electrons have been collected at the anode. (The avalanche is sometimes referred to as a Townsend avalanche.)

Gas gain is a function of, among other things, anode voltage, anode radius, gas density, and gas composition. It is vital to be able to identify gain changes caused by fluctuations in these parameters lest they be mistakenly interpreted as aging: a model for gas gain is required.

When developing an expression for gas gain, the following simplifying assumptions are commonly made. (1) The multiplication process occurs only by electron collisions: photoelectric effects are negligible. (2) No electrons are lost by attachment processes to form negative ions. (3) There is no electron-ion recombination. (4) Space-charge effects are negligible.

Suppose that at a radius r there are $N(r)$ free electrons. The change in $N(r)$ over a path length dr is then given by

$$dN = N(r) \alpha dr, \quad (1.1)$$

where α is the linear ionization density. In the literature, α is commonly referred to as the first Townsend coefficient, which is defined as the mean number of electron-ion pairs (i.e., secondary electrons) produced by a free electron per

centimeter of path length. In general, α depends on the electron energy, and thus on the field strength and on the position in the counter (i.e., radius). Integration of equation (1.1) gives an expression for the gas gain, G :

$$\ln G = \int (dN/N) = \int \alpha(r) dr. \quad (1.2a)$$

or,

$$G = N_s/N_c \quad (1.2b)$$

The integration is over the range of radii from the critical radius, c , at which point the field is too weak to support gas gain, to the surface of the anode, a . N_c represents the number of electrons produced by the primary ionization.

The governing factor in avalanche formation is the electron energy distribution, which is largely determined by the amount of energy that an electron gains between inelastic collisions. This amount is proportional to the product of the field strength and the distance between collisions (mean free path); the mean free path is inversely proportional to the gas density. It is therefore common to introduce the term $S(r)$ as defined by

$$S(r) = E(r)/p, \quad (1.3)$$

where $E(r)$ is the field strength and p is the gas pressure. $S(r)$ is sometimes called the "reduced field."

In cylindrical geometry, the field strength is given by

$$E(r) = V_0/[r \ln(b/a)], \quad (1.4)$$

where V_0 is the voltage difference between the anode and the cathode, a is the anode radius, and b is the inner radius of

the proportional tube. Combining equations (1.3) and (1.4) gives

$$S(r) = V_0/[p r \ln(b/a)]. \quad (1.5)$$

The linear ionization density, α , is proportional to the product of the gas density (pressure) and the ionization cross-section. The ionization cross-section is a function of the electron energy distribution, which, in turn, is a function of S . It follows that α/p is a function of S . Equations (1.2a) and (1.5) can therefore be combined to give

$$\frac{\ln G}{p a S(a)} = \int_p \frac{\alpha}{S^2} dS. \quad (1.6)$$

The integral is evaluated between the value of S at the wire surface and the critical value of S , beyond which the field is too weak to support gas gain.

The functional form of the dependence of α on S is the fundamental difference between models for gas gain. Several commonly used models were summarized by Bambynek [8], who also discussed the effects of relaxing the above-noted assumptions.

1.2.2 Quenching Gases

Several processes can occur near anode wires that result in electron emission at the cathode (Table 1.1). Electrons emitted by these processes can create positive feedback that can overwhelm the real signal. To prevent this failure mode, a quenching gas is added. The quenching gas is

usually a polyatomic molecule, typically a hydrocarbon, so chosen because it has many degrees of freedom and therefore can absorb energy efficiently.

Table 1.1

Simple theory of processes occurring in the anode-cathode gap that demonstrates the need for quenching gases [9].

1. Counter gas is solely argon (Ar).

(a) $E/p < 2.5$ kV/cm-atm. Collisions of electrons with gas molecules are elastic.

(b) $E/p > 2.5$ kV/cm-atm. Collisions are inelastic.

(Ar^{**} lifetime $\sim 100 \mu\text{s}$) (Ar^* lifetime $\sim \text{ns}$)

(c) $E/p > 10$ kV/cm-atm. Collisions can be ionizing.

BAD EFFECTS:

$$(E_\gamma \approx I E_{\text{Ar}} - \phi_{\text{cathode}} \approx 15.8 - 5 \approx 11 \text{ eV})$$

2. Solution: Add quenching gas M.

(M^* relaxes without photon or electron emission)

(charge transfer collision)

A good quenching gas will relax by mechanisms other than photon or electron emission. Some of the acceptable

relaxation mechanisms are collisions, fragmentation, and distribution of energy into vibrational modes.

1.2.3 Counter Gases

Proper choice of a fill gas is imperative for proper operation of wire chambers and proportional counters. The gas amplification process is critically dependent on the migration of free electrons, and the fill gas must therefore have little propensity for electron attachment (i.e., it must not be too electronegative). An important design issue regarding sealing of the detector arises because oxygen in air is electronegative. Other restrictions on the gas concern electron diffusion (the spreading of a group of electrons in the direction of the electric field) and drift velocity. In some applications (e.g., vertex detectors), low diffusion and low drift velocities are necessary: a gas that does not have these properties, even if it causes no aging at all, would not be useful for a vertex detector. In other applications (e.g., wire calorimeters), non-hydrogen-containing gases (i.e., gases that contain neither molecular hydrogen nor hydrogenated compounds) may be needed. Such gases would be necessary when there is a high neutron-radiation background because collisions of slow neutrons with hydrogen cause protons to be freed, and the ionization trails left by these protons cause severe noise problems. Safety may also be a concern. There is recent interest in reducing the hydrocarbon content of wire chamber gases due

to the explosion hazard associated with flammable gas leaks [10], especially in underground experiments [11].

1.3 Wire Aging Phenomena

1.3.1 Types of Aging

There are several manifestations of wire aging that commonly occur in wire chambers. Of most interest to this discussion is the loss of gain, but other effects include loss of pulse height resolution, reduction of plateau, large and self-sustained currents, and sparking. Any or all of these may occur in a particular chamber. These effects have been shown to be due to the coating of chamber electrodes by polymer or other deposits. Coatings on wire- or continuous-cathode surfaces normally cause self-sustained currents, while anode coatings cause loss of gain and of pulse-height resolution.

1.3.2 Parameterization of Aging Rate

To determine the severity of anode wire aging, we must have a scale with which to measure aging. There are two measures useful in this regard. First, wire lifetime is commonly reported as coulombs of charge collected per centimeter of wire. The length of wire in this case refers to the irradiated portion of the wire that actually collects charge. In a wire chamber, where the events are expected to be more-or-less uniformly spaced, the physical length of the wire is used. In an accelerated aging test, a region on the

order of one centimeter is likely to be irradiated. Total charge is calculated by integrating the current. Wire lifetimes of approximately 0.3 C/cm are required at existing high energy physics experimental facilities; the proposed Superconducting Super Collider (SSC) may require wire lifetimes of approximately 1 C/cm.

The rate of wire aging is commonly expressed as the normalized rate of gain loss, R :

$$R = -(1/G)(dG/dQ) \quad (1.7)$$

where G is the gas gain, Q is the accumulated (integrated) charge per length of wire; R is normally expressed in units of %/C/cm. R is determined in aging tests by measuring the anode current as a function of accumulated charge (anode current and gas gain are taken to be linearly proportional to each other). Va'vra [12] suggested that $R < 10$ %/C/cm is a good (i.e., acceptable) aging rate, $10 < R < 30$ is a moderate rate, and $R > 30$ is a rapid aging rate. Kadyk [13] uses a more liberal classification: $R < 10$ is a negligible aging rate, $10 < R < 100$ is a moderate rate, and $R > 100$ is a rapid aging rate. Any classification of aging rates is, of course, somewhat subjective.

1.3.3 Cathode Coatings

Insulating coatings on the cathode can result in thin-film emission (of electrons), a process frequently referred to as the Malter effect [14]. The details of how a film may form are unknown; possible explanations are (1) that the

positive ions that drift to the cathode combine on the surface to form nonvolatile polymers, or (2) that large molecules formed in the gas phase drift to the cathode where they condense. Regardless of the actual mechanism, once an insulating film is formed on the cathode, the end result can be potentially fatal to the wire chamber. Positive ions produced in the avalanches continue to drift to the cathode surface, but they are prevented from reaching the wire by the insulating layer and hence are not neutralized. These positive ions, along with their induced image charges, act to produce an electric dipole field that can easily exceed the $\sim 10^7$ V/cm threshold required for field emission. Although some of the electrons so emitted will neutralize the positive ions, most will travel to the anode where they can induce more avalanches, which in turn produce more positive ions. As these positive ions accumulate on the cathode surface, the dipole field increases; this regenerative process results in a large self-sustained current and renders the chamber inoperable.

The discharge continues after the radiation source (particle beam) is removed, but can be stopped by turning off the high voltage on the anode. Once the charge on the cathode has dissipated (this may take several minutes), the chamber can operate normally when the high voltage is restored. The self-sustained discharge will resume, however, as charge builds up again. In practice, the discharge resumes abruptly after some threshold current is reached.

After a self-sustained current is achieved, the large current tends to increase locally the thickness and area of the deposit: the Malter effect (discharge) is contagious. It is easy to understand how the deposit could spread along a single wire. Less clear is how it might jump to other wires, but this, too, has been observed. Danilov, et al. [15] reported that over a period of two weeks, a Malter discharge spread to a region 15 wires wide by 18 wires deep! Wire currents in this region were as high as 1 μ A, one thousand times the normal.

The potential for Malter discharges is augmented in wire chambers relative to proportional tubes because of the smaller cathode area provided by the wires. The number of ions, and hence the amount of polymeric material produced by avalanches at the anode should depend only on the amount of radiation detected and the gain. A fixed amount of polymeric material can more easily coat the smaller cathode area in wire chambers, causing Malter discharges to occur 10-100 times earlier than in proportional tubes [16].

1.3.4 Anode Coatings

Because gas gain occurs in avalanches at the anode wire, anode coatings would be expected to influence the gain. The loss of gain can arise by either or both of two mechanisms. (1) A nonconductive coating (the kind normally expected) on the wire may cause electrons to accumulate, thereby reducing the effective field at the surface. Since

gain is dependent on the field, there is a loss of gain. (2) A conductive coating on the wire increases the effective wire radius and thus decreases the field, which has a $1/r$ dependence, at the wire surface. Again, there is the possibility for a loss of gain.

Due to the statistical nature of the deposition process, the possibility of gain nonuniformity arises. It is also easy to envision that defects (e.g., scratches or bumps) in the wire surface could result in locally larger electric fields, and thus locally accelerate aging rates. This is a particularly serious concern in wire chambers that use energy-loss resolution (dE/dx measurements) as a means of particle identification. Gain uniformity is assumed in this application because the amount of primary ionization is determined from the measured pulse height.

Wire coatings may be a polymer formed in the plasma in the avalanches. If the wire surface has active elements (i.e., is not gold plated), there may also be corrosion or oxidation processes that can form insulating layers.

It was shown long ago by Friedland and Katzenstein [17] that anode wire coatings are responsible for the loss of Geiger region* in Geiger-Mueller counters. A counter was

*The Geiger region is the portion of the curve of pulse size vs. voltage that is essentially constant: the Geiger discharge mechanism is in operation. A Geiger discharge starts with a single avalanche. The gain and the field strength are both very large ($>10^8$ and $\sim 10^6$ V/cm for gases at atmospheric pressure, respectively), however, and a sufficient number of photons is emitted due to relaxation processes that, statistically, some trigger other avalanches: the discharge spreads along the wire. Many positive ions are produced in these avalanches and their resulting space-charge effects eventually reduce the field below that required to

irradiated until it no longer had a Geiger region (10^{10} counts in this case). When the used gas was put into a counter with a new wire, the new counter had a Geiger region, but it exhibited multiple pulsing and large dark currents. When fresh gas was put into the counter with the used wire, the counter then had no Geiger region, but was free of multiple pulsing and dark currents. It was thus concluded that the loss of Geiger region was related to the used wire and that the multiple pulsing and dark currents were related to the used gas. The used wires could in this case be seen to have deposits on them.

1.3.5 Pulse-Height Resolution

Anode wire aging can also be characterized by a loss of pulse-height resolution. den Boggende, et al. [18] described how the appearance of the pulse-height spectrum of the 5.9 keV photons from an ^{55}Fe source deteriorated in a proportional counter with P-10 (90% argon + 10% methane) counter gas.

For a new wire, the spectrum has two distinct peaks: the main peak and a smaller "escape" peak at lower energy (Fig 1.1a). As the wire ages, the main peak gets wider (Figs. 1.1b,c), eventually splitting into two peaks

support gas gain. This limiting point is always reached after approximately the same number of avalanches have been created. All pulses in the Geiger discharge mode are therefore of the same amplitude, regardless of the amount of charge that initiated the pulse. This mode of operation is very different from the proportional mode in which wire chambers operate.

(Figs. 1.1d,e). This splitting occurs after 10^8 - 10^{10} counts; the degree of splitting observed depends on the counting rate, the splitting being more pronounced at higher rates. Noting that the aging effects disappeared after the wire was annealed, and that surface analysis of an aged wire revealed a strong carbon signal (unlike a new wire), the authors concluded that a carbon-based deposit had been formed on the wire, and concluded that the gas was the most likely source of carbon.

The mechanism for formation of the two peaks is not clear. The authors speculated that it might be due to formation of coatings of unequal thickness on the sides of the wire nearest and furthest from the radiation source: the anisotropy of the incident radiation would cause the side of the wire nearest the radiation source to accumulate deposits more readily than the opposite side of the wire. The sides of the wire perpendicular to the incident radiation would be expected to detect little radiation and thus to accumulate very little coating.

Because gain is strongly dependent on the radius at which the electrons are detected, the side of the wire nearest the radiation source would lose gain more rapidly than would the opposite side of the wire. With two different surface radii, the pulse-height spectrum could be explained: the double peak is actually two overlapping main peaks produced by two anode regions having distinctly different gains. To test this hypothesis, the wire was irradiated from

Fig. 1.1. Five successive pulse-height distributions as they develop during irradiation with a 5.9 keV x-ray source of a proportional counter filled with 90% argon + 10% methane [18].

the other side so that the coating thickness was equal on both sides. The pulse height spectrum returned to normal (one main and one escape peak), although the peaks were somewhat wider than would have been observed with a new wire [18].

Based on their studies of proportional counters with argon/methane and xenon/methane gases, Smith and Turner [19] expressed agreement with the asymmetric deposition mechanism. Turala [20] reported that electron micrographs of aged wires revealed significant asymmetries in the deposits. Whatever the exact mechanism, this pattern of the loss of pulse-height resolution has been verified many times in wire aging studies and is often used as a measure of the extent of wire aging. It is important to note, however, that argon must be present in the counter gas for the escape peak, and hence the pattern of deterioration of the pulse-height spectrum shown in Fig. 1.1, to be observed. (Argon need not be present for deposits to be formed on the wires.)

1.4 Plasma Chemistry

There is an enormous number of reactions that can potentially occur in the avalanches. Indeed, all possible reactions probably do occur; their rates determine their relative importance. It is, naturally, unrealistic to attempt to create a complete picture of the avalanche process. As Va'vra pointed out [4], to do this would require knowledge of all collision cross-sections and reaction probabilities

for all species (molecules, radicals, ions, radical ions, atoms, electrons, photons, etc.) with all other species as functions of temperature, pressure, electron and photon energies, and probably a host of other variables.

The avalanche environment is a plasma, and it may be possible to draw qualitative comparisons between the reactions in wire plasmas and those in other, better-understood plasmas. Low-pressure rf-discharge plasmas, in particular, have been used extensively by the microelectronics and coatings industries for purposes of inorganic and hydrocarbon (polymer) film deposition. Although many of the parameters characterizing these two regimes are expected to be vastly different (Table 1.2), there is no *a priori* reason to expect the reaction mechanisms to differ. Reaction rates will certainly vary, however. With knowledge of the conditions under which polymers are formed, it may be possible to choose wire chamber operating conditions in which they will not form.

It is not the purpose of this discussion to review extensively the principles of plasma polymerization; several comprehensive references are available [21-23]. Hess [24] provided a summary of the fundamental plasma processes believed to occur in low-pressure rf-discharge plasmas and suggested possible similarities to wire chamber plasmas. The two recent reviews [4,5] of wire aging also stress the possible relation of this plasma chemistry regime to that of wire chambers.

Table 1.2

Comparison of basic operating conditions [4,24]. Anode wire is assumed to be 20-50 μm diameter.

Parameter	Low-P rf discharges	Wire Chambers
electron energy	1-10 eV	5-10 eV
effective volume	100-1000 cm^3	10^{-10} - 10^{-18} cm^3
electron density	10^9 - 10^{12} cm^{-3}	10^{14} - 10^{17} cm^{-3}
power density	0.01-10 W/cm^3	10^8 - 10^{12} W/cm^3
gas pressure	0.1-5 torr	760-5000 torr
E/p	10-50 $\text{V}/\text{cm-torr}$	100-400 $\text{V}/\text{cm-torr}$
type of field	rf, 50 kHz-40 MHz	dc
space velocity*	0.01-0.5 min^{-1}	0.01-0.001 min^{-1}

*The space velocity is the ratio of the volumetric flowrate at the inlet conditions of a chemical reactor (e.g., wire chamber) to the volume of the reactor.

Due to the extreme complexity of the plasma environment, it is common to characterize the plasma by a few macroscopic variables, e.g., pressure, power density, gas flowrate, and gas composition. The deposition rate and the morphology of the polymer deposit (e.g., powder, film, oil) are then determined as functions of these variables.

Another approach is to model the plasma as accurately as practical as, for example, Jensen, et al. [25] did with ethane. This work may have some relation to the chemistry of wire plasmas that include ethane.

1.4.1 Plasma Polymerization Model

We start by mentioning the classes of reactions by which reactive species can be formed in the plasma environ-

ment. These reactions, which are summarized in Table 1.3, include collisions of neutral species with electrons, photons, and heavy particles. The generic molecule AB is used to represent any molecular species; M represents a third body (molecule, ion, or atom) that can transfer energy or momentum in a collision. These processes can occur in the gas phase or on a surface.

Table 1.3

Reactions that form reactive species in the plasma. AB represents any molecular species. M represents any third body (molecule, ion, or atom) that can transfer energy in a collision.

Electron Impact:

Photodissociation:

Photoionization:

Heavy Particle Collisions:

The relative importance of dissociation and ionization reactions can be determined by comparing bond dissociation and ionization energies. A representative selection of these values are shown in Tables 1.4 and 1.5. It can be seen that dissociation energies are, on average, lower than ionization

energies. As noted in Table 1.2, electron energies in the plasma are expected to be in the 1-10 eV range; this energy is usually sufficient for dissociation but not for ionization. We thus conclude that neutral radicals are present in higher concentrations than are ions.

Table 1.4

Bond dissociation energies (E_d) and ionization energies (IE) for selected molecules [5].

Bond	E_d , eV	IE, eV	Bond	E_d , eV	IE, eV
H	-	13.6	NC-CN	5.6	13.6
Ar	-	15.8	O-N ₂	1.7	12.9
Xe	-	12.1	O-NO	3.2	9.8
H ₂	4.5	15.4	H-CH ₃	4.6	12.6
N ₂	9.8	15.6	H-CH ₂	4.8	9.8
O ₂	5.2	12.1	H-CH	4.4	10.4
Cl ₂	2.6	11.5	H-C	3.5	11.1
F ₂	1.6	15.7	H-C ₂ H ₅	4.3	11.5
Br ₂	2.0	10.5	H- <i>i</i> C ₃ H ₇	4.2	11.1
HF	5.9	15.8	H- <i>t</i> C ₄ H ₉	4.0	10.6
HCl	4.5	12.7	H-C ₆ H ₅	4.8	9.2
HBr	3.8	11.6	H-CN	5.4	13.8
CO	11.2	14.0	H-OH	5.2	12.6
NO	6.5	9.2	H-NH ₂	4.7	10.2
O=CO	5.5	13.8	H-CHO	3.8	10.9
H-CH(CH ₃)OH	4.0	10.5	H-CHCH ₂	4.6	10.5
H-CH ₂ OCH ₃	4.0	10.0	H-CH ₂ OH	4.1	10.8
H ₃ CO-OCH ₃	1.6	-	H ₃ C-CH ₃	3.9	11.5
HO- <i>i</i> C ₃ H ₇	4.0	10.2	H ₂ C=CH ₂	7.5	10.5
F-CH ₃	4.7	12.8	HC=CH	10.0	11.4
Cl-CH ₃	3.6	11.3	Cl-CF ₃	3.7	12.9
Br-CH ₃	3.0	10.5	Cl-CF ₂ Cl	3.3	12.3
			Cl-CFCl ₂	3.2	11.8

Table 1.5
Typical bond dissociation energies [26].

Bond	Dissociation energy, eV	Bond	Dissociation energy, eV
C-C	3.61	C=O	7.78
C=C	6.35	C-F	5.35
C-H	4.30	C-Cl	3.52
C-N	3.17	N-H	4.04
C=N	9.26	O-H	4.83
C-O	3.74	O-O	1.52

A qualitative picture of typical plasma-chemical reactions can be used to describe how larger hydrocarbons might be formed. Polymerization is comprised of three types of reactions: initiation, propagation, and termination. Because we expect radicals to be present in far larger concentrations than ions, a free-radical polymerization mechanism will be illustrated. A generalized polymerization scheme is constructed as follows. In the reactions below, $R\cdot$ represents a radical (the dot represents an unpaired electron), M represents a monomer, P represents a polymer, I represents an initiator, and A represents a transfer agent.

