# The Influence of Age and Storage Conditions on the Activity of Carbon in Cigarette Filters

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**Summary**

The use of activated carbon in cigarette filters is now well established and the ability of activated carbon to reduce the levels of compounds in cigarette smoke is well known. It is also known that during storage the carbon in a cigarette filter tends to undergo a reduction in activity. The factors governing this change in activity are not yet fully understood. An acceptable measure of the activity of carbon to cigarette smoke is the retention of vapour phase compounds. The current study looks at the effect of age and conditions of storage on the activity of carbon in a cigarette filter.

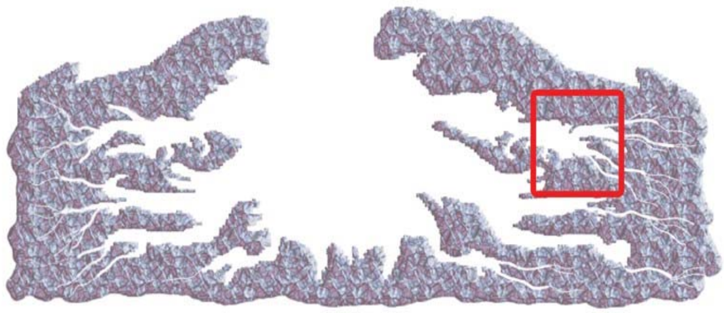
Carbon filter samples have been stored under four different conditions. These are temperature, -18C, low water content, temperature 4C, low water content, temperature 22C, 60%RH and temperature 35C, 75% RH. For each storage condition the vapour phase retention of the carbon has been measured as a function of sample age for up to six months ageing. Other important filter properties such as the hydrolysis of the plasticiser have also been studied as a function of storage temperature and age.

The effect of storage conditions on the change in activity of the carbon on storage as measured by the retention of major vapour phase aldehydes, ketones, hydrocarbons and Acrylonitrile determined using standard ISO smoking and GC analysis will be discussed. The rates of plasticiser hydrolysis as measured by the generation of Acetic acid in the filters are also discussed. Recommendations for optimum storage conditions are given.

## The Influence of Age and Storage Conditions on the Activity of Carbon in Cigarette Filters

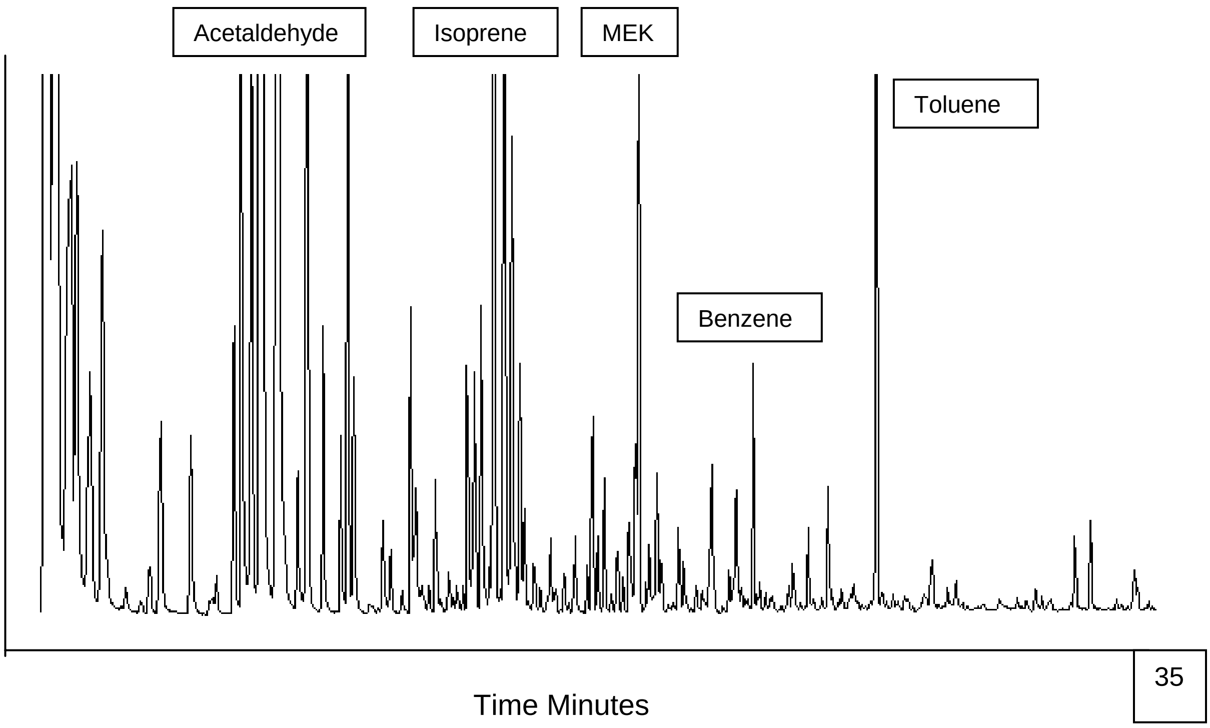
The use of activated carbon in cigarette filters is now well established and the ability of activated carbon to reduce the levels of many compounds in cigarette smoke is well known. It is now also known that the ability of carbon to remove compounds from smoke can change as it ages in a cigarette. The reasons for and extent of the change in activity are perhaps less well known and very little work has been done on the effect of storage conditions on the activity of carbon in filter rods or cigarettes. In particular, is any deactivation of the carbon caused by volatile materials from tobacco or by materials from the filter? To look at the possible difference in ageing between carbon in filter rods and carbon in cigarettes, ageing trials have been carried out by ageing the samples as assembled cigarettes and as filter rods. To measure the activity of the carbon in the filter the retention of a number of vapour phase compounds have been measured.