Initiation: These reactions produce reactive species (radicals in this case). The reactivity of radicals is due to their unpaired electron(s).

Propagation: These reactions produce species of increasing molecular weight by repeatedly adding small units. (The small units need not all be identical.) The unpaired electron from the initiator is left unpaired in these reactions, and thus can continue to react. It is during this stage, as molecules get heavier, that they may begin to condense onto the wire.

$R_n\cdot$ represents a radical with n =number of monomers in the molecule. Propagation can occur homogeneously (when the radical is in the gas phase) or heterogeneously (when the radical is on a surface).

Termination: These reactions occur when two radicals react to form a chemical bond, thereby destroying the reactivity of both. Termination can occur by recombination (1.18) or by disproportionation (1.19).

One of the disproportionation products is unsaturated (it has a multiple bond). This multiple bond can react with other radicals to cause branching or cross-linking.

Chain Transfer: This type of reaction is a cross between initiation and termination. In chain transfer reactions, a large (polymeric) radical reacts with a small molecule (the

transfer agent) so that the large radical is terminated and the reactivity is transferred to the small molecule, which then starts to grow.

The type of reaction scheme described above, expanded to account for many of the possible reactions, has been used to describe the observed polymerization kinetics of ethane in a low-pressure rf discharge [25]. The set of reactions is shown in Table 1.6.

Table 1.6

Set of reactions used to describe the low-pressure, rf discharge polymerization kinetics of ethane [25]. Subscripts g and s refer to gas-phase and surface-phase molecules, respectively. Subscripts n and m refer to the number of monomers in the molecule. Σ represents a surface.

<u>Initiation by electrons</u>		<u>Homogeneous propagation</u>	
1.	$e + C_2H_6 \rightarrow 2CH_3^\bullet + e$	13.	$R_{g,n} + C_2H_6 \rightarrow R_{g,n+1}$
2.	$e + C_2H_6 \rightarrow CH_3^\bullet + CH_2^\bullet + e$	14.	$R_{g,n} + C_2H_2 \rightarrow R_{g,n+1}$
3.	$e + C_2H_6 \rightarrow C_2H_5^\bullet + H_2 + e$		
4.	$e + C_2H_4 \rightarrow C_2H_3^\bullet + H_2 + e$	<u>Heterogeneous propagation</u>	
5.	$e + H_2 \rightarrow 2H^\bullet + e$	15.	$R_{s,n} + C_2H_4 \rightarrow R_{s,n+1}$
6.	$e + P_g \rightarrow R_{g,n}^\bullet + H_2$	16.	$R_{s,n} + C_2H_2 \rightarrow R_{s,n+1}$
<u>Initiation by atomic hydrogen</u>		<u>Homogeneous termination</u>	
7.	$H^\bullet + C_2H_6 \rightarrow C_2H_5^\bullet + H_2$	17.	$2H^\bullet + M \rightarrow H_2 + M$
8.	$H^\bullet + C_2H_4 \rightarrow C_2H_3^\bullet$	18.	$H^\bullet + CH_3^\bullet + M \rightarrow CH_4 + M$
9.	$H^\bullet + C_2H_2 \rightarrow C_2H_3^\bullet$	19.	$H^\bullet + C_2H_3^\bullet \rightarrow C_2H_2 + H_2$
10.	$H^\bullet + C_2H_5^\bullet \rightarrow 2CH_3^\bullet$	20.	$H^\bullet + C_2H_5^\bullet \rightarrow C_2H_4 + H_2$
		21.	$R_{g,n}^\bullet + R_{g,m}^\bullet \rightarrow P_{g,n+m}$
<u>Heterogeneous initiation</u>		<u>Heterogeneous termination</u>	
11.	$H^\bullet + P_s \rightarrow R_{s,n}^\bullet + H_2$	22.	$R_{s,n}^\bullet + H^\bullet \rightarrow P_{s,n}$
12.	$R_{g,n}^\bullet + \Sigma \rightarrow R_{s,n}^\bullet$	23.	$R_{s,n}^\bullet + R_{g,m}^\bullet \rightarrow P_{s,n+m}$

1.4.2 Ablation

Ablation refers to a process wherein the molecules of a surface are removed and caused to enter the gas phase. There are two mechanisms by which this may occur: reactive and nonreactive. A reactive mechanism is a chemical mechanism: the gas reacts with the surface and is consumed. The reaction products are often volatile, but need not be. In the latter case, there must also be a nonreactive mechanism that effects removal of the surface. A nonreactive mechanism is a physical mechanism: momentum transfer processes between the gas and the surface cause nonvolatile species to be removed from the surface. The term etching refers to removal of material by means of chemical reactions. The term sputtering refers to removal of material by physical (momentum transfer) means. The dominant factors that influence ablation are the gas composition and the particle bombardment energies.

Yasuda [27] discussed the concept of competitive ablation and polymerization (CAP). In this process, a steady-state between polymer deposition and ablation is achieved. It may be profitable to consider this mechanism in wire chambers: perhaps we can find gases whose chemistry will lean more towards ablation than polymerization.

The chemistry of the plasma can be affected by addition (intentional or nonintentional) of small concentrations of certain components in the gas phase. Some compounds will aid ablation by reacting to form stable, volatile compounds that will not coat wires. A list of reactions that form volatile

products by reaction with methylene (CH_2) is shown in Table 1.7.

Table 1.7

Formation of stable, volatile species in the plasma [21].

1. $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	5. $\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}_2$
2. $2\text{CH}_2 + \text{N}_2 \rightarrow 2\text{HCN} + \text{H}_2$	6. $\text{CH}_2 + \text{CO}_2 \rightarrow 2\text{CO} + \text{H}_2$
3. $\text{CH}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2$	7. $\text{CH}_2 + \text{CF}_4 \rightarrow \text{C}_2\text{H}_2\text{F}_4$
4. $\text{CH}_2 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	

1.4.3 Atmospheric Pressure Plasma Chemistry

The plasma chemistry results discussed thus far all refer to the low-pressure (<5 torr) regime, and the degree to which these results may be used to interpret high pressure plasmas (~760 torr) is an open question. Hess [21] cited results of Fraser, et al. [28] demonstrating that in a 60 Hz, 1 atm plasma of methane in nitrogen, the reaction mechanisms are similar to those at low pressure. In this study, 560 ppm of methane and varying amounts (35-1100 ppm) of oxygen were introduced into a nitrogen discharge, and the concentrations of the primary products determined using gas chromatography and mass spectrometry. As shown in Table 1.8, methane was only partly dissociated; the extent of dissociation was independent of the amount of oxygen added. The dissociation products of methane are expected to be radicals

($\text{CH}_3\cdot$, $\text{H}\cdot$, and $\text{CH}_2\cdot$). This is supported by the observations that at low oxygen concentrations the major products are H_2 and HCN , and at higher oxygen concentrations the major reaction products are CO and CO_2 , which are presumably formed by oxidation of the carbon radicals. An important point to note is that in this atmospheric pressure plasma, stable, volatile oxygenated species are formed. More recent work by Tevault [29] on the oxidation of methane in air/methane plasmas at atmospheric pressure confirmed that methane decomposition to radicals is limited by the power input. The trend towards lower CO/CO_2 ratios with larger oxygen concentrations was also seen.

Table 1.8

Effect of oxygen addition on effluent yield for AC discharges in N_2/CH_4 [28]. Conditions are 60 Hz, 1 atm, 1 mA current, and 350 cm^3/min total flowrate with 560 ppm of CH_4 in the feed.

effluent species	Input O_2 concentration, ppm		
	35	500	1100
O_2	25	75	800
CH_4	345	360	360
C_2H_6	0.7	< 0.2	< 0.2
H_2	370	110	90
HCN	100	10	7.3
NCCN	1.2	< 0.2	< 0.2
CH_3CN	0.6	< 0.4	< 0.4
CO	4.8	45	60
CO_2	4.0	135	125

1.5 Wire Deposits

No study of wire aging would be complete without some information regarding the condition of the aged wires. Are they covered with deposits? What do the deposits look like? Is there corrosion or pitting? The visual appearance may offer insight into the types of fundamental processes at work. It is certainly important to know the composition of the deposits if one hopes to understand the chemical reactions that formed them.

1.5.1 Appearance

Many researchers have investigated the surfaces of damaged wires, primarily by electron microscopy. It is thus known that there is an enormous range of morphologies that the deposits can assume. The deposits may be solids (whiskers, powders, films) or liquids. The morphologies that have been observed include flakes [30], fuzz [31], and bubble-like growths [32]. Many striking photographs of these and other morphologies are in the Proceedings [3].

1.5.2 Analysis Techniques

Analysis of wire deposits is naturally an important step in the process of determining the source of the deposits. Techniques that have been used or suggested for wire analysis are mass spectroscopy (MS), secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), x-ray fluorescence spectroscopy (XRF), x-ray photoelectron

spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and laser microprobe mass analysis (LAMMA).

Mass spectroscopy (MS) separates ions by their mass-to-charge ratio. MS must, therefore, be combined with some method of vaporizing the sample to produce gas-phase molecules. Thermal fragmentation (pyrolysis), for example, is a convenient method of vaporizing the sample. Indeed, pyrolysis has been used widely in conjunction with gas chromatography (GC) for identification of polymers [33]. Much has been learned by MS analysis of wire deposits. Williams [34] provided a comprehensive description of the type of information that can be derived from MS, especially as this technique relates to analysis of wire deposits.

Boerner and Heuer [32] suggested that SIMS and LAMMA might be particularly appropriate to analysis of wire deposits. The SIMS technique uses an ion beam to sputter material off a sample; the sputtered (secondary) ions are analyzed by mass-spectroscopic methods such as magnetic prism or quadrupole analyzers. As the surface is removed by sputtering, a depth-composition profile is obtained. This technique may be useful in tandem with pyrolysis MS.

The LAMMA technique uses a pulsed UV-laser beam to vaporize and ionize part of the surface on which it is focused. The ejected ions are analyzed by a time-of-flight mass spectrometer. LAMMA has the advantage of a very small spot size ($\sim 1 \mu\text{m}$ dia), but it analyzes the composition to a depth of several microns, and so is more of a bulk analysis

technique. The very small spot size may be useful, however, if it is desirable to analyze independently specific regions of wire coatings. Such a case might occur when small irregularities in the wire surface play a large role in the aging, possibly by creating nonuniformities in the coating. (One would expect the chemistry in the avalanche to be independent of the surface, however.)

The FTIR technique relies on absorption of infrared radiation by molecular vibrations. The infrared region, typically 4000 to 700 cm^{-1} , is scanned and the absorption spectrum recorded. The peaks correspond to the characteristic frequencies of molecular vibrations. This technique is useful only for samples that are transparent to the infrared beam, but it is nondestructive.

The XRF technique uses x-ray bombardment to stimulate the emission of x-rays from the bombarded sample. The XPS technique (also referred to as ESCA) also uses x-ray bombardment, but it stimulates photoelectron emission. The energy of the emitted radiation is characteristic of specific elements; neither of these techniques can detect hydrogen, however. Because the attenuation length for electrons is shorter than for x-rays, the analysis depth of XPS is less than for XRF.

The AES technique uses electron bombardment to stimulate the emission of Auger electrons, which are ejected from an atom in response to core-level ionization. AES is used to determine the elemental composition of a surface to a depth

of a few nanometers. Elemental composition determined by AES can be used, for example, to resolve ambiguities that may arise in mass spectral identification in the event that a particular spectrum could plausibly have been generated by widely different compounds.

It was noted above that the SIMS technique uses an ion beam to sputter ions from the surface. It is common to employ such a sputtering technique in conjunction with AES so that a composition-depth profile can be obtained. As the analysis proceeds, the surface is etched and the thickness of layers can, in principle, be determined. Kwong, et al. [35] estimated the deposit thickness on a wire at $0.1\text{ }\mu\text{m}$ in this way. Kotthaus [36] also used this technique, and estimated deposit thicknesses at $<1\text{ }\mu\text{m}$. It should be noted, however, that etch rates are dependent on the composition of the surface being etched. It is therefore extremely difficult (some would say impossible) to know that the instrument is accurately calibrated when estimating the thickness of a sample whose composition is not known *a priori*. It is also possible to combine ion-beam sputtering with XRF or XPS, although it is not common practice to do so.

The relative advantages and disadvantages of the techniques discussed above are summarized in Table 1.9. An introduction to methods of surface analysis can be found in Sze [37]; a comprehensive treatment is given by Feldman and Mayer [38].

Table 1.9

Surface analysis techniques. All techniques listed can detect chemical composition, but none can detect morphology.

Technique	detect hydrogen	detect bonding	analysis depth	etch capability	spot diameter
MS	Y	Y	-	-	-
SIMS	Y	Y	10 Å	Y	50 µm-1 mm
AES	N	Y	50 Å	Y	50 µm
XRF	N	N	>3 µm	N	0.1-1 cm
XPS	N	Y	50 Å	N	0.1-1 cm
FTIR	Y	Y	-	N	-
LAMMA	Y	Y	5 µm	N	1 µm

1.5.3 Composition

Hydrocarbon residues are the most common type of wire deposits, but halogens, sulfur, and silicon are frequently observed contaminants in the deposits.

Williams [34] reported that phthalate esters were found in the deposits on both anode and cathode wires. Mass spectral data suggested that these phthalates were unreacted and it was thus suggested that they had been incorporated physically into the deposit, and probably did not play a significant role in any chemical reactions. It was not determined whether the phthalates were randomly incorporated into the deposits or whether there was some mechanism by which they were concentrated there. The source of the phthalates was suggested to be the plastic insulation on signal cables in the detector. (Phthalates are used as plasticizers; they are added to otherwise rigid plastics to render them flexible.)

1.6 Chemistry of Wire Aging

Wire aging is an extremely complex chemical process. Most studies of wire aging have largely ignored the chemical aspects, focusing instead on what were perceived to be remedies applicable to certain specific cases. A generalized understanding of wire aging must, however, go beyond the "cookbook" that has developed and attempt to quantify, or at least identify, the dominant chemical reactions. It might still be necessary to proceed largely by trial-and-error, but with some understanding of the chemistry, attention could be directed towards the more important variables.

This discussion will review some of what is known or speculated about the chemical reaction mechanisms of wire aging and try to fit this into the framework of plasma chemistry. Naturally, specific results from low-pressure plasma chemistry should not be expected to hold at high pressures, but the fundamental mechanisms should be similar, and qualitative comparisons should be possible.

1.6.1 Appearance of Wire Plasmas

It is common in plasma chemistry studies to describe the appearance of the plasma, but there is relatively little literature that describes the appearance of the plasma sheaths around wires. Sadrozinski [39] reported a test cell with Lucite sides made expressly for viewing the discharge, but did not mention what the appearance of the discharge was. Kotthaus [36] reported glow and spark discharges in a

test cell that had a glass bottom, but did not describe the appearance of the discharges other than to say that sparking was seen. Charpak, et al. [16] reported that the glow resulting from self-sustained (Malter) discharges in a multi-wire proportional counter (MWPC) could be seen when the room was darkened. The glow appeared as small, bright dots in the region where sense and high-voltage wires crossed.

Atac used an image intensifier/video camera assembly to observe wires operating in the self-quenching streamer* mode [40] and in the proportional and in a Geiger-like mode [41].

Streamers were photographed at different anode voltages, gas pressures, and gas compositions. In a 49.3% argon + 49.3% ethane + 1.4% ethanol gas mixture, streamers were 150-200 μm wide and 1.5-3 mm long over a voltage range of 3200-3600 V (Fig. 1.2). As the gas pressure was increased from 1 atm to 2 atm, the streamer length decreased from 3 mm to <1 mm. In a 50% argon + 50% ethane gas mixture, the streamer length decreased from 4 mm to 1 mm over the same pressure range. Addition of 2% nitrogen to the 50% argon + 50% ethane mixture resulted in closely-spaced double streamers (Fig. 1.3a) and in branching of the streamer tail (Fig. 1.3b).

*The streamer mode occurs in a regime of field strength and gas pressure similar to that in which the Geiger mode occurs (see footnote on page 15). Streamers are formed when there is sufficient quenching to prevent the avalanches from spreading along the wire.

In the proportional mode, there was sufficient photon activity to make the wire, or at least its position, visible (Fig. 1.4). The illuminated region extended further from the wire at higher voltages (i.e., at higher gains).

In the Geiger-like mode, bright spots first appeared around the anode wire (Fig. 1.5a), followed several seconds later by more bright spots (Fig. 1.5b), followed by the bright region spreading rapidly along the entire wire (Fig. 1.5c). Only Fig. 1.5c shows the Geiger discharge; the bright spots shown in Figs. 1.5a and 1.5b were thought to be caused by localized parasitic discharges.

Fig. 1.2. Individual self-quenching streamers at various voltages. Anode wire position is indicated at the sides of the pictures. Photographic negatives are shown for clarity [40].

Fig. 1.3. Double (a) and multiple-branch (b) streamer formation with the addition of nitrogen gas. Anode wire position is indicated at the sides of the pictures. Photographic negatives are shown for clarity [40].

Fig. 1.4. Photon activity around the anode wires of a test drift chamber at 2500 V. Photographic negative is shown for clarity [41].

(a)

(b)

(c)

Fig. 1.5. (a) Bright spots along the anode wire. (b) More bright spots appear after several seconds. (c) Discharge spreads along wire. Photographic negatives are shown for clarity [41].

1.6.2 Effects of Wire Composition

There is considerable evidence to suggest that the anode wire material must be compatible with the gas lest there be chemical reactions of the surface elements that cause aging. Alcohol (methanol, ethanol, or isopropanol) additives are effective in suppressing aging in argon/ethane gas mixtures when gold-plated wires are used. However, when resistive wires, such as Stablohm or Nicotin wires, are used with alcohol additives, there can be rapid aging. Stablohm 800 (California Fine Wire, Grover City, CA) is an alloy consisting of 75% nickel, 20% chromium, and 5% (aluminum + copper). Nicotin (Microfil, Renens, Switzerland) is an alloy consisting of 40% cobalt, 20% chromium, 16% nickel, 13% iron, and 11% molybdenum. Atac [42] reported that both Stablohm and Nicotin wires age rapidly when methanol or ethanol is present, but not when isopropanol is present.

To determine whether specific elements in these alloys might be responsible for this aging, several wires of different materials were tested with different alcohol additives to determine their aging behavior [42]. Nickel and aluminum wires did age, but copper, stainless steel, and platinum wires did not. Atac concluded that nickel and aluminum oxides, which are insulators, had formed, and likely did so in the resistive alloys as well. The loss of gain was attributed to a lowering of the electric field caused by charge accumulating on the surface of the insulating oxide

layer. To explain the lack of aging experienced with isopropanol, it was suggested that oxidation of the wire was due to reactions with oxygen radicals, and that isopropanol may dissociate in such a way as to form acetone rather than oxygen radicals:

Indeed, acetone was found in the effluent gas of a test chamber in which isopropanol was used as an additive, lending credence to this hypothesis. Atac did not, however, determine whether acetone causes wire oxidation by performing an aging test in which acetone was used in lieu of an alcohol.

Jibaly, et al. [43,44] also reported aging that is dependent on wire composition. Dimethyl ether was found to cause rapid aging when used with Nicotin or Stablohm wires, but not when used with stainless steel, molybdenum, or gold-plated tungsten wires. It is interesting to note that these groupings of wire materials are essentially identical to those reported by Atac [42]. The structure of dimethyl ether is very similar to that of an alcohol, and it may be reasonable to suppose that dimethyl ether dissociates to form oxygen radicals in the same way that small alcohols do. Bond strengths in alcohols and ethers are expected to be comparable [45].

Kadyk, et al. [46] reported that low aging rates can be achieved when dimethyl ether is used with Nicotin or

Stablohm wires provided that the gas tubing is rigorously free of plastics. The reason for the discrepancy between these results and those of Jibaly, et al. [43,44] and earlier results of Kadyk [47] is not clear at present.

1.6.3 Chemistry of Deposits

1.6.3.1 Carbon Deposits

Gases that do not contain hydrogen, such as carbon dioxide, have been proposed as nonpolymerizing replacements for hydrocarbon quenching gases. However, it has been observed that carbon dioxide-based gases also cause aging, usually by forming deposits on the cathodes.

Carbonized deposits have been observed in beryllium-cathode proportional counters [48,49]. Consistent with loss of carbon dioxide quenching gas, these counters also exhibited shifts in gain and the double-peaked pulse-height spectrum described by den Boggende [18]. Bawdekar [49] proposed a mechanism by which this carbon might be deposited.

After the original ionization of argon, a carbon dioxide ion is produced in a charge-transfer collision. The CO_2^+ ion then migrates toward the cathode, where it is suggested that it may undergo reactions as shown in Scheme 1.1.

The sequence starts as the CO_2^+ ion approaches the cathode surface and causes an electron to be extracted by field emission. The neutralized CO_2 now has an excitation energy of 10.48 eV, having lost 3.92 eV to overcome the work function of the beryllium. The excited CO_2 collides with the

surface, where it dissociates and extracts another electron from the metal. The remaining 1.06 eV is dissipated into the cathode. The beryllium surface is oxidized and a CO molecule is released into the counter gas. The CO subsequently undergoes an analogous series of reactions, as shown in Scheme 1.2. Reaction 3 of Scheme 1.2 leads to carbon deposition on the cathode surface.

Scheme 1.1

Reaction scheme of carbon dioxide [49]. Energies are in eV.

	Reaction	E_{in}	ΔE_{rx}	E_{out}
1.	CO_2^+	0.0	14.4 IE	14.4
2.	$CO_2^+ + e \rightarrow CO_2^*$	14.4	-3.92 ϕ_{Be}	10.48
3.	$CO_2^* \rightarrow CO + O + e$	10.48	$\begin{bmatrix} -5.5 & E_{diss} \\ -3.92 & \phi_{Be} \end{bmatrix}$	1.06
4.	$Be + O \rightarrow BeO$	-	-	-

Scheme 1.2

Reaction scheme of carbon monoxide [49]. Energies are in eV.

	Reaction	E_{in}	ΔE_{rx}	E_{out}
1.	CO^+	0.0	14.1 IE	14.1
2.	$CO^+ + e \rightarrow CO^*$	14.1	-3.92 ϕ_{Be}	10.18
3.	$CO^* \rightarrow C + O$	10.18	-10.00 E_{diss}	0.18
4.	$Be + O \rightarrow BeO$	-	-	-

Carbon deposits may also be produced from hydrocarbon deposits. Sauli [6] suggested that hydrocarbon deposits might be, at least partially, reduced to carbon by chemical

or thermal effects resulting from electron bombardment caused by the avalanches.

1.6.3.2 Silicon Deposits

Silicon has been implicated many times in wire aging processes: analysis of deposits on aged wires often show a significant silicon presence [30,34-36,50]. Spinka [50], in particular, in a semi-quantitative analysis, compared the silicon abundance on an aged anode wire to the estimated silicon abundance in the gas. The film thickness was estimated at $1\text{ }\mu\text{m}$ in two ways. (1) Based on the fact that the film was visible to the eye, its thickness must be substantially greater than the wavelength of light, $\sim 5000\text{ }\text{\AA}$. (2) If the loss of gain was assumed to result from a surface deposit with a dielectric constant similar to that of glass, the deposit would need to be on the order of $1\text{ }\mu\text{m}$ thick. In both cases, these estimates implied that one silicon atom was deposited on the surface for every ~ 125 electrons collected. It was therefore concluded that there is a tremendously efficient mechanism by which silicon is deposited.

The potential sources of silicon in the system included G-10 fiberglass walls and a silicone oil bubbler on the gas line. The G-10 was ruled out as the source of the silicon on the grounds that (1) etching of the surface could not plausibly account for all of the silicon deposited on the wire, and (2) the vapor pressure of the G-10 must be vanishingly

small. The silicone oil bubbler was determined to be the most likely source.

Adam, et al. [51] also reported an extensive silicon presence in wire deposits. In this case the potential sources of silicon were also the G-10 walls and a silicone oil bubbler. Attempts to remove the silicon with a cold trap (-79°C) or with a sacrificial prechamber with high voltage both failed to prevent deposits from forming.

Silicon-based films have long been known to form from low concentrations of silicone oil vapors. Christy [52] studied the formation of such films in a vacuum by the influence of a low-energy electron beam. Dow 704 diffusion pump oil was used as the source of the silicon. The deposition rate was rather insensitive to the total pressure, which was on the order of 10^{-5} torr, but was strongly dependent on the silicone oil partial pressure. The vapor pressure of the oil was varied by changing the temperature of the oil. Cooling the oil from room temperature by circulating liquid nitrogen through baffles in the oil reservoir reduced the film deposition rate by a factor of ten. (System constraints precluded increasing the vapor pressure of the oil by heating it.)

Recent aging test results by Kadyk [46] are in general agreement with this picture. A 50% argon + 50% ethane gas mixture, bubbled through Dow 704 oil to create an 18 ppb silicone oil concentration, aged rapidly ($R \sim 50 \text{ } \mu\text{C/cm}$), presumably due to deposition of a silicon-based film.

1.6.3.3 Hydrocarbon Deposits

Williams [34] reported hydrocarbon deposits that were largely linear hydrocarbons, but noted that there was evidence that unsaturated and branched hydrocarbons were also present. It was suggested that reactive species were concentrated in the region near the wire where they polymerized by mechanisms assumed to be similar to those of low-pressure rf-discharge plasma chemistry. It was added that radicals could be trapped in the polymer film and would subsequently react over a time-scale of hours to cause additional crosslinking.

1.6.3.4 Whiskers

Whiskers are a common feature on aged wires that often occur in wire chambers that use hydrocarbon quenching gases. Kwong, et al. [35] included a photograph of a cathode wire with charred spots that are postulated to be locations of whiskers that had burned off. Sadrozinski [39], using a test chamber with Lucite sides, reported observing whisker formation: it is a rapid process, about 1 mm/5 min. Some of the factors affecting whisker growth were investigated by Foster [53]. Argon/ethane gases were observed to grow whiskers on the cathode. The tips of the growing whiskers glowed brightly as glow discharges surrounding them approached the anode. Argon/ethane was found to support whisker growth with as little as 5% ethane. Argon/isobutane mixtures required at

least 9% isobutane to grow whiskers. Alcohol additives suppressed, but did not eliminate, the whisker growth.

Argon/carbon dioxide gases did not support whisker growth. Moreover, if carbon dioxide was used in place of ethane in a chamber that already had whiskers, the whisker tips would glow red while the whisker was consumed. Sadrozinski [39] observed the same phenomenon when carbon dioxide was used in lieu of ethane. It is possible that an ablation process was responsible for removing the whiskers. Alternatively, carbon dioxide in the gas may have provided oxygen that reacted with the whisker material to form a volatile product such as CO.

1.6.4 Chemistry of Gases

1.6.4.1 Hydrogen

The smaller hydrocarbons that are used in wire chambers are enriched in hydrogen relative to their larger homologs. Methane, the smallest saturated hydrocarbon, has a hydrogen:carbon ratio of 4:1. In the limit of an infinite alkane, the hydrogen:carbon ratio reaches 2:1 as the end effects due to the CH_3 groups vanish. It might reasonably be supposed, therefore, that the presence of molecular hydrogen in a wire chamber gas might help to inhibit polymer growth. There are two possible effects to consider: the thermodynamic effect and the kinetic effect. Hydrogen is produced as the polymer forms from smaller, saturated hydrocarbons. Representative stoichiometry is shown by reaction (1.23).

Thermodynamics indicates that an excess of hydrogen atoms would tend to shift the reaction equilibrium to the left, towards smaller rather than larger species. (This would, however, tend to be counteracted by polymer deposition, which would tend to shift the reaction equilibrium to the right, i.e., toward production of larger species.) Kinetics indicates that with an excess of hydrogen atoms, growing polymers would be more likely to react with a hydrogen atom than with a carbon radical, thereby forming smaller rather than larger products. The kinetics of polymerization would be shifted towards production of smaller species.

Spielberg and Tsarnas [54] proposed that methane dissociates in an avalanche by

so that $\text{CH}_2:$ is a major dissociation product. The diradical $\text{CH}_2:$ is an extremely reactive species known as a carbene. The use of carbenes in organic synthesis reactions is well-known [55], as is their propensity to undergo insertion reactions of the type

Under discharge conditions, carbenes are known to react preferentially with hydrogen over methane. This was determined by an isotopic labeling study [56].

The observed product distribution suggested that reaction (1.27) is approximately 200 times faster than reaction (1.26).

In view of such chemical expectations, Sipila and Jarvinen [57] added small amounts (0.1% to 0.5%) of hydrogen to argon/methane and to argon/isobutane in sealed proportional counters and found that aging rates were reduced by a factor of 20 relative to the same gases without the hydrogen. Several points should be noted, however. (1) The tests were at very low gain (~200), much lower than is typically used in wire chambers. (2) Permanently sealed counters generally have the worst lifetimes, and so would be most likely to show improvement. (3) Hydrogen did not reduce the aging rate of an argon/acetylene mixture. This was thought to be due to the much larger reaction rates (by a factor of 150 to 200) of carbenes with acetylene than with hydrogen [58]. Such relative reaction rates would be expected, given the attraction of the electron deficient carbene to the electron-rich acetylene.

Despite the many factors suggesting that hydrogen should be a beneficial additive in wire chambers, there are reports indicating that the benefit may be very small.

Dwurażny, et al. [31] tested sealed proportional counters with 0.5% hydrogen in argon/isopentane, but found no improvement in lifetime relative to the case without hydrogen. They speculated that the lack of effect was due to

depletion of the hydrogen, which they expected to occur quickly because there was so little hydrogen.

Nelson [59], in aging tests with straw tubes*, reported that argon/hydrocarbon mixtures were unsatisfactory for his application, and that addition of hydrogen to these gases made very little difference.

Juricic and Kadyk [47] reported accelerated aging tests comparing 50% argon + 50% ethane with and without a 1% hydrogen additive with Stablohm wire. There was no significant decrease in the aging rate when hydrogen was present. In fact, their results were generally worse with hydrogen than without, and they concluded that there was no evidence of improvement with the addition of hydrogen.

1.6.4.2 Oxygen

The classic example of applied chemistry in a wire chamber is the ~1000-fold improvement in chamber lifetime achieved by the addition of ~4% methylal ($\text{CH}_3\text{OCH}_2\text{OCH}_3$, sometimes called "formaldehyde, dimethyl acetal") to "Magic Gas" [16]. To minimize polymerization of hydrocarbon quenching gases on the wires, the idea developed of adding a non-polymerizing buffer gas that would have the lowest ionization potential of any gas in the mixture. The hydrocarbons would

*Straw tubes are basically four-to-eight-millimeter ID proportional tubes with aluminized-mylar walls. The optimal thickness of the aluminum coating is still under investigation, but is expected to be in the 0.1-10 μm range. A detector could be comprised of an array of straw tubes.

behave as before and would still be ionized, but charge-transfer collisions would ensure that only ions of the buffer gas would reach the cathode. There, upon neutralization, they would not polymerize.

It has generally been observed that oxygenated additives (usually alcohols) are beneficial to chamber operation. In low-pressure rf-discharge plasma chemistry, it is believed that organic groups containing oxygen (e.g., carboxyl groups, esters, ketones, aldehydes, ethers, and alcohols) do not generally form polymers [60]. This may be due to the relative stability of oxygen radicals compared to carbon radicals. Further, the small oxygenated molecules likely to be formed (e.g., H_2O , CO_2 , CO) are volatile and should not contribute to wire coating. Oxygen plasmas are used for etching and there is the speculation that added oxygen may act to increase the etch rate of wire deposits, possibly shifting the polymerization/ablation balance more towards ablation.

Molecular oxygen may also be beneficial, if present in sufficient concentrations. In an aging test [46], addition of 1000 ppm of molecular oxygen to 50% argon + 50% ethane was found not to affect the aging rate relative to the same gas without the oxygen. Addition of 3000 ppm of oxygen decreased the aging rate, relative to the control, by a factor of three. Oxygen at the 6000 ppm level is believed to have stabilized the operation of a drift chamber [4].

1.6.4.3 Halogens

There are two issues to consider regarding the possible effects of halogens on aging. First, halogens are known to catalyze polymerization of hydrocarbons in the low-pressure rf-discharge regime [61]. It is therefore conceivable that they behave similarly in wire chamber plasmas, enhancing the aging rate. Some halogens are very electronegative, and easily attach electrons, thereby forming negative ions. Such negative ions are then attracted to the anode by electrostatic forces, and are neutralized upon arrival. Neutral halogens may remain, and thus be concentrated in the immediate vicinity of the anode, where they can be involved in avalanches and may act to catalyze polymerization. Second, if halogens attach electrons, these electrons are no longer able to initiate avalanches because they do not gain sufficient energy from the field between collisions. It has been suggested [46] that increases in Freon concentrations, caused by differential evaporation rates of low-boiling gases and high-boiling Freons, may give the appearance of aging. Freon 11 would be likely to give this effect as it is extremely electronegative [46] and its boiling point (25°C) is much higher than the boiling points of typical wire chamber gases.

Juricic and Kadyk [47] reported that dimethyl ether with 10-20 ppm Freon 11 (CFCl_3) ages ~100 times more rapidly than does otherwise pure dimethyl ether. Jibaly, et al.

[43,44] also reported that Freon 11 causes aging in dimethyl ether.

Another conceivable role of halogenated hydrocarbons is that of transfer agents in polymerization. A transfer agent is a small molecule that has a weak bond. A growing polymer may easily extract the weakly bonded atom (or group of atoms) from the transfer agent, leaving the remaining small fragment of the molecule to start a new polymer chain, as shown in reaction (1.18). Because carbon-halogen bonds are generally weaker than carbon-carbon and carbon-hydrogen bonds, alkyl halides can be used as transfer agents. To be effective, however, the transfer agent needs to be present in large excess (it might be used as the solvent for a polymerization reaction). This mechanism probably plays little role in plasma polymerization. The concept of the transfer agent may be applicable, however, if an appropriate transfer agent could be found.

An interesting gas that displays virtually no aging with lifetimes up to 8 C/cm is 80% Freon 14 (CF_4) + 20% isobutane [62,63]. We noted earlier that halogens catalyze plasma polymerization, yet in this case we have to presume that there is little or no polymerization. It is known from plasma chemistry studies that CF_4 alone does not polymerize to form a $-(\text{CF}_2)_x-$ polymer (similar to Teflon, PTFE) in a manner analogous to formation of $-(\text{CH}_2)_x-$ (polyethylene) from hydrocarbons [64]. This is believed to be a consequence of the small bond energy of the F-F bond (1.6 eV). For poly-

merization to occur, F_2 would have to be produced. Any F_2 so produced, however, would be readily dissociated in the discharge to form $F\cdot$, which is extremely reactive and would tend to shift the polymerization/ablation balance towards ablation. In the presence of hydrogen, however, a PTFE-like polymer does form. This is attributed to the formation of strong H-F bonds (5.9 eV); hydrogen scavenges the fluorine radicals resulting in CH_x formation.

We can make two suppositions regarding the CF_4 /isobutane gas. (1) Few hydrogen radicals are produced, thereby preventing deposition of $-(CF_2)_x-$. (2) Isobutane dissociates to form methylene ($CH_2\cdot$), which reacts rapidly with CF_4 to form $C_2H_2F_4$, as by reaction 7 of Table 1.7.

1.6.4.4 Inorganic Gases

There is the possibility that inorganic gases (i.e., those that do not contain carbon) might be used as an alternative to hydrocarbon quenching gases. With no carbon source present, polymers presumably could not form, and long lifetimes should be expected. That adequate quenching cannot be achieved easily is probably the reason that this approach has not received much attention.

Attempts along these lines have met with some success, however. Dwurazny, et al. [65] investigated wire lifetimes in several different mixtures of noble gases, nitrogen, hydrogen, and ammonia. No loss of pulse-height resolution and very little loss of gain ($R \sim 9\%$ /C/cm) were observed for

argon/nitrogen and argon/krypton/hydrogen mixtures after collecting charge on the order of 1 C/cm. Electron microscopy revealed no changes to the anode wire surfaces after this irradiation.

1.6.4.5 Water

Water is often added to the gas mixture when Malter discharges are experienced because of its observed tendency to restore normal operation [30,66-68]. There are two theories for this. (1) Water may act to turn an otherwise insulating layer on the cathode into a better conductor. With an electrical path to the cathode now available, positive charge on the layer bleeds off, and the discharge ceases. (2) Water is a polyatomic molecule and may act as a potent quenching agent [4].

Danilov, et al. [15] reported that addition of 0.2% water to propane reduced the aging rate by one order of magnitude and delayed the onset of Malter breakdown by a comparable factor. This may be significant in that, in addition to helping to cure Malter discharges after the fact, water may also act before the fact to inhibit the chemical reactions that cause aging.

1.6.5 Effects of Tubings

It was noted previously that phthalate esters, which may be used as plasticizers, have been found in wire deposits. Plastic tubing is often used in gas distribution

systems for wire chambers, and it is possible that tubing outgas components contribute to aging. Kotthaus [36] reported that Tygon (a plasticized polyvinylchloride (PVC)) tubing greatly accelerated the aging rate of a chamber with argon/ethane gas, and that the accelerated aging continued after the Tygon was removed. As the specific batch and manufacturer of this tubing were not identified, it is not known what compound in the tubing might have been responsible for the aging.

It is known that plastic tubings outgas many components. Wise, et al. [69] recently analyzed some tubing outgas components and found a large variety of compounds, although phthalate esters were not among these. Water was often seen to be among the components and was found in all of the plastic tubings that were tested. As discussed above (section 1.6.4.5), there is evidence that water is beneficial to the chamber. Indeed, there has been good experience [70] with Rilsan (a type of nylon), which would be expected to outgas water. In this laboratory we have observed that use of nylon tubing suppresses Malter breakdowns that occurred when copper or stainless steel tubing was used. This result is described more completely in section 3.1.

1.6.6 Very Rapid Aging

There are several examples of gases that cause extremely rapid aging [5]. The first, 49.5% argon + 49.5% ethane + 1% ammonia, resulted in a measured value of

R~2500 %/C/cm. The irradiated region of the wire had a visible deposit with a flaky, reptilian appearance. The second, 50% argon + 40% Freon 14 (CF_4) + 10% oxygen, resulted in a measured value of R~130,000 %/C/cm. In this case, no deposit could be seen on the wire. It is obvious that these gas mixtures are not viable candidates for use in wire chambers. The chemistry of these gases may, however, provide insights as to the types of reactions and trace contaminants that should be avoided. (It is interesting to compare the aging properties of the 50% argon + 40% CF_4 + 10% O_2 to the 80% CF_4 + 20% isobutane discussed earlier (section 1.6.4.3): their apparent chemistry is the reverse of what we might anticipate based on low-pressure rf-discharge plasma chemistry.) The magnitudes of these aging rates are depicted vividly in Fig. 1.6.

The third case of rapid aging occurs with a real wire chamber gas containing tetrakis-(dimethylamino)ethylene (TMAE). When ~0.08% of TMAE was added to methane, the measured aging rate was R~1,300,000 %/C/cm [71,72]. After exposure to air (for periods ranging from ten minutes to several hours), liquid droplets could be seen to form on the aged wires. The wires in this case were 7 μm diameter carbon fibers, but the composition of the wire surface did not seem to affect the aging rate: gold-plated wires also aged rapidly with this gas mixture.

TMAE is a photoionizing compound that is used to convert UV photons to electrons, which can be detected in wire

chambers. TMAE has a low ionization potential (5.4 eV) and a low dissociation energy (~2.9 eV). The conjugated pi orbitals in TMAE make it especially likely to polymerize via a free radical mechanism. That it has a low dissociation energy suggests that it may readily dissociate, and subsequently polymerize, in an avalanche. It is likely that the deposits were composed, at least in part, of TMAE. Analysis of the liquid droplets revealed the presence of tertiary amides. Although the amide oxygen may have been due to the oxidation, the tertiary nitrogen was probably from TMAE.

Fig. 1.6. Aging tests with three different gases showing variations in the magnitude of aging rates. (a) 50% argon + 50% ethane. (b) 49.5% argon + 49.5% ethane + 1% ammonia. (c) 50% argon + 40% CF_4 + 10% O_2 .

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2 Experimental Apparatus

The goal of this project is to understand the chemistry of radiation-induced plasma reactions occurring in wire chambers that are believed to be responsible for wire aging phenomena. To allow systematic and detailed study of these reactions, we have constructed an apparatus for analyzing trace constituents in gases. A proportional tube irradiated by an ^{55}Fe source is used as a model wire chamber. By comparing the observed products in the tube effluent to the reactants (which may include contaminants and/or deliberate additives), it is hoped that the dominant reactions can be deduced. By correlating these reactions with the aging phenomena resulting from the same gas, it is further hoped that the detrimental reactions may be identified, and appropriate measures taken to reduce or eliminate them in full-scale wire chambers.

There are two phases to this project. (1) As part of a continuing set of studies, tests are made of the aging phenomena associated with typical, proposed, or potentially instructive sets of operating conditions to determine the suitability of these conditions for their intended application, typically in large high energy physics experiments. These tests are also useful in identifying for further study

systems that are prone to aging. (2) As a new line of investigations, components in a gas, especially the reaction products in a proportional tube effluent, are concentrated by several orders of magnitude in a cryotrap to provide the sensitivity needed for detection and identification. These components are analyzed by gas chromatography/mass spectrometry so that the chemistry of wire aging can be studied. The apparatus described in this chapter was built specifically for this application. The two phases operate concurrently but independently of each other.

2.1 Rationale for System

It is expected that the plasma forms a sheath around a wire that extends on the order of ten mean free path-lengths for ionization from the surface of the wire. (We run the proportional tubes at gains of about 20,000; it requires 14.3 mean free path-lengths to achieve this gain.) For a typical wire of 50 μm diameter installed in a proportional tube of 3/8" ID, and an ionization mean free path of 3 μm , the plasma volume will be $\sim 7 \times 10^{-6}$ of the total gas volume. Individual products will, of course, be present in even lower volume fractions. The analytical problem of measuring these reaction products is nontrivial; extraction of a sample from a small volume is mechanically complex. Further, although the expected products are primarily hydrocarbons, many of the main gas components are also hydrocarbons. Standard adsorptive techniques used in chromatography to analyze

trace hydrocarbons in air [1-3] are therefore of little interest, as they do not provide the discrimination necessary for successful separation and analysis.