Activated carbon is a relatively unique adsorbent because of its extended surface area, microporous structure and high adsorption capacity. It has a large well developed internal pore structure giving it the ability to adsorb more volatile materials from smoke than other adsorbents. The molecules are retained on the surface of the carbon by non specific forces and are thus also relatively easily desorbed. Adsorption occurs when the interaction potential is equal to the work done to bring the molecule to the adsorbed state. This essentially means that for vapour phase adsorption, pores in the size range 5 to 25 Å give the greatest force of adsorption and hence retain the majority of compounds. A representation of a carbon granule is shown below:-



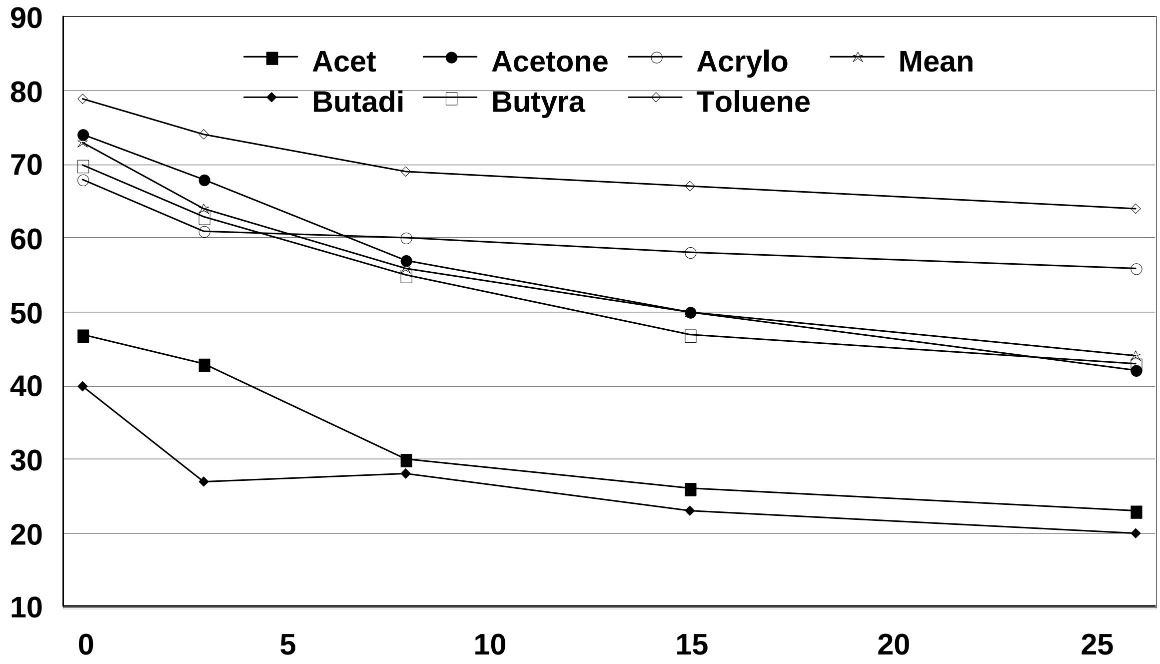
For adsorption to occur the vapour molecules diffuse via the macro and meso pores into the micropores where the majority of adsorption occurs. Despite the large surface area carbon does have a finite capacity and as the micropores fill with molecules, the capacity for further adsorption is diminished. In a filter rod carbon is exposed to a number of vapours from Triacetin, spin finish and adhesives which could cause a decrease in smoke compound reduction. Once the filters are assembled into cigarettes, further adsorption of volatile materials from the tobacco can occur which may further reduce the capability of the carbon to adsorb compounds from smoke. An interesting question is which of these possibilities causes the greater deactivation of the carbon and if it is from the filter can the way the filter is stored affect the level of deactivation.