To solve this problem, cold trapping was used, with separation effected by exploiting the difference in volatility (i.e., boiling points) of the various components. By maintaining a suitable cold trap (cryotrap) at a temperature above the boiling point of the highest-boiling principal gas component, the heavier species will be preferentially condensed.

2.2 Operational Overview

The experimental apparatus, shown schematically in Figs 2.1-2.4, incorporates a Varian 3400 Gas Chromatograph (Varian Instruments Division, Walnut Creek, CA) and a Finnigan Ion Trap Mass Spectrometer (Finnigan MAT, San Jose, CA), which are used to perform gas chromatography/mass spectrometry (GC/MS) analyses of cryotrapped samples. The cryotrap is a nickel tube 10" x 1/16" OD x 0.040" ID connected to a six-port, two-position sampling valve (Valco 6UWT, Valco Instruments, Houston, TX), the "sample valve." A four-port, two-position valve (Valco 4T), the "purge valve," is used to select between two inlet streams: a helium purge stream and a sample stream. Both valves and all tubing between them and the gas chromatograph are in a heated enclosure (valve oven) to prevent loss of samples by adsorp-

tion and contamination of samples by desorption of previous samples. The valve oven is maintained at 200°C.

A cryotrapping cycle consists of five parts, starting with the valves in their standby positions (Fig. 2.1).

- (1) The cryotrap is baked while under pure helium flow to remove residual impurities. This step was necessitated by the observation that sufficient material would accumulate in the cryotrap in as little as two hours to cause misleading changes in the background.
- (2) The cryotrap, still under helium flow, is cooled with liquid nitrogen and its temperature allowed to stabilize at a prechosen setpoint. Temperature control is achieved by computerized regulation of the coolant flow.
- (3) The purge valve is rotated (Fig. 2.2), allowing a sample gas (e.g., proportional tube effluent) to flow through the cryotrap for a preset cryotrapping period.
- (4) At the end of the cryotrapping period, the purge valve is returned to its standby position (Fig. 2.3), allowing helium to displace the sample gas remaining in the trap. When the residual sample gas was not purged, a masking effect was observed, wherein many of the smaller GC/MS peaks were obscured, and the larger peaks were of highly variable size. (See section 2.8 for further discussion of this phenomenon.)
- (5) The sample valve is rotated (Fig. 2.4), causing the cryotrap to be in the flowpath of the carrier gas (helium) which enters the GC column. The cryotrap is electrically heated by passing a current through the nickel tube, thereby driving the previously condensed species into

STANDBY, BAKE, AND STABILIZE MODES

Fig. 2.1. Configuration of the valve oven during the standby, bake, and stabilize portions of a cryotrapping cycle.

LOAD MODE

Fig. 2.2. Configuration of the valve oven during the load portion of a cryotrapping cycle.

PURGE MODE

Fig. 2.3. Configuration of the valve oven during the purge portion of a cryotrapping cycle. Note the liquid nitrogen spray at the front end of the GC column.

TRANSFER MODE

Fig 2.4. Configuration of the valve oven during the transfer portion of a cryotrapping cycle.

the carrier gas. These species are recondensed (focused) on a ~3 mm column segment near the beginning of the GC column so that standard GC analysis techniques can be used. After the sample is transferred and focused, both valves are returned to their standby positions (Fig. 2.1) and the GC/MS analysis procedure is initiated. Operation of the entire system is under the control of two PC/AT computers: one to drive the cryotrapping cycle and to sample relevant wire chamber parameters (anode voltage and current and gas temperature, pressure, and flowrate), and the other to communicate with the mass spectrometer for data acquisition and analysis.

2.3 Equipment Descriptions

Some of the more important details, features, and peculiarities of the equipment are described in this section. The large commercial items are discussed briefly to familiarize the reader with their operation. Much of the information in this section refers specifically to the current system configuration.

2.3.1 Electronic Instrumentation

The instrumentation used to monitor the proportional tube and to interface with the cryotrapping controls is an expansion of the system used for wire aging tests [4]. The anode wire potential is provided by a Bertan 1755P 5 kV power supply (Bertan Associates, Syosset, NY). The wire cur-

rent is digitized by a Keithley 485 autoranging picoammeter (Keithley Instruments, Cleveland, OH). The tube effluent is discharged to atmospheric pressure, which is monitored by a Setra 270 precision barometer (Setra Systems, Acton, MA). Gas flowrates are monitored by Matheson #601 rotameters (Matheson Gas Products, Newark, CA) and by Omega FMA-213 flowmeters (Omega Engineering, Stamford, CT); both devices are installed downstream of the test chamber to avoid any possible contamination due to outgassing. Temperatures are measured with YSI-44201 thermistors (Yellow Springs Instruments, Yellow Springs, OH) or with copper/constantan thermocouples. With the exception of the picoammeters, the monitors are scanned by a Hewlett-Packard 3495A scanner (Hewlett-Packard, Loveland, CO) and digitized by a Keithley 196 digital multimeter.

Communication between the PC/AT computer and the instruments occurs via a general purpose interface bus (GPIB) (National Instruments, Austin, TX), the IEEE 488 standard. The GPIB is also used to send instructions to a relay driver unit that can control up to 16 solenoids and/or relays. Each instruction sent to the driver consists of a two-byte word containing programming information for all 16 channels. The functions of the solenoids controlled by this unit are listed in Table 2.1.

Table 2.1

The following are the channel assignments of the relay driver unit as of March 31, 1990.

Channel	Solenoid Function	Channel	Solenoid Function
1.....	move to LOAD position	9.....	Cryotrap coolant-COARSE
2.....	move to TRANSFER position	10.....	Cryotrap coolant-FINE
3.....	move to PURGE position	11.....	Coolant to Focus Spray
4.....	move to SAMPLE position	12.....	-
5.....	-	13.....	-
6.....	-	14.....	-
7.....	GC start	15.....	-
8.....	GC reset	16.....	Cryotrap Heater

2.3.2 Varian 3400 Gas Chromatograph

The gas chromatograph is fitted with two DB-5 capillary columns, each of 30 m length, 0.25 mm ID, and 0.25 μ m phase thickness (J&W Scientific, Folsom, CA). The DB-5 column is a general-purpose column, well suited to experimental work where the nature of the analytes is unknown. One column connects the valve oven/cryotrap to the Ion Trap mass spectrometer. The second column connects a Septum Programmable Injector, SPI, (Varian 1093), to an electron capture detector (ECD). There is also a split/splitless injector (Varian 1075) that is not currently in use. Although not used for analysis of the proportional tube effluent, these extras are convenient for analyzing other samples. For example, by connecting an injector to the mass spectrometer, prospective GC temperature programs can be evaluated much more quickly than when using the cryotrap. Or, by using the ECD as the detector for the cryotrap system, we could look for electronegative compounds in the proportional tube effluent that might

be present below the sensitivity threshold of the mass spectrometer.

To effect separations of volatile organic compounds (C_4 and smaller), the GC oven is equipped with a liquid nitrogen-cooled cryogenic unit that can cool the oven to -99°C . The oven can be heated to 400°C , but we keep it below 325°C to prevent damage to the columns.

The temperature program normally used for analysis of the proportional tube effluent consists of a ramp to 250°C at $10^{\circ}\text{C}/\text{min}$ after an initial three-minute hold at -50°C . A helium carrier gas pressure of 15 psig is used.

Automated operation of the system requires that the GC "reset" function be accessible to the computer via the interface bus. The GC was not designed, however, to allow the "reset" function to be activated by an external signal. To overcome this difficulty, a relay was added in parallel to the "reset" switch that is on the GC front panel.

2.3.3 Finnigan Ion Trap Detector

The Finnigan Ion Trap detector is a versatile, low-cost mass spectrometer designed specifically for use as a detector in gas chromatography; it has a mass range of 25 to 650 amu with unit mass resolution. Its design sensitivity specification is identification of 100 pg of hexachlorobenzene with a signal-to-noise ratio of at least 10:1, but we have found 1 ng (1000 pg) to be the lower limit at which

mass spectral identification of an unknown can reasonably be expected to be made.

The high sensitivity of this instrument relative to that of a quadrupole mass spectrometer is due to the automatic gain control software developed by Finnigan. This algorithm regulates the ionization time so that equal numbers of ions are created regardless of the concentration of the sample being analyzed, thereby greatly reducing loss of resolution due to space-charge effects.

2.3.4 Valve Oven and Cryotrap

The valve oven maintains the two switching valves and the other plumbing associated with the cryotrap at an elevated temperature to inhibit vapor condensation. (This is standard practice in chromatography since deposits accumulate on local cold spots.) The sample inlet port is immediately outside the valve oven wall so that the path length from the proportional tube to the oven is minimized, and the discharge products have a reduced chance of condensing.

It should be noted, however, that because neither the inlet port nor the proportional tube are heated, they must be considered as cold spots. Although both could be heated, we chose not to do so initially because heating the proportional tube could, in principle, affect reaction rates and relative products abundances. (Proportional tubes are normally used at room temperature.) The possibility that reaction products are condensed in the unheated inlet port

and/or proportional tube is of sufficient concern that the effect of heating these areas should be investigated and provisions for heating them implemented if necessary.

The cryotrap extends outside the oven walls, since it serves as an intentional cold spot during part of its normal operation. During the bake and transfer stages, the trap is electrically heated by passing a current through the nickel tube. The electrical connections to the tube are both inside the oven, ensuring that the entire length of tubing is heated. Electrical connections to the tube are made with copper clamps, which are gold-plated to reduce copper corrosion. Without gold plating, a (green) copper oxide developed on the clamps. The increased resistance caused by this growing oxide was evidenced by a gradual increase in the power needed to heat the trap. The problem has not reoccurred since the clamps were plated. The gold plating is not impervious, however; a bluish corrosion has developed underneath the plating.

Gold-plated spade lugs crimped onto the electrical cables are attached to the copper clamps with stainless steel machine screws. There is some green oxide on the wire strands near the crimped area.

Because the cryotrap has a low resistance ($R=L\rho/A=0.044\ \Omega$; $L\sim 75\text{ cm}$, the length of the cryotrap tube that is heated; $A=0.0117\text{ cm}^2$; $\rho=6.84\ \mu\Omega\text{-cm}$ at 20°C [5]) it is necessary to use a low voltage, high current power supply. Since a commercial transformer with the desired power

rating was not available, a transformer was specially wound for this application. The need to reach higher cryotrap temperatures later rendered this transformer inadequate, and a modified welding transformer was obtained instead. The power delivered (at the transformer output terminals) is 3.25 volts over the current range of 19 amps (with the cryotrap hot, -200°C) to 25 amps (with the cryotrap cold, -70°C). These values indicate a resistance of $\sim 0.16 \Omega$. The discrepancy between this value and the resistance of the nickel tube alone can be explained by taking into account the resistance of the cable and the connections.

To ensure that the power intended to heat that cryotrap is not dissipated inside the valve oven (which, due to its larger cross-sectional area, may have a lower resistance than the cryotrap), it was necessary to electrically insulate one end of the cryotrap from the valve oven. (This also prevents a possible short circuit between the welding transformer and the valve oven heater.) A short (2.5 inch) length of specially ground quartz tubing is used as an insulator. Special grinding was necessary to adapt the quartz glass, which is only available in metric sizes, to the Valco fittings (Valco Instruments, Houston, TX) used in the oven, which are only available in English sizes*. The difficulty

*The quartz segment is held in place by 1/8" polyimide ferrules (Valco ZF2V). As a special order, Valco will manufacture a ferrule with the external dimensions of a 1/8" ferrule, but with a hole of any desired diameter (e.g., 4 mm). This is probably the best option available if the quartz segment ever needs to be replaced.

in finding a viable solution to this problem cannot be overemphasized.

The cryotrap tube is mounted in a brass case, through which the liquid nitrogen coolant flows. The brass case is in turn mounted in a NEMA fiberglass box, and insulated with Kaowool ceramic fiber (Thermal Ceramics, Augusta, GA).

The sample flows from the valve oven to the GC oven through a piece of deactivated fused silica capillary column. This column is two meters long; the ~1.5 meter length that is inside the GC oven functions as a guard column. The connection between the deactivated column and the DB-5 column is made with a Press-Tight connector (Restek, Bellefonte, PA).

The column between the valve oven and the GC oven is inside a heated tube. At the GC oven wall, the column runs through a heated brass block with a 1/16" OD snout (Fig 2.5). The end of the snout is the only part of the block in contact with the inside of the GC oven. In this way, the sample in the column is kept hot until it is inside the GC oven, at which point the cryofocusing occurs.

2.3.5 Liquid Nitrogen Distribution System

In this system, liquid nitrogen is used to cool the cryotrap, the focus spray, and the gas chromatograph. The supply lines are 1/4" Poly-Flo tubing (Imperial Eastman, Manitowoc, WI) that are insulated with 3/8" ID Armaflex neoprene foam tubing (Armstrong World Industries, Lancaster,

Fig. 2.5. The heater block at the GC oven wall.

PA). The ends of the Armaflex are glued to blocks of 3/4" thick neoprene foam, and all are kept under slight compression so that a tight seal is obtained. This greatly reduces frost accumulation at the joints.

Liquid nitrogen is fed to the cryotrap through two Asco 8263B206LT solenoids (Automatic Switch, Florham Park, NJ) in parallel. One solenoid (the fine flow) has a needle valve in series with it to throttle the flow; there is no additional resistance in series with the other solenoid (the coarse flow). The coarse flow is used when the cryotrap is initially being cooled to minimize the time required. Once the trap is cool, very little liquid nitrogen is needed to keep it cool, and the fine flow is used. This permits better temperature control and reduces liquid nitrogen consumption.

The liquid nitrogen supply line to the focus spray is copper rather than the usual Poly-Flo. The substitution was made after a plastic strengthening insert in the end of a plastic tube connected to a fitting in the GC oven wall melted shut after repeated cycling to high temperatures.

2.3.6 Proportional Counter Tube

As a model wire chamber, we use a single-wire proportional tube. Originally, aluminum tubes (Fig. 2.6) were used, but they were later replaced by copper tubes (Fig. 2.7). Both types of tubes have similar internal dimensions and cross-sectional areas. The change to copper was prompted by the propensity of aluminum tubes to fail by

electrical breakdown. We believe this failure mode to be associated with the insulating characteristics of the native aluminum oxide, inducing a self-sustained discharge analogous to a Malter discharge [6]. Indeed, Malter's experiments were conducted using aluminum oxide as an insulating layer. Atac suggested that a Malter-like discharge will not occur with cupric oxide because cupric oxide is a semiconductor [7].

The aluminum tubes are not reused after a test run; after use they are analyzed or stored. The copper tubes, on the other hand, are cleaned and rebuilt after each test, and the used anode wires are stored. Cleaning procedures that have been used include treatment with nitric acid, ultrasonic cleaning in isopropanol, baking in air, and vacuum baking. The standard cleaning procedure is: (1) mechanically clean the tube to remove the glue, (2) ultrasonically clean the tube shell twice, for 15 minutes and with fresh isopropanol each time, and (3) bake the tube in air at $\sim 120^{\circ}\text{C}$ for one hour.

The tubes used for analysis with the cryotrap are very similar to that shown in Fig. 2.7, except that they are shorter (4.5 inch) and have a longer window (3 inch). They are strung with a $50\text{ }\mu\text{m}$ diameter, gold-plated tungsten wire (Luma Metall, Kalmar, Sweden); the gold plating is nominally $0.5\text{ }\mu\text{m}$ thick. The window (0.5 mil aluminum foil) is sealed to the tube with five-minute epoxy (Hardman, Belleville,

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Fig. 2.6. Aluminum tube and fittings used for anode wire lifetime tests. A simple representation of wire, coating, and equipotential lines.

Fig. 2.7. Copper tube and fittings used for anode wire lifetime tests.

NJ). The feedthroughs are molded from a fiberglass-epoxy material.

2.3.7 Radiation Source

The 5.9 keV photons emitted by an ^{55}Fe source are used to simulate ionizing particle radiation. A 10 mCi line source six centimeters long is normally used for tests in which the proportional tube effluent is analyzed. Aging tests are run with 1 mCi or 2 mCi point sources. All of the sources were supplied by Isotope Products Laboratories, Burbank, CA.

The line source is mounted on an 8 cm x 0.8 cm x 0.2 cm aluminum baseplate. Spacers approximately two millimeters thick are glued to the ends of the baseplate to prevent the source from touching and possibly puncturing the proportional tube window.

2.3.8 Permeation Device

There are times when it has been desirable to introduce low (ppb to ppm) levels of a specific additive to gases used for wire aging tests or for plasma chemistry studies using the GC/MS system. Successive dilution of a concentrated mixture is both inconvenient and wasteful. Gas permeation is a method that creates low concentration mixtures by permeating the additive through a Teflon membrane into the main gas. Permeation tubes were initially proposed by O'Keeffe and Ortman [8] as a method of preparing primary standards for

use in trace gas analyses. Scaringelli, et al. [9] gave many practical details regarding the construction, calibration, and use of permeation tubes.

We use a Kin-Tek Precision Gas Standards Generator, Model 570-C (Kin-Tek Laboratories, Texas City, TX), with a digital temperature controller adjustable from 25°C to 150°C in 0.1°C increments. Experimental permeation data for many compounds are supplied by the manufacturer; these data have an exponential dependence on inverse temperature.

2.4 Software

The software used to run the cryotrapping cycle is a derivative/modification of a program written to control data sampling and display functions for wire aging tests [10]. These programs are written in FORTRAN (Microsoft, Redmond, WA) and use HALO graphic routines (Media Cybernetics, Silver Spring, MD) for all on-screen output.

2.4.1 Cryotrapping Cycle Control Parameters

The names and functions of the parameters used to control a cryotrapping cycle are described below in the order in which the user is prompted to enter them. The default values of these parameters have been determined from long experience with the system and are shown Table 2.2.

Cryotrapping duration: The length of time in minutes that the cryotrap is held at the temperature setpoint while a sample gas is flowing.

Cryotrapping temperature: The cryotrapping temperature setpoint in degrees Centigrade.

Bake time: The length of time in minutes that the cryotrap is baked under helium purge gas before starting to cryotrap.

Purge time: The length of time in seconds that the cryotrap is purged with helium after completing the requested duration of cryotrapping but before beginning to transfer the sample to the focus spray in the GC. The cryotrap is held at the temperature setpoint during the purge. If the purge time is set to zero, the purge valve is not rotated, and no purge gas flows into the cryotrap; this feature is intended primarily for diagnostic use.

Transfer duration: The length of time in minutes that the cryotrap is heated while transferring the sample into the GC.

Focus precooling time: The length of time in seconds that is allowed for the focus spray to reach liquid nitrogen temperature before the transfer is started.

GC reset time: The length of time in seconds that the GC reset function is activated before the end of the transfer (and corresponding start of the GC temperature program).

Stabilization time: The length of time in minutes that the cryotrap is allowed to stabilize at the temperature setpoint under helium flow before the sample gas is allowed to flow into the cryotrap.

Upper deviation limit: The temperature deviation above the setpoint in degrees Centigrade below which the temperature is considered to be acceptable and above which the temperature is considered to be too high. The role of this parameter in the temperature control algorithm is described in section 2.4.3.

Extreme deviation limit: The temperature deviation above the setpoint in degrees Centigrade below which the temperature is considered to be too high and above which the temperature is considered to be "much too" high. The role of this parameter in the temperature control algorithm is described in section 2.4.3.

Lower deviation limit: The temperature deviation below the setpoint in degrees Centigrade above which the temperature is considered to be acceptable and below which the temperature is considered to be too low. The role of this parameter

in the temperature control algorithm is described in section 2.4.3.

Table 2.2

Default values for the cryotrapping control parameters.

Cryotrapping duration	15 min
Cryotrapping temperature	-80 °C (but depends on sample gas)
Recommended cryotrapping temperatures for several gases:	
helium	-100 °C
methane	-80 °C
ethane	-70 °C
propane	-30 °C
isobutane	0 °C
Bake time	5 min
Purge time	100 sec
Transfer duration	9 min
Focus precooling time	105 sec
GC reset time	160 sec
Stabilization time	4 min
Upper deviation limit	2 °C
Extreme deviation limit	5 °C
Lower deviation limit	2 °C

These parameters may be entered as integers only. To allow flexibility in setting these parameters, those that need fine adjustment are measured in seconds while those that need only coarser adjustment are measured in minutes. The complete timing diagram for a cryotrapping cycle is shown in Fig 2.8.

Fig. 2.8. (Figure on page 92.) Timing diagram for a cryotrapping cycle. Typical time values are indicated, but the time axis is not drawn to scale. Pulses are three seconds wide. The cool-down step has no set time; it is under feedback control and depends on the initial temperature of the liquid nitrogen distribution system and the pressure in the dewar.

2.4.2 Temperature Measurement

Reliable measurements of cryotrap temperature are needed for effective temperature control. In most instances, temperatures are measured with copper/constantan (type T) thermocouples; a commercially available heated transfer line (EnviroChem, Kemblesville, PA) came with an iron/constantan (type J) thermocouple. The copper/constantan thermocouple was chosen because it is most suited to low temperature work: its wire materials are better able to maintain their homogeneity at low temperatures than are the materials used in other types of thermocouples [11]. This thermocouple is also convenient to work with because it has only one thermal reference junction, the other being a nonthermal copper/copper junction. The measured thermocouple voltages are converted to temperatures by sets of equations (Tables 2.3 and 2.4) that we developed to approximate the thermocouple tables. The reference junctions are at room temperature, but no correction is made for variations in room temperature. Although room temperature could be measured with a thermistor, it was convenient to make all calculations with the reference temperature assumed to be 22°C. This value is a reasonably accurate average temperature in the laboratory, and so introduces little error. Temperature changes monitored during aging tests show little diurnal variation, although there are seasonal variations of 2-3°C.

Table 2.3

Equations relating thermocouple voltage to temperature for iron/constantan (Type J) thermocouples. T is in degrees Centigrade. V is in millivolts. The reference junctions are assumed to be at 0°C.

<u>Temp. Range</u>		<u>Voltage Range</u>		Equation
Low T	High T	Low V	High V	
0	100	0	5.268	$T = 18.983V + 0.4$
100	300	5.269	16.325	$T = 18.088V + 5.066$
300	500	16.326	27.388	$T = 18.079V + 5.046$
500	700	27.389	39.130	$T = 17.033V + 35.276$
700	760	39.131	42.922	$T = 15.823V + 81.051$

Table 2.4

Equations relating thermocouple voltage to temperature for copper/constantan (Type T) thermocouples. T is in degrees Centigrade. V is in millivolts. The reference junction is assumed to be at 0°C.

<u>Temp. Range</u>		Equation
Low T	High T	
-200	-100	$T = 76.92[-4.175 + (2.6V + 17.0)^{0.5}]$
-100	100	$T = 100.00[-3.840 + (2.0V + 14.8)^{0.5}]$
100	250	$T = 166.67[-4.120 + (1.2V + 17.2)^{0.5}]$
250	400	$T = 250.00[-4.610 + (0.8V + 21.9)^{0.5}]$

A platinum resistance element, PT-139AW (Yellow Springs Instruments, Yellow Springs, OH) was initially used to measure the cryotrap temperature, but was rejected. Because of its large physical size (1/8" dia x 1" length), it was difficult to put this device into good thermal contact with the 1/16" OD cryotrap tube. Consequently, we could not ascertain whether it was more responsive to the coolant (liquid nitrogen) temperature than to the cryotrap temperature. It was

also difficult to make good electrical connections to this device.

2.4.3 Temperature Control

Temperature control of the cryotrap is perhaps the most important of the automated functions. If the cryotrap gets too cold, components of the sample gas can condense, diluting the signal from the heavier species of interest. In extreme cases, enough of the sample gas can condense to plug the cryotrap completely. This is particularly prone to occur when carbon dioxide is a component of the sample gas. When the cryotrap does get too cold, common sense suggests that no additional coolant should be used until the trap has warmed. When this method was used, however, and coolant subsequently supplied, it was usually observed that the liquid nitrogen distribution lines had warmed so that the trap initially rose in temperature when the liquid nitrogen flow was resumed. This effect gives rise to the possibility of boiling off some of the collected sample.

To achieve close temperature control, the cryotrap is equipped with three copper/constantan thermocouples that are each silver-soldered to the exterior surface of the cryotrap tube. The three thermocouples are designated inlet, middle, and outlet, with their positions referring to the direction of coolant flow. (The sample gas flows cocurrent with the coolant; this was a construction error, but it does not appear to have impaired the heat transfer process. The

topology of the cryotrap is such that effecting countercurrent flow would be inconvenient.) Around the nominal temperature setpoint, there is an accepted tolerance of temperature variation that is defined by an "upper deviation limit" and a "lower deviation limit." These two quantities, in conjunction with the nominal setpoint, are used to determine when the trap is too warm or too cold, respectively. There is also an "extreme deviation limit" that tells when the trap is "much too warm." The values of these parameters are normally: upper deviation limit = 2, lower deviation limit = 2, and extreme deviation limit = 5.

The temperature controller reads the inlet temperature when deciding whether the trap is too cold, and the outlet temperature when deciding whether the trap is too warm. The middle temperature is monitored for the benefit of the operator, but plays no role in the temperature control algorithm. The three thermocouples are scanned in sequential order at the maximum rate that the system can achieve (approximately 1.3 thermocouple readings per second). Whenever the most recent reading indicates that the temperature is within the desired limits, the coolant flow is not altered. If the trap is too warm (outlet temperature - upper deviation limit > setpoint), the fine coolant flow is activated. If the trap is "much too warm" (outlet temperature - extreme deviation limit > setpoint), both the fine and coarse coolant flows are activated. If the trap is too cold (inlet temperature + lower deviation limit < setpoint), all

coolant flow is terminated. In practice, this control scheme maintains the outlet temperature at a value equal to the setpoint plus the upper deviation limit. A temperature gradient of four or five degrees Centigrade across the trap is normally observed. A plot of the controlled cryotrap temperatures versus time of operation is shown in Fig. 2.9.

Temperature control of the focus spray is somewhat problematic. Because it is designed to keep the column as close to liquid nitrogen temperature as possible, the coolant flow is activated for as long as the column must be kept cold. The only difficulty is determining when the column has reached liquid nitrogen temperature. An algorithm to determine this might involve monitoring both the column temperature and its first time derivative. But because the column usually does not cool monotonically (in fact, it can oscillate over a range of as much as 50°C), this algorithm could be unreliable. Further, it is desirable to minimize the dead time in the cryotrap temperature control loop; this rules out time-consuming algorithms, and is most conveniently accomplished by having no algorithm at all, but rather by precooling the column and assuming that it will be cold when necessary. With an appropriate precooling time (the default is 105 seconds), this assumption causes no difficulty.

The behavior of the focus spray is extremely sensitive to the pressure in the liquid nitrogen dewar. The default precooling time was determined for operation with a "fully

Fig. 2.9. Controlled cryotrap temperatures vs. time of operation.

pressurized" dewar; that is, one under at least 50 psig. Under full pressure, the focus spray temperature oscillates for about ten seconds as it cools; under a marginal pressure of 35 psig, the oscillations can last for four to six minutes. To address this problem, there is a provision in the program that allows the user to change the control parameters during a cryotrapping cycle.

Cooling the gas chromatograph column oven poses few problems; it is relatively insensitive to dewar pressure. It also has an output that unambiguously indicates its "ready" status. The GC is sufficiently reliable, however, that it has not been necessary to make the timing contingent upon the GC "ready" status.

2.5 Cryotrapping

Capillary cold traps are pervasive in gas chromatography and are used for two main purposes: sample enrichment and solute band concentration. The utility of sample enrichment is obvious; solute band concentration is effected to localize the sample at the column inlet so that resolution of the separation is not compromised. In our system, the cryotrap is used for sample enrichment and the focus spray is used for solute band concentration. Numerous authors have reported cold-trapping schemes; several [12-14] discussed equipment design issues that may be worthy of consideration if the system is ever rebuilt.

2.5.1 Capillary Cold-Trapping Techniques

In its simplest form, a capillary cold trap is a loop of capillary column that is immersed in a coolant (liquid nitrogen, dry ice/methanol, etc.). In automated (and therefore reproducible and repetitive) operation, however, immersion schemes are impractical. A preferable method is to use a flow system. The crudest flow technique involves spraying liquid nitrogen past the column into the GC oven. This technique was tried, but caused two problems: 1) in addition to cooling the column, the excess liquid nitrogen dumped into the oven made its temperature difficult to control, and 2) the large amount of liquid nitrogen directed at the oven wall caused the wall and the section of the column cage closest to the wall to freeze. Because the loops of the column in the cage are of equal diameter, the frozen section consisted of a number of equally spaced column segments. Carbon dioxide that was not condensed in the spray at the beginning of the column was condensed instead in the frozen segments. Consequently, evenly spaced peaks of carbon dioxide were observed to elute during the first minute of the GC analysis (Fig. 2.10).

Fig 2.10. This chromatogram shows the effect of cooling one side of the column cage. The evenly spaced peaks are all carbon dioxide.

A number of quite sophisticated capillary cold-trapping techniques have been reported. The difficulty in all schemes is that when the GC temperature program starts after the cold-trapping step, the column temperature must follow the GC oven temperature, unaffected by the thermal inertia of the focusing apparatus. For cold-trapping/reinjection techniques, the focusing apparatus must be rapidly heated. Kalman, et al. [15] reported a cold-trapping method that involves placing a ten centimeter-length of copper tube around part of the column. The copper tube carries, alternately, liquid nitrogen and hot air. For reinjection techniques, electrical circuits for rapid heating have been reported [16,17]. Despite the problems that we encountered

when flowing liquid nitrogen into the oven, the problem is apparently not insoluble. Rijks, et al. [18] recently reported a particularly elegant cold trapping/thermodesorption technique that involves cold nitrogen gas flowing into the oven with no apparent undesired side effects. (It is possible, however, that their GC had a larger oven than ours does and/or they were able to use a lower nitrogen flowrate than we do. Either or both of these would help to resolve the difficulties that we encountered.)

2.5.2 Design of the Focus Spray

Our focusing apparatus, shown in Fig. 2.11, is a modification of the apparatus used for the crude focusing technique described in section 2.5.1. Liquid nitrogen enters through the tube (front), reverses direction before impinging on the column, and exits the GC oven, thereby eliminating the problems associated with dumping liquid nitrogen into the oven. To protect the floor, the excess liquid nitrogen is discharged into a box of sacrificial material (styrofoam packing). The large (1/2" square) hole size in the focusing tube allows sufficient air flow by the column that the column temperature follows the oven temperature without additional heating. A copper/constantan thermocouple placed adjacent to the column in the area of the liquid nitrogen spray monitors the temperature. One drawback to this technique is the rather large amount of liquid nitrogen required. There is also some question regarding the trapping

Fig. 2.11. The focus spray apparatus.

FOCUS SPRAY APPARATUS

efficiency in view of the short length of column (~3 mm) that is actually cooled to liquid nitrogen temperature. (See further discussion in section 2.5.3).

An alternative to the localized methods is to use what Pankow termed "whole column trapping" [19]. In this method, the GC oven is held at a low temperature, e.g., -80°C, while the focusing takes place. The temperature chosen must be low enough that the species of interest will condense. There is a built-in monitor for trapping efficiency in the form of peak shape: sharp, symmetric peaks likely represent quantitative trapping. Breakthrough results in wide peaks, which can be identified easily. This technique has been tried on our system and appears to work; it has not been thoroughly explored because our analytical procedure has already been standardized. Since this technique has the potential to simplify the analytical procedure and to reduce greatly liquid nitrogen consumption, it is a viable alternative to our current practice.

2.5.3 Efficiency of Cold Traps

In general, the lower the temperature, the more efficient the cold trap. However, since the temperature to which the cryotrap may be cooled is limited by the boiling point of the sample gas, other factors must be considered.

The importance of a negative axial temperature gradient was first discussed by Kaiser [20], who concluded that too large a gradient or too low a temperature could cause micro-

fog (aerosol) formation. These condensed particles are rapidly swept out of the trap by flowing gas, resulting in low and erratic trapping efficiency.

Hagman [21] and Graydon [22] both reported that at low temperature, there is no difference in the trapping efficiency of coated and uncoated columns, consistent with the belief that the coating (i.e., the column phase) behaves as a solid at the low temperatures typical of cryotrapping.

The ratio of gas-phase residence time of a molecule in the trap to the time for a molecule to diffuse to the wall is probably the single most important parameter in determining the necessary size (length) of a cold trap. The time required for a molecule to diffuse to the wall is commonly [16,21] calculated with the Einstein diffusion relation, $\tau = r^2/4D$, where τ is the diffusion time, r is the radius of the trap and D is the diffusivity of the particular species in the main gas. Diffusivities can be estimated conveniently with the Fuller-Schettler-Giddings correlation [23].

Table 2.5 shows diffusivities and diffusion times that are calculated by this approach for a range of conditions. It can be seen readily that the ratio of residence time to diffusion time is at least ten in the cryotrap, but only about unity in the focus spray at liquid nitrogen temperature. With a focusing temperature of -80°C , however, as might be used in the "whole column trapping" method, the ratio is closer to ten. But since the entire column is cooled for whole column trapping, the focusing region is

longer than in the current method (perhaps 10 cm vs. 3 mm), and consequently the residence time, and hence the ratio, are further enhanced by at least one order of magnitude.

Table 2.5

(a) Diffusion times for anticipated species in the cryotrap. Cryotrap length is 25 cm. Cryotrap diameter is 0.040". Gas pressure in the trap is 1 atm. Gas flowrate is 20 cm³/min. Average linear velocity is 30 cm/sec. Average residence time is 0.83 sec. Minimum residence time ($t_{\min}$) is 0.42 sec (laminar flow in the trap).

T (C)	main gas	diffusing species	diffusivity (cm ² /sec)	τ_d (sec)	$t_{\min}/\tau_d$
-100	He	C ₁₂ H ₂₆	0.070	0.009	46.7
-70	C ₂ H ₆	C ₆ H ₁₄	0.031	0.021	20.0
-70	C ₂ H ₆	C ₁₂ H ₂₆	0.022	0.029	14.5
-50	C ₂ H ₆	C ₆ H ₁₄	0.037	0.017	24.7
-50	C ₂ H ₆	C ₁₂ H ₂₆	0.026	0.025	16.8
-50	C ₃ H ₈	C ₁₂ H ₂₆	0.020	0.032	13.1

(b) Diffusion times for anticipated species in the focus spray. Focus spray length is 3 mm. Capillary column diameter is 0.25 mm. Gas pressure in the column is 2 atm. Average linear velocity is 30 cm/sec. Maximum linear velocity is 60 cm/sec. Minimum residence time ($t_{\min}$) is 0.005 sec (laminar flow in the column).

T (C)	main gas	diffusing species	diffusivity (cm ² /sec)	τ_d (sec)	$t_{\min}/\tau_d$
-196	He	C ₆ H ₁₄	0.0128	0.0031	1.61
-196	He	C ₁₂ H ₂₆	0.0085	0.0046	1.09
-80	He	C ₆ H ₁₄	0.064	0.0006	8.3
-80	He	C ₁₂ H ₂₆	0.043	0.0009	5.6

2.6 Peak Identification

The two-dimensional nature of gas chromatography/mass spectrometry makes it a powerful analytic tool. One-dimensional GC reveals only peak size and location, but in GC/MS, each peak is also analyzed by mass spectrometry. A vivid diagram of the two-dimensional nature of this process is shown in Fig. 2.12.

2-D GC/MS PLOT

ITDS DEMO DATA Feb-14-1987

Fig 2.12. This figure shows the two-dimensional nature of GC/MS. The GC chromatogram is at the bottom. Mass spectra of each scan are at the top. These data are from the Finnigan demonstration datafile DEMO.DAT.

Mass spectrometric identification is made by comparing the spectrum of the unknown to the NBS library of 42,222 standard mass spectra. The library search procedure usually gives at least a qualitative identification, and in isolated cases gives a definitive identification. There are, however, a number of difficulties in relying solely on this approach.

(1) Although the sample spectra should in principle be identical to the standard spectra, minor differences are often observed in practice (Fig. 2.13). (2) Many of the components being analyzed are hydrocarbons, the mass spectra of which may display very little variation from each other, especially when the hydrocarbons are members of a homologous series. In many instances, the library search may give a qualitative identification such as a branched C_7 - C_9 alkane, or a linear, C_8 - C_{10} alkene. In other instances, a molecular formula (e.g., C_5H_{10}), but not a specific isomer, can be identified.

Fig. 2.13(a). This figure shows the difference between the experimental mass spectrum for dimethyl ether (top) and the NBS standard spectrum (bottom). Notice the slight differences at masses 46 and 47.

Fig 2.13(b). This figure shows the difference between the experimental mass spectrum for ethanol (top) and the NBS standard spectrum (bottom). Notice the slight differences at masses 20, 26-29, 46 and 47.

In addition to providing a means of separation, gas chromatography yields a retention time that is (almost always) unique to a compound. If it were possible to search a library of retention times and cross reference the results to those of a mass spectral search, a much more unambiguous identification should be possible.

Methods of describing GC retention data are well developed. The Kovats retention index system [24] relates retention time to the retention times of a homologous series of alkanes. Rohrschneider [25] expanded the retention index concept to distinguish between the contributions due to the analyte and those due to the column phase. McReynolds [26] gave a method of defining column phases in terms of a small number of parameters. Ettre summarized the salient issues of

retention index systems in an excellent series of articles [27].

Several investigators [28,29] have developed computerized table-matching programs, but they seem to rely on a large body of in-house retention data and do not appear to be of much general utility. Because retention times depend on many factors, most importantly column type, initial column temperature, and temperature programming rate, it is a challenging problem to develop a system that can predict retention times from a small amount of experimental data. The issue is further complicated by the experimental difficulty in reliable and accurate measurement of retention data. Rijks, et al. [30] have developed an algorithm that uses isothermal data compiled at two different temperatures to predict retention temperatures (and thus retention times) under temperature-programmed conditions. Although this algorithm can be used only on column phases for which experimental data are available, it is nevertheless extremely attractive. Sadtler (Sadtler Research Laboratories, Philadelphia, PA) is developing a program* to implement the Rijks algorithm, but it is still in the early stages of development, and suffers from a relatively small (<3000 compounds) library of retention data.

The most rigorous means of identification is comparison of both the mass spectrum and the retention time of an

*Sadtler GCI program for Microsoft Windows. We have been evaluating a pre-release version of this program.

unknown to those of known compounds whose data were obtained on our system. Naturally, to make a valid comparison of the retention times, the knowns and the unknowns would need to be analyzed under identical temperature-programming conditions.

2.7 Calibration

2.7.1 Preparation of Calibration Standards

The cryotrap is designed to process gaseous samples, and consequently any calibration standards used must be gaseous. Standards are prepared as follows: Several three-millimeter diameter glass beads are placed in a one-liter glass bulb equipped with two stopcocks, one at each end, and a side septum. The glass beads provide a means of agitating the sample inside the bulb to ensure homogeneity. The bulb is purged several times with helium, and the stopcocks closed such that the bulb is filled with helium. There is no reason that other gases could not be used, although it is preferable not to use molecular-oxygen-containing gases, as repeated exposure to oxygen may damage the heated transfer lines. Helium is especially convenient because it does not condense at liquid nitrogen temperature. One-microliter quantities of liquids are injected into the bulb through the septum. The one-microliter of liquid to one-liter of gas dilution is such that the concentration in the gas phase, in $\text{ng}/\mu\text{l}$, is equal to the liquid density, in g/cm^3 . To ensure that the injected samples are fully vaporized, the following

criterion has been adopted: the vapor pressure of the standard at 0°C must be greater than ten times the partial pressure that would result if the injected sample is fully vaporized. Vapor pressures are calculated from tabulated data [31]. A list of compounds that have been used as calibration standards, with some of their vapor pressure data, is shown in Table 2.6.

Table 2.6

Calibration standards used for the cryotrap/GC/MS system. Because of their low vapor pressures, undecane and dodecane are rarely used.

Compound	normal bp (K)	liquid density (g/cm ³)	<u>vapor pressures</u>	
			at 0C (Torr)	at 25C (Torr)
n-pentane	309.2	0.626	183.0	511.5
methyl chloride	313.0	1.317	144.5	429.8
methylal	315.0	0.888	130.4	397.6
acetone	329.2	0.79	70.2	231.1
methanol	337.7	0.791	30.5	127.2
n-hexane	341.9	0.659	45.3	151.1
carbon tetrachloride	349.9	1.584	33.4	114.4
ethanol	351.4	0.789	12.1	59.2
isopropanol	355.4	0.786	7.7	43.5
n-heptane	371.6	0.684	11.3	45.5
iso-octane	372.4	0.692	13.1	49.4
n-octane	398.8	0.703	2.9	13.9
n-decane	447.3	0.73	0.2	1.4
n-undecane	469.1	0.74	0.054	0.44
dodecane	489.5	0.748	0.015	0.14

To inject standards into the cryotrap, a septum was installed in the side-arm of a 1/4" Swagelok union tee (Swagelok, Solon, OH), which is installed immediately out-

side of the valve oven. A sample gas, usually either helium or argon/ethane, is flowed through the system. One or more injections of the gaseous sample are made into the septum. In all other aspects, the procedure is identical to a standard cryotrapping cycle.

2.7.2 Calibration Response

There is some concern that the response of the cryotrap to a pulse input of condensible species (as from an injection) may be different from the response to a continuous input (as would be expected when running a proportional tube). Calibration results measured when multiple (up to seven) injections were made over a period of several minutes revealed no evidence of any difference in response.

The most accurate calibration standards are the heavier hydrocarbons (C_7 and larger). Smaller hydrocarbons (C_5 and smaller) have a considerably lower response, particularly when ethane is present in the main sample gas. This result may be due to preferential solvation of these components by the ethane rather than by the column phase. Calibration curves for two standards (n-heptane and n-decane) are shown in Fig. 2.14. It is an interesting coincidence that the quantitative response of the mass spectrometer to these two compounds is virtually identical. Standards with hydroxyl groups (i.e., alcohols) are usually not readily detected unless present above a threshold amount of approximately 150 ng. This threshold is thought to be due to the presence

of active (e.g., metal) sites in the system, quite possibly the cryotrap. It is known that alcohols are particularly sensitive to active sites; indeed, the Grob test of column efficiency, for example, is a particularly rigorous test for active sites.