To try to ascertain the mechanism of deactivation a comparison has been made of the performance of carbon filters when stored as assembled cigarettes and when stored as filters. For this work the measurement of vapour phase retention was used as an acceptable way of evaluating the carbon filter performance. Determination of vapour phase activity involved the smoking of 8 cigarettes per determination according to ISO standard procedures using a low dead volume linear smoking machine. The vapour phase was collected after passing through a Cambridge filter holder using a Tedlar gas sampling bag. After collection the smoke was immediately analysed using a GC equipped with a heated gas sampling valve with a 2 cm$^3$ gas sample loop and a capillary GC column. The GC conditions were column 25M x 0.25 mm ID coating Poaraplot Q with a film thickness of 8 microns. The oven was temperature programmed from 50C, held for 1 minute, to 90C at 50C per minute. The temperature was then increased at 3C per minute to 185C. A rapid temperature step of 50C per minute up to 230C held for 5 minutes then followed. Carrier gas was hydrogen with a flow rate of 2 ml/minute. The injection was split with a split flow of 10 ml/minute. The heated sampling value was held at 120C, the injector at 200C and the FID detector at 250C. Under these conditions the total run time was about 35 minutes and a typical chromatogram is shown with some of the major peaks identified.




The area's of 12 peaks were measured, 5 aldehydes – Acetaldehyde, Acrolein, Propionaldehyde, Butyraldehyde and Crotronaldehyde, 4 hydrocarbons – 1,3 Butadiene, Isoprene, Benzene and Toluene, 2 ketones – Acetone and Methyl Ethyl Ketone and Acrylonitrile.  Each result is the mean of at least three replicate determinations. To determine the retention of the filters, a control cigarette with an acetate filter was also analysed. The retention of the compound of interest was determined by the indirect calculation method. For example, the retention of Acetone was the Acetone peak area of the control cigarette minus the Acetone peak area of the test cigarette divided by the Acetone peak area of the control cigarette multiplied by 100. Although 12 compounds have been measured, to simplify the expression of results, data from six vapour phase compounds with boiling points in the range -4.5 to 111C are given in data that follows. These are 1, 3 Butadiene, Acetaldehyde, Acetone, Acrylonitrile, Butyraldehyde and Toluene. Also shown in the data is a mean vapour phase retention value which is the average percentage retention of all twelve compounds analysed.

The first experiment was carried out using assembled cigarettes. These were manufactured using a dual filter containing a 15 mm length carbon on tow filter segment with approximately 90 mg of carbon per tip. Immediately after manufacture the filters were assembled into cigarettes and stored under normal laboratory conditions of 22C and 60%RH. The cigarettes were sampled and tested for vapour phase retention using cigarettes made with an acetate filter of the same filter PD as a control cigarette. The plot, of cigarette age in weeks (x axis) against percentage retention (Y axis) shown below gives the measured retention of the six compounds and the mean value over a period of 26 weeks. From this plot it can be seen that in general carbon activity towards the higher boiling point compounds is higher and declines less over the period of the study. For example, the retention of Toluene with a boiling point of 111C is significantly higher than the retention of 1, 3 Butadiene which has a boiling point of -4.5C.