A possible improvement to the cryotrap might be to replace the nickel tube currently in use with glass-lined stainless steel tubing or with fused silica-lined stainless steel tubing (e.g., SilcoSteel, Restek, Bellefonte, PA). The SilcoSteel, because it is more flexible and, according to the manufacturer, more inert, would probably be the better choice. It is unclear, however, whether either of these lined tubings could withstand repeated cycling to the extreme temperatures used in the cryotrapping system.

Calibration Plot for n-HEPTANE
(Peak Area of Sample) vs (Amount of Sample Injected)

Fig 2.14(a). Calibration plot for n-heptane showing a linear fit of peak area vs. nanograms of sample. Also shown is the one-standard-deviation range.

Calibration Plot for n-DECANE
(Peak Area of Sample) vs (Amount of Sample Injected)

Fig 2.14(b). Calibration plot for n-decane showing a linear fit of peak area vs. nanograms of sample. Also shown is the one standard-deviation-range.

2.8 Interference with Chromatograms

In many instances in which long lengths of tubing, particularly plastic tubing, are used upstream of the cryotrap, a structure frequently appears in the chromatograms in the 1000-1200 scan region. This structure interferes with early-eluting compounds, resulting in lack of knowledge of quantity and chemical character of eluents in this region. As shown in Fig. 2.15, there is considerable reason to believe that water is largely responsible for this peak. Close inspection reveals that the peak starts at 0°C, and thus likely corresponds to the melting of an accumulation of ice. Icing and plugging of capillary cold traps used for analysis of air samples has been reported [13,15]; the severity of

this problem is directly related to the humidity of the sample. In our system, hygroscopic filters (Supelco OMI-1, Supelco, Bellefonte, PA) on the carrier gas and/or sample gas lines have eliminated this problem. An especially wet gas supply bottle may have been the source of much of the water. A related, but essentially harmless, manifestation of water interference is shown in Fig. 2.16.

Fig. 2.15. This chromatogram shows the total ion response (top) and the m/z -18 ion response that is characteristic of water (bottom). The correlation between the large structure (top) and water (bottom) is evident.

100% = 17935

SVEN99 Sep-12-1989

Fig. 2.16. This chromatogram shows a distinct glitch in the baseline (top) that is correlated with water (bottom). This glitch does not interfere with interpretation of the chromatogram.

When ethane (or another hydrocarbon) is present in the sample gas and the cryotrap is not purged with helium before the transfer, the resulting chromatogram will be unreliable. The ethane elutes in a large "solvent" peak, but it "masks" the other components so that they are visible only if present above some threshold, which, unfortunately, fluctuates in an as-yet undetermined manner. This effect is not understood at present, but may be similar to what Grob calls a "matrix" effect [32], wherein a large concentration of high-boiling materials ("dirt") causes a reduction in the absolute peak areas of late-eluting compounds. Grob states that a 10% concentration of "dirt" can result in an 80% reduction in peak areas [33]. No interference due to water has been observed when the cryotrap is not purged.

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3 Results

Qualitative results that demonstrate the viability of the system described in chapter 2 as a method of investigating the plasma chemistry of wire chambers are presented in this chapter. Unpublished results of attempts to induce aging in 50% argon + 50% ethane are described in Appendix C. Publications detailing (1) preliminary analyses of the reaction products in a proportional tube effluent, and (2) anode wire aging results, both done in conjunction with the present work, are abstracted in Appendices D and E, respectively.

The beneficial effects of adding oxygen or oxygenated compounds to wire chamber gases were discussed in Chapter 1. These effects include reducing the aging rate and suppressing self-sustained discharges. In particular, Danilov, et al. [1] reported that 0.2% of water in propane reduced both the aging rate and the inception period for Malter breakdowns by about one order of magnitude; this result suggested that oxygen may act to inhibit polymer growth in wire chambers. It was also noted that oxygenated compounds do not generally undergo plasma polymerization [2]. With these results in mind, we investigated the effect of removing oxygen and water from the chamber gas by means of

hygroscopic filters and observed the resulting product-distribution effects.

3.1 Aging Tests

We mention here two instances in which oxygen/water were shown to prevent Malter breakdowns in aging tests. The techniques used to collect aging data have already been described [3].

The first test involved a straw tube operating with several different gas mixtures including (1) 80% Freon 14 (CF_4) + 20% isobutane, (2) 90% CF_4 + 10% dimethyl ether, and (3) 50% argon + 50% ethane. Malter breakdowns occurred virtually instantaneously for all three gases when stainless steel tubing was used as the gas supply tubing. The Malter breakdowns could be suppressed in two ways, however: (1) by continuing to use the stainless steel tubing but by bubbling the gas through water at a temperature appropriate to add 500-1000 ppm of water to the gas (the concentration of water was determined by assuming that the gas exiting the bubbler was saturated with water at the temperature of the bubbler), or (2) by substituting nylon (Nylo-Seal, Imperial Eastman, Manitowoc, WI) tubing for the stainless steel. In all cases, returning the stainless steel or the Nylo-Seal caused the Malter breakdown to resume or to be suppressed, respectively. These results were recently quoted by Va'vra [4].

To confirm this result, a second test was run in which the gas was filtered to remove oxygen and water. Two aging

tests using Nylo-Seal tubing were run simultaneously from a single cylinder of 50% argon + 50% ethane. The gas was split into two streams, one of which was routed through a Supelco OMI-1 filter (Supelco, Bellefonte, PA), which removes oxygen and water to a level of ~50 ppb. Copper tubing was used downstream of this filter since it is impermeable to air. (The copper tubing was verified to be free of water outgassing by analyzing its outgas components with the cryo-trap.) All other conditions in these two tests were as identical as possible.

As shown in Fig. 3.1, the proportional tube that was using unfiltered gas exhibited virtually no aging and did not experience a Malter breakdown. The wire running on the filtered gas, however, experienced a Malter breakdown within 30 mC/cm of accumulated charge. There were two brief periods in which the breakdown was suppressed, however. The first occurred when the filter reached its maximum capacity, and the second occurred when the used filter was removed from the plumbing. We suspect that in both cases the oxygen/water level in the gas increased sufficiently to suppress the breakdown. That this effect was only temporary may be attributed to the presence of very heavy coatings on the wire and/or the cathode wall.

Fig. 3.1(a). Aging test (RUN285) with unfiltered gas. A Malter breakdown did not occur. A simultaneous test with filtered gas is shown in Fig. 3.1(b).

Fig. 3.1(b). Aging test (RUN286) showing effect of filtering the gas to remove oxygen and water. A Malter breakdown began at 30 mC/cm of collected charge. The filter ran out at point A. The used filter was removed from the plumbing at point B.

3.2 Reaction Products

Analysis of the products in the proportional tube effluent revealed a correlation between the identity and concentration of the products and the presence of an oxygen/water filter. This correlation is in general agreement with the above-noted aging test results. Without a filter, the products had lower molecular weights and included more oxygenated compounds. With a filter, the product distribution was skewed towards higher-molecular-weight compounds and the number of oxygenated compounds was reduced. The effects of removing oxygen and water were investigated in several different gases. Details are given below.

3.2.1 Experimental

Analyses of the reaction products in the proportional tube effluent were performed using the apparatus described in Chapter 2. The 10 mCi ^{55}Fe line source described in section 2.3.7 was used as the source of ionizing radiation. An attempt was made to maintain a constant current in all tests, but this was difficult. The current tended to fluctuate and there were fairly frequent occurrences of Malter breakdowns. Currents, voltages and incidences of Malter breakdowns are summarized in Appendix B.

In all cases, the gas flowrate was approximately $20\text{ cm}^3/\text{min}$. Cryotrapping was normally done for 15 minutes; this time is also noted in Appendix B. All other cryotrapping control parameters were set at their default val-

ues, which are listed in section 2.4. Cryotrapping temperatures depended on the type of sample gas used and were set as follows: methane, -80°C ; ethane, -70°C ; propane, -30°C ; isobutane, 0°C .

All gases used in these tests were supplied by Matheron Gas Products, Newark, CA. Grades and compositions of the gases were: methane, CP grade; argon/methane, 80% HP argon + 20% CP methane; ethane, CP grade; argon/ethane, 50% HP argon + 50% CP ethane; propane, instrument grade; argon/isobutane, 25% argon + 75% isobutane, unknown grades.

A DB-5 capillary column of 30 m length, 0.25 mm ID, and $0.25\text{ }\mu\text{m}$ phase thickness was used for these analyses. The GC temperature program was a ramp to 250°C at $10^{\circ}\text{C}/\text{min}$ after an initial three-minute hold at -50°C . The helium carrier gas pressure was 15 psig. Retention times and positions in the chromatograms are referred to in scans; the duration of one scan is one-half second.

Identification of chromatographic peaks was done by comparison of their mass spectra to results of mass-spectral library searches. Mass spectra of the peaks identified in this chapter are shown in Appendix A.

3.2.2 Chromatographic Background

To determine the normal chromatographic background, a test was run by flowing 50% argon + 50% ethane through the proportional tube in the absence of high voltage and ionizing radiation. As shown in Fig. 3.2, the only peaks of note

occur before scan 210. These peaks (described below) are artifacts of the cryotrapping system. Similar tests in which only the high voltage was applied or in which only ionizing radiation (^{55}Fe source) was present gave virtually identical results. The same dependence on high voltage and ionizing radiation was observed for all other gas mixtures tested.

There are several peaks and a high baseline in the 1-200 scan region of Fig. 3.2. The peaks are from carbon dioxide; the high baseline is due primarily to nitrogen and oxygen. The carbon dioxide peaks are probably produced by a phenomenon similar to that described in section 2.5.1. Carbon dioxide is observed in all analyses and is presumed to come from air leaks. The duration of the high baseline corresponds to the dead time of the GC column. During the cryofocusing stage, noncondensable species are distributed throughout the column and therefore cannot be resolved into distinct peaks. These species elute instead as one wide peak, which appears as a high baseline. (Samples that are analyzed by the GC travel the entire length of the column and must therefore have retention times greater than or equal to the column dead time.)

The two large peaks in the 200-210 scan region are carbon dioxide and ethane that were condensed in the focus spray. The ethane is a residue of the argon/ethane that was flowed through the cryotrap. (With the exception of methane, which is not detected readily by the mass spectrometer, all

hydrocarbons that are primary components of the sample gas are observed in the background analysis.)

Except where explicitly stated otherwise, all subsequent chromatograms in this chapter depict analyses of the proportional tube effluent when the high voltage was applied and the ^{55}Fe source was present, so that current was being drawn to support a plasma discharge in which chemical reactions can potentially occur.

Fig. 3.2. (Figure on page 131.) Chromatogram showing normal background and artifacts of the cryotrapping system. This analysis used filtered argon/ethane. The vertical scale is the total ion response of the mass spectrometer.

100% = 160,000 ARCON/ETHANE (50/50), FILTERED, BACKGROUND ANALYSIS

UVEN30

100% = 160,000

UVEN30

100% = 160,000

UVEN30

100% = 160,000

UVEN30

3.2.3 Ethane

There is a plethora of reaction products when filtered argon/ethane (Fig. 3.3) or filtered ethane (Fig. 3.4) is used. As shown in these figures, the major reaction products occur in the 1900-2900 scan region. The maximum peak intensities occur at scan 2100, although this is not clearly depicted in the figures. As discussed in section 2.6, unambiguous identification of hydrocarbons by their mass spectra is difficult. Most of these compounds can, however, be identified as methyl-branched alkenes with 8-13 carbon atoms (i.e., there is evidence of gas-phase polymerization). Identification of specific molecular formulae or configurational isomers is virtually impossible without comparison to standards, but is probably unnecessary for a qualitative understanding of the reaction mechanisms. Table 3.1 shows tentative identities of selected peaks; these identifications are representative of the types of products formed.

Although the higher-molecular-weight reaction products observed when using filtered ethane are very similar to those produced when using filtered argon/ethane, there appear to be some differences in the relative intensities of peaks in the 1200-1800 scan region. Whether these differences are due to the presence of argon or, rather, are due to changes in the plasma chemistry caused by variations in pressure, power density, etc., is not clear at present, and this issue is still under investigation.

The reaction products of the unfiltered argon/ethane are shown in Fig. 3.5. Most notable is that the maximum of peak intensity has shifted dramatically towards shorter retention times: the bulk of the products occur in the 900-1400 scan region, indicating that these products are collectively of considerably lower molecular weight than those produced when the gas is filtered. Identities of the major products are shown in Table 3.2; reliable mass-spectral identification is possible in this case because the molecules are smaller and their mass spectra more distinct. The major peaks are low-molecular-weight alkenes, specifically butylenes, pentenes, and hexenes, but some alcohols are observed as well. It should be noted that these small alkenes (and to a lesser extent the alcohols) are also produced when the gas is filtered. Indeed, retention times (and hence identities) of all peaks for both the filtered and the unfiltered gases are identical; it is only their relative intensities that change. That oxygenated compounds (i.e., alcohols) should be produced when the gas is not filtered is in accordance with expectations that small concentrations of additives in the gas phase can change greatly the plasma chemistry [5].

The unfiltered ethane used in these analyses had a sufficiently high concentration of water that chromatographic interference (see section 2.8) was usually experienced. Because there was only one test (Fig. 3.6) in which the 1200-1800 scan region was not obscured by water interfer-

ence, comparisons and conclusions could not be made. The identifiable peaks in Fig. 3.6 are, however, identical to those produced by reactions of unfiltered argon/ethane. The labeled peaks are identified in Table 3.2.

Table 3.1

Tentative identification of some products formed by reaction of filtered argon/ethane and of filtered ethane. Peak numbers refer to the labeled peaks in Figs. 3.3 and 3.4. Although tentative, these identifications are qualitatively correct and represent the type of species produced in the discharge. Mass spectra of the numbered peaks are shown in Appendix A.

peak	scan	product
1	949	2-pentene isomer
2	987	pentadiene isomer
3	1035	2-pentene isomer
4	1272	hexene isomer
5	1374	hexene isomer
6	1891	dimethyl heptane
7	1940	trimethyl hexene
8	1959	trimethyl pentane
9	1974	trimethyl hexene
10	2029	trimethyl hexene
11	2088	methyl heptene
12	2115	dimethyl octene
13	2171	dimethyl octene
14	2203	methyl nonene
15	2237	decene isomer
16	2244	substituted cyclopentane (C ₁₀)
17	2291	trimethyl pentene
18	2320	tetramethyl hexene
19	2348	methyl decene
20	2375	isobutylene trimer
21	2448	substituted cyclohexane (C ₉)
22	2609	trimethyl nonene
23	2848	tetradecene isomer

Table 3.2

Major products formed by reaction of unfiltered argon/ethane and of unfiltered ethane. Peak numbers refer to the labeled peaks in Figs. 3.5 and 3.6. It is possible that one of the hexene isomers is actually a dihydro-methyl-furan (C_5H_6O). Mass spectra of the numbered peaks are shown in Appendix A.

peak	scan	product
-	505	butylene isomer
1	945	pentene isomer
2	970	ethanol
3	1035	pentene isomer
4	1118	t-butanol
5	1270	hexene isomer
6	1303	2-butanone
7	1308	hexene isomer
8	1333	hexene isomer
9	1338	hexene isomer
10	1372	hexene isomer

Fig. 3.3. (Figure on page 137.) Chromatogram showing reaction products of filtered argon/ethane. The vertical scale is the total ion response of the mass spectrometer. Notice that the 0-600 scan region is not shown. Numbered peaks are identified in Table 3.1.

Fig. 3.4. (Figure on page 138.) Chromatogram showing reaction products of filtered ethane. The vertical scale is the total ion response of the mass spectrometer. Notice that the 0-600 scan region is not shown. Numbered peaks are identified in Table 3.1.

Fig. 3.5. (Figure on page 139.) Chromatogram showing reaction products of unfiltered argon/ethane. The vertical scale is the total ion response of the mass spectrometer. Notice that the 0-600 scan region is not shown. Notice also that the vertical scale differs in the four segments. Numbered peaks are identified in Table 3.2.

Fig. 3.6. (Figure on page 140.) Chromatogram showing reaction products of unfiltered ethane. The vertical scale is the total ion response of the mass spectrometer. Notice that the 0-600 scan region is not shown. Numbered peaks are identified in Table 3.2.

100% = 1,300,000 ARGON/ETHANE (50/50), FILTERED

UVEN29

100% = 1,300,000

UVEN29

100% = 1,300,000

UVEN29

100% = 1,300,000

UVEN29

100% = 1,120,000 ETHANE, FILTERED

UVEN71

TOT

100% = 1,120,000

UVEN71

TOT

100% = 1,120,000

UVEN71

TOT

100% = 1,120,000

UVEN71

TOT

140

100% = 110,000 ETHANE, UNFILTERED

UVEN65

100% = 110,000

UVEN65

100% = 110,000

UVEN65

100% = 110,000

UVEN65

3.2.4 Propane

Most noticeable about the proportional-tube reaction products of propane is that there are so few of them. This is especially interesting considering the large number of products formed by reaction of ethane, and may therefore indicate that different reactions dominate the chemistry of the two gases.

Reaction products from unfiltered propane (shown in Fig. 3.7 and Table 3.3) include three groups: alcohols, hexenes, and heptenes. All of these products occur in the 1000-1700 scan region. As with the products from ethane that eluted in this region, these products are of sufficiently low molecular weight that reliable mass-spectral identification can be made. Relative peak heights among each group were reproducible in all tests, but relative peak heights between groups were not reproducible. Hexenes (perhaps produced by a dimerization reaction of propane) were always the most abundant group, however. It is interesting to note that production of hexenes and heptenes from propane represents an absolutely and relatively lower degree of polymerization than was observed with ethane.

In an attempt to increase the oxygen content of the gas, a three-inch segment of Nylo-Seal tubing was inserted into the gas supply line to permit diffusion of atmospheric oxygen into the gas. No differences in the reaction products were observed as a result of this action. It is possible, however, that the concentration of oxygen introduced by dif-

fusion through this segment was insufficient to alter noticeably the plasma chemistry. A longer length of Nylo-Seal (4 ft) caused water interference that obscured the relevant scan region of the chromatogram, making it impossible to determine whether or not product-distribution changes had occurred.

When the propane was filtered (Fig. 3.8), there was a general trend towards higher-molecular-weight alkanes with longer retention times, and peaks in the 1800-2400 scan region were always seen, although reproducibility both of specific peaks and of relative peak areas was poor. Two generalizations can be made, however. (1) The alcohol peaks at scans 1092 and 1290 are reduced greatly in magnitude when the gas is filtered, and (2) there is a definite, albeit poorly reproducible, indication of higher-molecular-weight species being produced when the gas is filtered. These results are consistent with those observed for ethane.

Table 3.3

Products formed by reaction of propane. Peak numbers refer to the labeled peaks in Figs. 3.7 and 3.8. Mass spectra of the numbered peaks are shown in Appendix A.

peak	scan	compound	products w/out filter	products with filter
1	202	carbon dioxide	BKG	BKG
2	257	propane	BKG	BKG
3	1004	propylene oxide	Y	N
4	1092	2-propanol	Y	N
5	1271	hexene isomer	Y	Y
6	1290	1-propanol	Y	N
7	1311	hexene isomer	Y	N
8	1335	hexene isomer	Y	Y
9	1375	hexene isomer	Y	Y
10	1482	heptene isomer	Y	Y
11	1576	heptene isomer	Y	Y
12	1648	heptene isomer	Y	Y

Fig. 3.7. (Figure on page 145.) Chromatogram showing reaction products of unfiltered propane. The vertical scale is the total ion response of the mass spectrometer. Numbered peaks are identified in Table 3.3. The peaks that elute before scan 200 are from carbon dioxide; they and the high baseline are artifacts of the cryotrapping system (see section 3.2.2).

Fig. 3.8. (Figure on page 146.) Chromatogram showing reaction products of filtered propane. The vertical scale is the total ion response of the mass spectrometer. Notice that peaks appear in the 1800-2400 scan region. Numbered peaks are identified in Table 3.3. The peaks that elute before scan 200 are from carbon dioxide; they and the high baseline are artifacts of the cryotrapping system (see section 3.2.2).

100% = 63,000 PROPANE, UNFILTERED

UVEN82

100% = 63,000

UVEN82

100% = 63,000

UVEN82

100% = 63,000

UVEN82

100% = 190,000 PROPANE, FILTERED

UUVEN76

100% = 63,000

UUVEN76

100% = 190,000

UUVEN76

100% = 190,000

UUVEN76

3.2.5 Isobutane

Like propane, there are very few reaction products from isobutane. Typical chromatograms of the major reaction products from both filtered and unfiltered isobutane are shown in Figs. 3.9 and 3.10, respectively. Many of the peaks (including products, background components, and contaminants) in these figures are identified in Table 3.4. It should be noted that the contaminants could not be detected in the filtered gas, probably because insufficient time was allowed for the filter to saturate.

The products observed from the filtered gas are primarily hydrocarbons, although three peaks appear to be oxygenated compounds. Most of the products occur in the 2900-3050 scan region and appear to have 11-13 carbon atoms. One peak (scan 2960) can be assigned to the isobutylene trimer; this seems reasonable in view of the fact that a butylene isomer (scan 505) is also a major product. It is likely that this isomer is isobutylene rather than one of the linear butylenes because the structures of isobutane and isobutylene are so similar. Mass-spectral data suggests that many of these hydrocarbons are highly methyl-branched, consistent with the expectation that isobutylene forms methyl-branched polymers.

When the gas is not filtered, all major products contain oxygen. Pentadiene is the only product in this case that does not contain oxygen, and it is present at small concentrations. All oxygenated products are of lower molecu-

lar weight than the hydrocarbons formed by reactions in the filtered gas, consistent with the observed chromatographic and mass spectrometric patterns for ethane and propane.

Table 3.4

Products formed by reaction of argon/isobutane. Peak numbers refer to labeled peaks in Figs. 3.9 and 3.10. Mass spectra of the numbered peaks are shown in Appendix A.

peak	scan	products with filter	products without filter	background contaminants
-	505	butylene isomer		
1	950	pentene isomer		
2	985	pentadiene		
3	1040	C ₄ aldehyde		
4	1055	methylal		
5	1185	unidentified		
6	1395	unidentified.....		unidentified
7	1635	heptene isomer		
8	1645	C ₆ /C ₇ ether		
9	1825	C ₅ -C ₆ ketone		
10	1870	hexenone isomer		
11	1935	C ₆ methyl ether		
12	2050	xylene		
13	2240	branched C ₉ alkane		
14	2255	octene isomer		
15	2375	octene isomer		
16	2395	C ₈ -C ₁₀ alcohol		
17	2615	octene isomer		
18	2900	C ₁₁ alkane		
19	2955	C ₁₁ alkane		
20	2960	isobutylene trimer		
21	2985	C ₁₁ -C ₁₂ alkene		
22	2990	branched C ₁₂ alkene		
-	3000	branched C ₁₂ alkene		
-	3040	branched C ₁₂ alkene		

Fig. 3.9. (Figure on page 150.) Chromatogram showing reaction products of filtered argon/isobutane. The vertical scale is the total ion response of the mass spectrometer. Notice that the 1-600 scan region is not shown. Notice also that the 2400-3000 scan region is shown with a larger vertical scale. Numbered peaks are identified in Table 3.4.

Fig. 3.10. (Figure on page 151.) Chromatogram showing reaction products of unfiltered argon/isobutane. The vertical scale is the total ion response of the mass spectrometer. Notice that the 1-600 scan region is not shown. Numbered peaks are identified in Table 3.4.

100% = 110,000 ARGON/isoBUTANE (25/75), FILTERED

UVEN57

100% = 110,000

UVEN57

100% = 110,000

UVEN57

100% = 220,000

UVEN57

100% = 360,000 ARGON/isoBUTANE (25/75), UNFILTERED

UVEN61

TOT

100% = 360,000

UVEN61

TOT

100% = 360,000

UVEN61

TOT

100% = 360,000

UVEN61

TOT

3.2.6 Methane

The discharge products formed from argon/methane display an anomalous behavior among the gases discussed here: there is no discernible shift to lower molecular weight products when the gas is not filtered. For both filtered and unfiltered gases, the products are largely hydrocarbons, as expected, but there are also some oxygenated compounds. Like ethane (but unlike propane and isobutane), there are many products formed by reactions in argon/methane.

Methane (without argon) was also used in these tests, but it was heavily contaminated with aromatic compounds (benzene, toluene, and xylenes) and with C₇-C₁₁ alkanes. A chromatogram showing a background analysis of this contaminated methane is shown in Fig. 3.11 and an accompanying list of some of the identifiable contaminants is shown in Table 3.5. Because the contaminants and the reaction products of methane eluted in the same region, it was not possible to make good comparisons or conclusions regarding the exact nature of the products.

Table 3.5

Background contaminants in unfiltered methane. Peak numbers refer to the labeled peaks in Fig. 3.11. Mass spectra of the numbered peaks are shown in Appendix A.

peak	scan	compound
1	1483	benzene
2	1606	heptane
3	1788	toluene
4	1879	trimethyl hexane
5	1962	ethyl cyclohexane
6	2033	ethyl benzene
7	2054	xylene isomer
8	2111	xylene isomer
9	2127	tetramethyl pentane
10	2356	undecane
11	2569	methyl decane
12	2769	dodecane

Fig. 3.11. (Figure on page 155.) Chromatogram showing background contaminants in unfiltered methane (i.e., no reactions occurring in the proportional tube). The vertical scale is the total ion response of the mass spectrometer. Notice that the 1-600 scan region is not shown. Numbered peaks are identified in Table 3.5.

100% = 2,100,000 METHANE, UNFILTERED, BACKGROUND ANALYSIS

UVEN51

100% = 2,100,000

UVEN51

100% = 2,100,000

UVEN51

100% = 2,100,000

UVEN51

Typical chromatograms of the products of filtered and unfiltered argon/methane are shown in Figs. 3.12 and 3.13, respectively, and an accompanying list of representative products is shown in Table 3.6. It is interesting to note that the products formed by methane are generally of lower molecular weight than those formed by ethane. For methane, the most abundant products occur in the 1200-1800 scan region, while for ethane the most abundant products occur in the 1900-2900 scan region. That methane forms lighter products than does ethane is consistent with the notion that methane is a smaller monomer than ethane and that assemblage of polymers from methane should be more difficult. Since methane has only one carbon atom, little ethylene or acetylene, which are known to polymerize readily in low-pressure rf discharges [6], may be produced.

The apparent insensitivity of the chemistry of methane to the concentration of oxygen/water almost certainly indicates that different reactions dominate the polymerization of methane than dominate the polymerization of its larger homologs.

Table 3.6

Representative products formed by reaction of argon/methane. Peak numbers refer to the labeled peaks in Figs. 3.12 and 3.13. Mass spectra of the numbered peaks are shown in Appendix A.

peak	scan	compound	products w/out filter	products with filter
1	202	carbon dioxide	BKG	BKG
2	253	propylene	Y	Y
3	504	butylene isomer	Y	Y
4	949	pentene isomer	Y	Y
5	965	acetone	Y	Y
6	1036	pentene isomer	Y	Y
7	1075	2-propanol	Y	Y
8	1271	hexene isomer	N	Y
9	1335	C ₆ ether	Y	Y
10	1375	hexene isomer	Y	Y
11	1519	branched C ₇ ether	Y	Y
12	1610	C ₇ ether	Y	Y
13	1715	C ₈ /C ₉ alkane	N	Y
14	1795	C ₈ /C ₉ aldehyde	Y	Y
15	1805	C ₈ /C ₉ alcohol/ether	Y	Y

Fig. 3.12. (Figure on page 159.) Chromatogram showing reaction products of filtered argon/methane. The vertical scale is the total ion response of the mass spectrometer. Numbered peaks are identified in Table 3.6. The peaks that elute before scan 200 are from carbon dioxide; they and the high baseline are artifacts of the cryotrapping system (see section 3.2.2).

Fig. 3.13. (Figure on page 160.) Chromatogram showing reaction products of unfiltered argon/methane. The vertical scale is the total ion response of the mass spectrometer. Numbered peaks are identified in Table 3.6. The peaks that elute before scan 200 are from carbon dioxide; they and the high baseline are artifacts of the cryotrapping system (see section 3.2.2).

100% = 235,000 ARGON/METHANE (80/20), FILTERED

UUVN42

100% = 235,000

UUVN42

100% = 235,000

UUVN42

100% = 235,000

UUVN42

100% = 180,000 ARGON/METHANE (80/20), UNFILTERED

UVEN41

3.3 Discussion

3.3.1 Oxygen

The observed reaction products display similarities in the different gases tested. Alcohols and alkenes are common products. There is a shift towards production of higher-mass products when the gas is filtered to remove oxygen and water. A possible explanation for this result is that oxygen and/or water act as chain transfer agents in the gas phase.

Oxygenated products are observed even when the gas is filtered. This can be attributed to the (atmospheric) air background; sources include diffusion through tubing, outgassing from walls, surface oxides, and leaks too small to be detected. Naturally, there would be some oxygen even in the absence of these sources: no filter is perfect.

That alcohols are usually beneficial additives to wire chambers may be explained by the presence of oxygen: it may not matter in what form the oxygen is added. This suggests that other small oxygenated additives (e.g., aldehydes, ketones, esters) may also inhibit polymer formation.

It is obvious that any polymer deposited on a wire (or any other surface) will not be detected in these analyses. We may reasonably presume, however, that the product distribution will be such that increased higher-mass product abundances are indicative of increased polymer deposition. In this case, the results shown here strongly suggest that oxygen and/or water acts to inhibit polymer growth in the wire chamber environment.

3.3.2 Alkenes

Alkenes are a product class normally expected from plasma chemistry, and could be formed by recombination (coupling) reactions of the type

or by disproportionation reactions of the type

Obviously, the ability to detect hydrogen would permit clearer elucidation of the occurrence of reaction (3.1). Hydrogen cannot be detected by the current system configuration for two reasons, however. (1) The cryotrap will not concentrate compounds with boiling points lower than that of the sample gas, and (2) the range of the Ion Trap mass spectrometer does not extend below 10 amu. Different types of detectors, such as flame-ionization or thermal-conductivity detectors, could, however, be used to detect hydrogen. A system to detect the light gaseous products evolved during the plasma polymerization of ethane has been described [7], but this system probably would not provide the sensitivity needed for our application because it would necessitate analysis of the entire proportional tube effluent rather than only of the cryotrapped species.

An interesting comparison between the lowest-molecular-weight reaction products from argon/methane and argon/ethane can be made. As shown in Fig. 3.14 and Table 3.7, propylene is at least three times more abundant as a product from methane than as a product from ethane. This is in spite of

the higher current (11 μA vs. 4.7 μA) used in the case of the ethane and the larger mole fraction (0.50 vs. 0.20) of ethane. In general, only trace amounts of propylene are observed as a product from ethane (Figs. 3.14c and 3.14d). That propylene, with three carbons, cannot be made easily from ethane, with two carbons, may suggest that one-carbon fragments ($\text{CH}_3\cdot$ and/or $\text{CH}_2\cdot$) are either not among the major dissociation products of ethane or that they do not react readily with ethane. (It is also possible that one-carbon fragments are among the major dissociation products of ethane, but that they recombine virtually instantaneously.)

Table 3.7

Identities of peaks shown in Fig. 3.14. Mass spectra of the numbered peaks are shown in Appendix A.

<u>produced from methane</u>			<u>produced from ethane</u>		
peak	scan	compound	peak	scan	compound
1	202	carbon dioxide	7	203	carbon dioxide
2	253	propylene	8	208	ethane
3	504	butylene isomer	9	255	propylene
4	529	butane	10	505	butylene isomer
5	537	butadiene	11	595	butylene isomer
6	591	butylene isomer			

Fig. 3.14. (Figure on page 165.) Comparative chromatograms showing some reaction products of filtered argon/methane, filtered argon/ethane, and filtered ethane. The vertical scale is the total ion response of the mass spectrometer. Numbered peaks are identified in Table 3.7. The peaks that elute before scan 200 are from carbon dioxide; they and the high baseline are artifacts of the cryotrapping system (see section 3.2.2).

100% = 117,000 ARGON/METHANE (80/20), FILTERED

UVEN42

100% = 160,000 ARGON/ETHANE (50/50), FILTERED

UVEN29

100% = 100,000 ETHANE, FILTERED

UVEN65

100% = 160,000 ARGON/ETHANE (50/50), FILTERED

UVEN33

3.3.3 Malter Breakdowns

There is concern as to whether the occurrence of Malter breakdowns influences the chemistry of the discharge. It seems unlikely that the chemistry of the avalanche would be affected, since the avalanche formation process should be independent of the mechanism by which the initiating electron is produced. It is possible, however, that chemical reactions at the cathode would be influenced by the occurrence of Malter breakdowns. It is also possible that a Malter breakdown could spread along the wire and result in etching of portions of the fiberglass-epoxy feedthroughs. Because our analysis system (cryotrap) agglomerates all reaction products in the proportional tube effluent, either of these two eventualities would affect the observed product distribution. The chemistry could also be affected by any changes in current density that might be caused by Malter breakdowns. It has not been possible thus far to determine definitively whether or not Malter breakdowns influence the chemistry in the proportional tube. There does not appear to be any general correlation between the observed products and the occurrence of Malter breakdowns, however.

References

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4 Summary and Conclusions

4.1 Summary

The wire chamber aging problem is very complex and the mechanisms of aging phenomena are only partially understood. With careful and directed analysis, however, it should be possible to describe qualitatively the dominant chemical reactions that cause aging.

Studies of wire aging have been largely trial-and-error experiments aimed at discovering satisfactory sets of operating conditions. Indeed, part of our experimental procedure is to continue this line of investigations by performing accelerated aging tests. These tests are useful both to identify conditions that might be used in full-scale wire chambers and to identify for further study conditions that cause rapid aging.

To understand better the plasma-chemical reactions thought to be responsible for wire aging, we have constructed a system to allow systematic and detailed study of the plasma reactions occurring in wire chambers. A proportional counter tube irradiated by an ^{55}Fe source is used as a model wire chamber. Condensible trace species in the proportional tube effluent are concentrated by several orders of magnitude in a cryotrap to provide the sensitivity

needed for detection and identification; separation and analysis are performed by gas chromatography/mass spectrometry. By correlating wire aging rates with the reaction products in the proportional tube effluent, it is hoped that the dominant reactions responsible for wire aging can be identified and appropriate measures taken to prevent polymer deposits in full-scale wire chambers.

4.2 Conclusions

The system described in Chapter 2 has been used successfully to detect and identify many reaction products in the effluent from a proportional tube. Several different gases were tested and their reaction products analyzed. A large number of reaction products were observed for methane and ethane, but very few were observed for propane and isobutane. It was determined that the presence of oxygen and/or water in ethane, propane, or isobutane (but not methane) influenced the product distribution: oxygen caused the products to be of generally lower molecular weights. Low-molecular-weight alcohols were produced in much greater abundances when the gas was not filtered to remove water and oxygen. The hydrocarbon products when the gas was filtered were mostly methyl-branched alkanes and alkenes with 7-13 carbon atoms. These results are in agreement with results from low-pressure rf-discharge plasma chemistry. These results also suggest that oxygenated compounds may retard

polymer growth in wire chambers, and so should be considered as potential additives to the chamber gas.

Several examples of the types of mechanistic information that might be deduced from these analyses were presented.

4.3 Future Work

Several still-unresolved issues were mentioned earlier, including the effect of argon on the plasma chemistry of hydrocarbon gases, the effect of Malter breakdowns on the chemistry, and the role of oxygenated species other than alcohols and water in wire chambers. Investigations into these issues are continuing.

The role of oxygen can be investigated in terms of both its concentration and its chemical form. By adding higher (and better-known) concentrations of oxygen (probably by using the permeation device), we can study how reaction rates scale with oxygen concentration. By adding different oxygenated species (e.g., O_2 , H_2O , alcohols, ketones, NO_x , etc.), we can study the effects of bond hybridization and bond strength.

Two gases that cause extremely rapid aging (49.5% argon + 49.5% ethane + 1% ammonia and 50% argon + 40% Freon 14 (CF_4) + 10% oxygen) are known. Silicone oil vapors at the 10 ppb level are also known to cause rapid aging. Other gases (e.g., 50% argon + 50% ethane and 80% CF_4 + 20% isobutane) cause very little aging. It will be interesting to

analyze the reaction products from these sets of gases to gain insight into the different reactions that so drastically influence aging rates.

Surface analyses will be used to provide information regarding the extent of wire coatings and their composition. This information will be used in conjunction with information derived from analyses of the gas-phase products to help elucidate mechanisms.

Using the permeation device, we plan to introduce halogenated compounds into the chamber gas. Halogens are known to catalyze the plasma polymerization of hydrocarbons, and it will be interesting to determine whether the same is true in wire chambers.

Appendix A

Mass Spectra

Mass spectra of the numbered peaks in the chromatograms in chapter 3 are shown here. To suggest its identity, each spectrum is accompanied by a possible match. The matches are not to be interpreted as definitive identifications. Rather, they are to be viewed as suggestions as to the qualitative nature of the unknown. Each match is described by three numbers: purity, fit, and reverse fit (rfit). Each of these numbers has a value between 0 and 1000, corresponding to a complete mismatch and a perfect match, respectively.

The fit measures the extent to which the standard spectrum is included in the unknown spectrum. The reverse fit measures the degree to which the unknown spectrum is included in the standard spectrum. The purity measures the degree to which each spectrum is included in the other (i.e., it incorporates both the fit and the reverse fit).

As a general guideline, a purity of 900 or higher indicates that the two compounds have closely related mass spectra and therefore similar structures. A purity of 600-900 indicates that the two compounds have similar fragment ions and therefore share important structural features. A purity of less than 600 suggests either that the two compounds are dissimilar or that the chromatographic peak

was incompletely resolved (i.e., the unknown spectrum is actually a combination of two or more mass spectra).

Each spectrum is identified by the chromatogram that it came from and by the peak identity number used in the table and figure(s).

Following are mass spectra of the numbered peaks (1-23) of Table 3.1 and Figs. 3.3 and 3.4. These pertained to analyses of the reaction products of filtered argon/ethane and filtered ethane. These spectra came from chromatogram file UVEN29.

100% UVEN29, PEAK 1

100% 2-PENTENE, (E)-

Formula: C₅H₁₀.

Purity 872

Fit 935

Rfit 872

100% UVEN29, PEAK 2

100% 1,3-PENTADIENE, (Z)-

Formula: C₅H₈.

Purity 771

Fit 929

Rfit 799

100% UVEN29, PEAK 3

100% 2-PENTENE, (Z)-

Formula: C₅H₁₀.

Purity 830

Fit 911

Rfit 843

100% UVEN29, PEAK 4

100% 1-PENTENE, 2-METHYL-

Formula: C₆H₁₂.

Purity 845

Fit 916

Rfit 861

100% UVEN29, PEAK 5

100% 2-PENTENE, 3-METHYL-, (2)-

Formula: C₆H₁₂.

Purity 812

Fit 959

Rfit 826

100% UVEN29, PEAK 6

100% HEPTANE, 3,3-DIMETHYL-

Formula: C₉H₂₀.

Purity 896

Fit 974

Rfit 896

100% UVEN29, PEAK 7

100% 2-HEXENE, 2,5,5-TRIMETHYL-

Formula: C₉H₁₈.

Purity 812

Fit 946

Rfit 812

100% UVEN29, PEAK 8

100% PENTANE, 2,3,4-TRIMETHYL-

Formula: C₈H₁₈.

Purity 714

Fit 856

Rfit 724

100% UVEN29, PEAK 9

100% UVEN29, PEAK 10

100% UVEN29, PEAK 11

100% UVEN29, PEAK 12

100% UVEN29, PEAK 13

100% 3-OCTENE, 2,6-DIMETHYL-

100% UVEN29, PEAK 14

100% 4-NONENE, 3-METHYL-, (2)-

100% UVEN29, PEAK 15

100% 1-DECENE

100% UVEN29, PEAK 16

100% CYCLOPENTANE, 1-METHYL-3-(2-METHYLPROPYL)-

100% UVEN29, PEAK 17

100% UVEN29, PEAK 18

100% UVEN29, PEAK 19

100% UVEN29, PEAK 20

100% UVEN29, PEAK 21

100% CYCLOHEXANE, 1-ETHYL-1-METHYL-

100% UVEN29, PEAK 22

100% 1-NONENE, 4,6,8-TRIMETHYL-

100% UVEN29, PEAK 23

100% 3-TETRADECENE, (E)-

Following are mass spectra of the numbered peaks (1-10) of Table 3.2 and Figs. 3.5 and 3.6. These pertained to analyses of the reaction products of unfiltered argon/ethane and unfiltered ethane. These spectra came from chromatogram file UVEN23.

100% UVEN23, PEAK 1

100% 2-PENTENE

Formula: C₅H₁₀.

Purity 750 Fit 843 Rfit 750

100% UVEN23, PEAK 2

100% ETHANOL (ACN)

Formula: C₂H₆O.

Purity 786 Fit 871 Rfit 825

100% UVEN23, PEAK 3

100% 2-BUTENE, 2-METHYL-

Formula: C₅H₁₀.

Purity 697 Fit 787 Rfit 704

100% UVEN23, PEAK 4

100% 2-PROPANOL, 2-METHYL-

Formula: C₄H₁₀O.

Purity 813 Fit 918 Rfit 825

100% UVEN23, PEAK 5

100% 1-PENTENE, 2-METHYL-

100% UVEN23, PEAK 6

100% 2-BUTANONE

100% UVEN23, PEAK 7

100% 2-PENTENE, 3-METHYL-, (E)-

100% UVEN23, PEAK 8

100% 1-BUTENE, 2,3-DIMETHYL-

100% UVEN23, PEAK 9

100% FURAN, 2,3-DIHYDRO-3-METHYL-

Formula: C₅H₈O.

Purity 752

Fit 908

Rfit 787

100% UVEN23, PEAK 10

100% 2-PENIENE, 4-METHYL-, (E)-

Formula: C₆H₁₂.

Purity 748

Fit 915

Rfit 756

Following are mass spectra of the numbered peaks (1-12) of Table 3.3 and Figs. 3.7 and 3.8. These pertained to analyses of the reaction products of unfiltered and filtered propane. These spectra came from chromatogram file UVEN82.

100% UVEN82, PEAK 1

100% UVEN82, PEAK 2

100% UVEN82, PEAK 3

100% UVEN82, PEAK 4

100% UVEN82, PEAK 5

Formula: C6.H12.

Purity 857

Fit 921

Rfit 873

100% UVEN82, PEAK 6

Formula: C3.H8.O.

Purity 814

Fit 898

Rfit 838

100% UVEN82, PEAK 7

Formula: C6.H12.

Purity 894

Fit 964

Rfit 823

100% UVEN82, PEAK 8

Formula: C6.H12.

Purity 796

Fit 927

Rfit 836

100% UVEN82, PEAK 9

100% UVEN82, PEAK 10

100% UVEN23, PEAK 11

100% UVEN82, PEAK 12

Following are mass spectra of the numbered peaks (1-22) of Table 3.4 and Figs. 3.9 and 3.10. These pertained to analyses of the reaction products of unfiltered and filtered argon/isobutane. Most of these spectra came from chromatogram file UVEN57; several came from chromatogram file UVEN61.

100% UVEN57, PEAK 1

100% 1-BUTENE, 3-METHYL-

Formula: C_5H_{10} .

Purity 728

Fit 825

Rfit 739

100% UVEN61, PEAK 2

100% 1,3-BUTADIENE, 2-METHYL-

Formula: C_5H_8 .

Purity 792

Fit 949

Rfit 792

100% UVEN57, PEAK 3

100% PROPANAL, 2-METHYL-

Formula: C_4H_8O .

Purity 662

Fit 745

Rfit 739

100% UVEN61, PEAK 4

100% METHANE, DIMETHOXY-

Formula: $C_3H_8O_2$.

Purity 875

Fit 883

Rfit 961

100% UVEN57, PEAK 5

100% UVEN57, PEAK 6

100% UVEN57, PEAK 7

100% UVEN61, PEAK 8

100% UVEN57, PEAK 9

Formula: $C_5H_{10}O$.

Purity 754

Fit 823

Rfit 772

100

100% UVEN57, PEAK 10

Formula: $C_5H_{10}O$.

Purity 846

Fit 961

Rfit 856

120

100% UVEN61, PEAK 11

Formula: $C_5H_{12}O$.

Purity 421

Fit 804

Rfit 463

120

100% UVEN61, PEAK 12

Formula: C_8H_{10} .

Purity 916

Fit 995

Rfit 916

100

100% UUVEN57, PEAK 13

100% PENTANE, 3-ETHYL-2,3-DIMETHYL-

Formula: C₉H₂₀. Purity 655 Fit 868 Rfit 701

100% UUVEN57, PEAK 14

100% 1-HEXENE, 5,5-DIMETHYL-

Formula: C₈H₁₆. Purity 726 Fit 896 Rfit 726

100% UUVEN57, PEAK 15

100% 2-PENTENE, 3,4,4-TRIMETHYL-

Formula: C₈H₁₆. Purity 740 Fit 927 Rfit 644

100% UUVEN51, PEAK 16

100% 2-OCTANOL

Formula: C₈H₁₈O. Purity 471 Fit 785 Rfit 522

100% UVEN57, PEAK 17

100% 2-PENTENE, 2,3,4-TRIMETHYL-

Formula: C_8H_{16} . Purity 739 Fit 826 Rfit 739

100% UVEN57, PEAK 18

100% OCTANE, 2,5,6-TRIMETHYL-

Formula: $C_{11}H_{24}$. Purity 659 Fit 804 Rfit 690

100% UVEN57, PEAK 19

100% DECANE, 5-METHYL-

Formula: $C_{11}H_{24}$. Purity 628 Fit 795 Rfit 681

100% UVEN57, PEAK 20

100% 1-PROPENE, 2-METHYL-, TRIMER

Formula: C_4H_8 . Purity 706 Fit 825 Rfit 706

100% DVENS7, PEAK 21

100% 1-DECENE, 8-METHYL-

Formula: C₁₁H₂₂.

Purity 693

Fit 915

Rfit 692

100% DVENS7, PEAK 22

100% 3-UNDECENE, 9-METHYL-, (E)-

Formula: C₁₂H₂₄.

Purity 756

Fit 813

Rfit 795

Following are mass spectra of the numbered peaks (1-12) of Table 3.5 and Fig. 3.11. These pertained to analyses of the background contaminants in unfiltered methane. These spectra came from chromatogram file UVEN51.

100% UVEN51, PEAK 1

100% BENZENE (ACN)(DOT)

Formula: C6.H6.

Purity 892

Fit 978

Rfit 899

100% UVEN51, PEAK 2

100% HEPTANE (DOT)

Formula: C7.H16.

Purity 907

Fit 953

Rfit 914

100% UVEN51, PEAK 3

100% BENZENE, METHYL-

Formula: C7.H8.

Purity 794

Fit 942

Rfit 817

100% UVEN51, PEAK 4

100% HEXANE, 2,3,4-TRIMETHYL-

Formula: C9.H20.

Purity 907

Fit 947

Rfit 916

100% UVEN51, PEAK 5

100% UVEN51, PEAK 6

100% UVEN51, PEAK 7

100% UVEN51, PEAK 8

100% UVEN51, PEAK 9

100% PENTANE, 2,2,3,4-TETRAMETHYL-

100% UVEN51, PEAK 10

100% UNDECANE

100% UVEN51, PEAK 11

100% DECANE, 5-METHYL-

100% UVEN51, PEAK 12

100% DODECANE

Following are mass spectra of the numbered peaks (1-15) of Table 3.6 and Figs. 3.12 and 3.13. These pertained to analyses of the reaction products of unfiltered and filtered argon/methane. These spectra came from chromatogram file UVEN42.

100% UVEN42, PEAK 1

100% CARBON DIOXIDE (ACN)

Formula: C.O2.

Purity 984

Fit 944

Rfit 954

100% UVEN42, PEAK 2

100% 1-PROPENE

Formula: C3.H6.

Purity 873

Fit 918

Rfit 877

100% UVEN42, PEAK 3

100% 1-PROPENE, 2-METHYL-

Formula: C4.H8.

Purity 876

Fit 922

Rfit 887

100% UVEN42, PEAK 4

100% 2-PENTENE, (E)-

Formula: C5.H10.

Purity 832

Fit 917

Rfit 848

100% UVEN42, PEAK 5

100% 2-PROPANONE

Formula: C_3H_6O .

Purity 765

Fit 828

Rfit 880

100% UVEN42, PEAK 6

100% 3-BUTENE, 2-METHYL-

Formula: C_5H_{10} .

Purity 831

Fit 948

Rfit 837

100% UVEN42, PEAK 7

100% 2-PROPANOL (ACN)

Formula: C_3H_8O .

Purity 862

Fit 951

Rfit 879

100% UVEN42, PEAK 8

100% 1-PENTENE, 2-METHYL-

Formula: C_6H_{12} .

Purity 895

Fit 950

Rfit 895

100% UVEN42, PEAK 9

100% 2-PENTANOL, 4-METHYL-

Formula: C6.H14.O.

Purity 766

Fit 895

Rfit 797

100% UVEN42, PEAK 10

100% 2-PENTENE, 3-METHYL-, (2)-

Formula: C5.H12.

Purity 764

Fit 932

Rfit 804

100% UVEN42, PEAK 11

100% PROPANE, 2-METHYL-2-(1-METHYLETHOXY)-

Formula: C7.H16.O.

Purity 949

Fit 980

Rfit 949

100% UVEN42, PEAK 12

100% PROPANE, 2-METHYL-1-PROPOXY-

Formula: C7.H16.O.

Purity 686

Fit 916

Rfit 789

100% UVEN42, PEAK 13

100% UVEN42, PEAK 14

100% UVEN42, PEAK 15

Following are mass spectra of the numbered peaks (1-11) of Table 3.13 and Fig. 3.14. These pertained to comparative analyses of the reaction products of filtered argon/methane, and filtered argon/ethane and filtered ethane. These spectra came from chromatogram files UVEN42 and UVEN29.

100% UVEN42, PEAK 1

100% UVEN42, PEAK 2

100% UVEN42, PEAK 3

100% UVEN42, PEAK 4

100% UVEN42, PEAK 5

100% 1,3-BUTADIENE

Formula: C₄H₆.

Purity 880

Fit 905

Rfit 896

100% UVEN42, PEAK 6

100% 2-BUTENE, (Z)-

Formula: C₄H₈.

Purity 889

Fit 931

Rfit 898

100% UVEN29, PEAK 7

100% CARBON DIOXIDE (ACN)

Formula: C.O₂.

Purity 921

Fit 954

Rfit 960

100% UVEN29, PEAK 8

100% ETHANE (DOT)

Formula: C₂H₆.

Purity 784

Fit 896

Rfit 814

100% UVEN29, PEAK 9

100% 1-PROPENE

Formula: C₃H₆.

Purity 826

Fit 848

Rfit 829

100% UVEN29, PEAK 10

100% 2-BUTENE, (Z)-

Formula: C₄H₈.

Purity 824

Fit 884

Rfit 860

100% UVEN29, PEAK 11

16% 1-BUTENE

Formula: C₄H₈.

Purity 836

Fit 893

Rfit 855

Appendix B**Summary of Datafiles**

Tables listing the datafiles and relevant conditions of the chromatograms run in conjunction with the results described in chapter 3 are included in this appendix. Column headings in the tables include: "filt," referring to the use of a Supelco OMI-1 filter to filter the gas, " ^{55}Fe ," referring to the presence of the ^{55}Fe source, "bkdn," referring to the occurrence of a Malter breakdown, and "time," referring to the length of time that the sample was cryotrapped. Other notation includes "bkg," referring to an analysis of the background components in the gas (in the absence of chemical reactions), and "water," referring to chromatographic interference caused by water (this phenomenon was described in section 2.8).

Table B.1
Methane analyses.

datafile	date	filt	⁵⁵ Fe	HV	I	bkdwn	time	other
UVEN45	3-01-90	Y	Y	2610	2.2	Y	15	
UVEN46	3-01-90	Y	Y	2730	3.7	Y	15	
UVEN47	3-02-90	Y	Y	2735	3.8	Y	15	
UVEN48	3-02-90	N	Y	2750	3.2	Y	15	
UVEN49	3-02-90	N	Y	2825	2.7	Y	15	
UVEN50	3-05-90	N	N	OFF	0	-	15	BKG
UVEN51	3-05-90	N	N	OFF	0	-	15	BKG

Table B.2
Argon/methane analyses.

datafile	date	filt	⁵⁵ Fe	HV	I	bkdwn	time	other
UVEN37	2-26-90	N	N	OFF	0	-	12	BKG
UVEN38	2-27-90	N	N	2400	3.9	Y	15	
UVEN39	2-27-90	N	Y	2200	5.1	Y	15	WATER
UVEN40	2-27-90	N	Y	2200	5.1	Y	15	
UVEN41	2-28-90	N	Y	2200	4.7	N	15	
UVEN42	2-28-90	Y	Y	2200	4.7	N	15	
UVEN43	2-28-90	Y	Y	2200	4.8	Y	15	
UVEN44	3-01-90	Y	Y	2200	5.1	Y	15	

Table B.3
Ethane analyses.

datafile	date	filt	⁵⁵ Fe	HV	I	bkdwn	time	other
UVEN62	3-12-90	N	N	OFF	0	-	15	BKG, WATER
UVEN63	3-12-90	N	N	OFF	0	-	10	BKG
UVEN64	3-12-90	N	Y	3500	2.5	Y	10	WATER
UVEN65	3-12-90	N	Y	3500	2.8	Y	10	WATER
UVEN66	3-13-90	N	Y	3500	3.3	Y	13	WATER
UVEN67	3-13-90	N	N	OFF	0	-	15	BKG, WATER
UVEN68	3-14-90	N	N	OFF	0	-	15	BKG, WATER
UVEN69	3-15-90	N	N	3500	7.7	Y	15	WATER
UVEN70	3-15-90	Y	N	OFF	0	-	15	BKG
UVEN71	3-15-90	Y	Y	3000	2.9	Y	15	
UVEN72	3-15-90	Y	Y	3000	4.0	Y	15	
UVEN73	3-15-90	Y	Y	2870	2.6	Y	15	

Table B.4
Argon/ethane analyses.

datafile	date	filt	⁵⁵ Fe	HV	I	bkdwn	time	other
UVEN23	2-07-90	N	Y	2600	7.4	Y	10	
UVEN26	2-09-90	Y	N	2520	10	Y	10	
UVEN27	2-09-90	Y	N	OFF	0	-	25	BKG
UVEN28	2-09-90	Y	N	2520	11.0	Y	12	
UVEN29	2-09-90	Y	N	2520	11.0	Y	12	
UVEN30	2-13-90	Y	N	OFF	0	-	20	BKG
UVEN31	2-13-90	Y	N	2300	5.3	Y	12	
UVEN33	2-16-90	Y	Y	2300	2.6	N	14	
UVEN34	2-16-90	N	Y	2300	2.7	N	19	
UVEN35	2-21-90	N	Y	2400	1.2	N	10	
UVEN36	2-26-90	N	Y	2500	2.0	N	10	

Table B.5
Propane analyses.

datafile	date	filt	⁵⁵ Fe	HV	I	bkdwn	time	other
UVEN52	3-05-90	N	N	OFF	0	-	15	BKG
UVEN53	3-05-90	N	N	OFF	0	-	15	BKG
UVEN54	3-05-90	N	Y	3350	0.7	N	15	
UVEN55	3-06-90	N	Y	3500	1.2	N	15	
UVEN56	3-06-90	Y	Y	3600	4.1	N	15	
UVEN74	3-16-90	Y	N	OFF	0	-	15	BKG
UVEN75	3-16-90	Y	Y	3410	2.7	Y	15	
UVEN76	3-16-90	Y	Y	3410	3.4	Y	15	
UVEN77	3-16-90	Y	Y	3410	4.1	Y	15	
UVEN79	3-24-90	N	N	OFF	0	-	15	WATER
UVEN80	3-24-90	N	N	OFF	0	-	15	BKG
UVEN81	3-24-90	N	Y	3610	1.5	N	15	Nylo-Seal
UVEN82	3-24-90	N	Y	4000	3.1	Y	15	Nylo-Seal

Table B.6
Argon/isobutane analyses.

datafile	date	filt	⁵⁵ Fe	HV	I	bkdwn	time	other
TVEN89	12-11-89	N	Y	OFF	0	-	10	BKG
TVEN90	12-11-89	N	Y	3200	2.1	N	10	
TVEN91	12-12-89	N	N	3300	2.0	Y	10	
TVEN92	12-13-89	N	Y	3250	3.2	N	10	
TVEN93	12-14-89	N	N	OFF	0	-	12	BKG
TVEN94	12-14-89	N	Y	3250	3.3	N	20	
TVEN95	12-14-89	N	Y	3250	2.6	N	20	
UVEN57	3-07-90	Y	Y	3000	1.2	N	15	
UVEN58	3-08-90	Y	Y	3400	5.0	Y	15	
UVEN59	3-08-90	Y	N	OFF	0	-	15	BKG
UVEN60	3-08-90	N	N	OFF	0	-	15	BKG
UVEN61	3-08-90	N	Y	3400	5.0	Y	15	

Appendix C

Effect of Freons on Aging

To make best use of the cryotrapping system to study the chemistry of wire aging, it would be desirable to compare the reaction products of gas mixtures that cause aging to those of gas mixtures that do not cause aging. In an attempt to find contaminants that would induce aging in 50% argon + 50% ethane, a series of tests was performed in which the permeation device (see section 2.3.8) was used to add Freons to the argon/ethane. Freons were chosen for three reasons. (1) There were previous reports that Freon 11 caused aging in dimethyl ether [1,2], and it was suspected that similar results might be found in argon/ethane. (2) Freons contain halogens, which are known to catalyze plasma polymerization of hydrocarbons in the low-pressure rf-discharge regime [3]. As suggested in section 1.4, there may be similarities between the low-pressure rf-discharge plasma regime and that of wire chambers. (3) Some Freons are very electronegative and are therefore expected to attach electrons and be drawn to the anode, where, if they do catalyze polymerization, they could most easily affect the aging rate. This possibility was discussed in section 1.6.4.3.

Aging tests were run using copper proportional tubes (shown in Fig. 2.7) strung with 50- μ m-diameter gold-plated

tungsten wires. The techniques used to collect aging data have already been described [4]. These aging tests were run only for relatively short periods in an exploratory mode, looking for large increases in the aging rates that could be seen readily. In no case was there evidence of any acceleration of aging rates. A summary of these results is provided in Table C.1.

Table C.1

Summary of aging results in which halogenated contaminants were deliberately added to 50% argon + 50% ethane. The irradiated region of the wire was 0.6 cm.

test name	additive	additive concentration	accumulated charge, mC	R, %/C/cm
RUN233	CFC1 ₃	8 ppm	23	note 1
RUN237	CHF ₂ Cl	8 ppm	90	-12.7
RUN241	CF ₂ Cl ₂	680 ppm	110	+1.0
RUN243	CH ₃ Cl	680 ppm	230	-7.1
RUN248	CH ₃ Cl	550 ppm	215	-7.4

Note 1. The current increased markedly during this test, probably due to a gradual decrease in the concentration of CFC1₃ (Freon 11) that was introduced. (The pressure of the Freon 11 in the permeation source (and therefore the permeation rate) was observed to decrease during the test.) There was no evidence of rapid aging.

A peculiar phenomenon was observed in the tests with methyl chloride (RUNS 243 and 248): periodic "spikes" in the current occurred after an inception period of approximately four days (Fig. C.1). Each spike was on the order of 20 minutes wide and had an amplitude thirty to fifty percent greater than the normal current.

Fig. C.1. Aging test with 680 ppm methyl chloride added to 50% argon + 50% ethane. Periodic "spikes" are observed. Notice that the current is shown with a suppressed zero.

By removing the source of ionizing radiation from the proportional tube and observing a nonzero current it was established that the tube was in some form of self-sustained discharge during the spikes, but that when the spike ended, so did the discharge. This suggested that the spikes were a consequence of cathode deposits.

Further attempts to reproduce this phenomenon (RUNS 277, 280, and 282) were of limited success. No spikes were observed in RUNS 277 and 280, possibly because the nylon tubing that was used for the gas supply lines allowed sufficient atmospheric oxygen to diffuse into the gas to either suppress self-sustained discharges or to prevent the polymerization presumed to have caused the cathode deposits. (RUNS 243 and 248 used copper tubing for the gas supply lines.) Copper tubing was used in RUN 282 and although spikes were observed, they were not periodic.

The mechanism of formation of the spikes is not understood at present. It should be noted, however, that similar behavior has been observed in tests that used stainless steel tubing for the gas supply lines and in which no contaminants were added to the argon/ethane (e.g., RUN 276) (see section 3.1 for further discussion).

References

- [1] I. Juricic and J. Kadyk, *IEEE Trans. Nucl. Sci.*, NS-34 (1987) 481.
- [2] M. Jibaly, P. Chrusch, G. Hilgenberg, S. Majewski, R. Wojcik, R. Weintraub, and F. Sauli, *Nucl. Instr. Meth.*, A273 (1988) 161.

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- [3] H. Kobayashi, M. Shen, and A.T. Bell, *J. Macromol. Sci., Chem.*, A8 (1974) 1345.
- [4] J. Kadyk, J. Wise, D. Hess, and M. Williams, accepted for publication in *IEEE Trans. Nucl. Sci.*, NS-37 (1990).

Appendix D

Published Results on Analysis of Reaction Products in a Proportional Tube Effluent

Results of preliminary analyses of the reaction products in a proportional tube effluent done as a prelude to the present work have recently been published [1]. This paper was presented at the 1989 IEEE Nuclear Science Symposium, San Francisco, CA, January 17-19, 1990. The abstract of the paper is reproduced below.

STUDY OF PLASMA CHEMISTRY IN WIRE CHAMBERS BY GC/MS

We have constructed an apparatus to allow systematic and detailed study of radiation-induced plasma-chemical reactions that may lead to wire aging. A proportional tube irradiated by an ^{55}Fe source is used as a model wire chamber. Less-volatile components in the tube effluent gas are concentrated by several orders of magnitude in a cryotrap to provide the sensitivity needed for detection. Separation and analysis are performed by gas chromatography/mass spectrometry. A strong signal from many products formed in the avalanche by plasma-chemical reactions has been observed.

Reference

- [1] J. Wise, J.A. Kadyk, D.W. Hess, and M.C. Williams, accepted for publication in *IEEE Trans. Nucl. Sci.*, NS-37 (1990).

Appendix E

Published Results on Anode Wire Aging

Results of anode wire aging tests done in conjunction with the present work have recently been published [1]. This paper was presented at the 1989 IEEE Nuclear Science Symposium, San Francisco, CA, January 17-19, 1990. The abstract of the paper is reproduced below.

ANODE WIRE AGING TESTS WITH SELECTED GASES

As a continuation of earlier wire aging investigations, additional candidates for wire chamber gases and wires have been tested. These include the gases: argon/ethane, HRS gas, dimethyl ether, carbon dioxide/ethane, and carbon tetrafluoride/isobutane. Wires used were: gold-plated tungsten, Stablohm, Nicotin, and stainless steel. Measurements were made of the effects upon wire aging of impurities from plumbing materials and of contamination from various types of oils. Attempts were made to induce wire aging by adding measured amounts of oxygen and halogen (methyl chloride) with negative results. Finally, the possible role of electronegativity in the wire aging process is discussed, and measurements of electronegativity are made of several single-carbon Freons, using both an electron capture detector and a wire chamber operating with dimethyl ether.

Reference

- [1] J. Kadyk, J. Wise, D. Hess, and M. Williams, accepted for publication in *IEEE Trans. Nucl. Sci.*, NS-37 (1990).