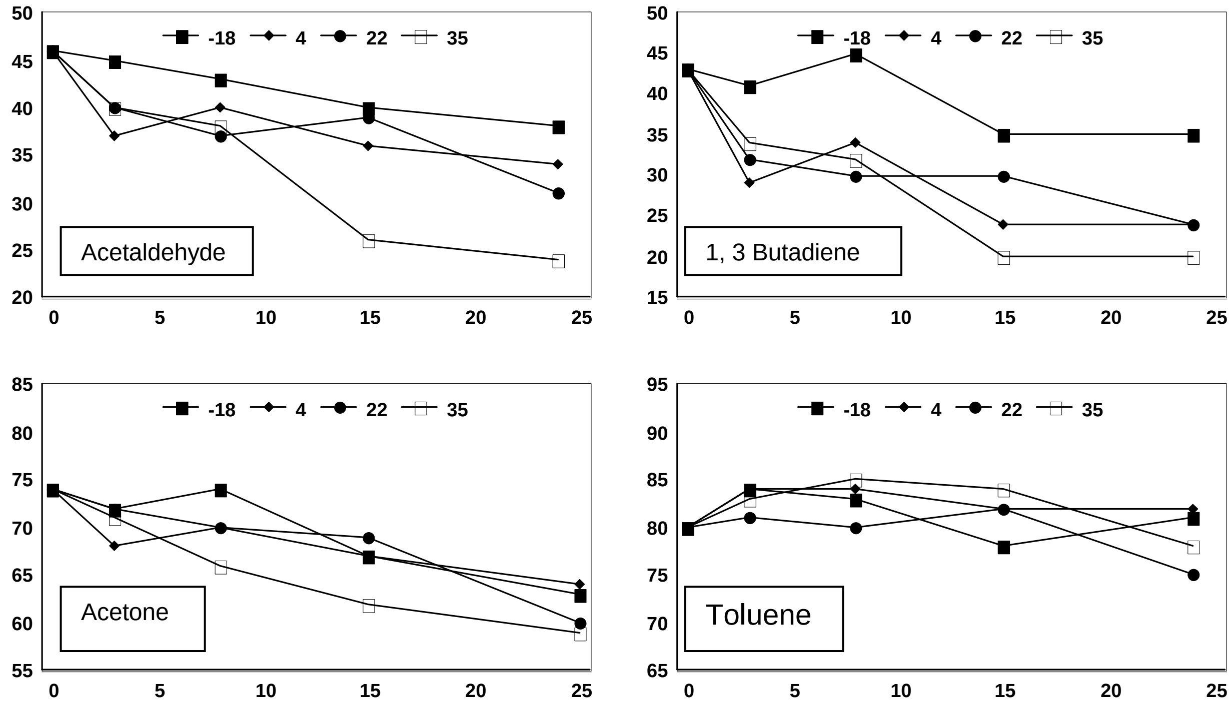

For both 1, 3 Butadiene and Acetaldehyde the retention of the compound is 50% or less than that of the initial value after 26 weeks, whereas, for less volatile compounds such as Toluene only about 20% of the initial retention is lost over the same storage period. On average, for this relatively high level of carbon the mean retention of the 12 compounds measured has fallen from 73 % to 44 % for six months storage.

Of course the main question is what actually causes this decline in the activity of the carbon with time. It is usually attributed to adsorption of volatile materials from the environment near the carbon that are more strongly absorbed than many smoke compounds. These adsorbed species block some of the active sites in the carbon and thus reduce the amount of compounds removed from smoke. But which materials actually cause the decrease in activity, are they from the filter or the tobacco or more likely a combination of both. Triacetin is often sited as one of the major causes of carbon deactivation but is this really true? If so can carbon filters be stored in a manner that would prevent or reduce the level of carbon deactivation? For the second part of our study we have looked at the change of activity in carbon filters stored as filters rather than cigarettes.

The filters used in this study were 25 mm dual filters of standard circumference with a 15 mm length segment of carbon on tow. The carbon was standard coconut shell carbon with a loading of just over 5 mg per mm of filter length to give a total loading of 80 mg carbon per tip. Immediately after manufacture the filter rods were randomised and divided into four sets of one thousand rods. These were stored in a cardboard container and placed in four different storage conditions. These were in a freezer temperature -18 C with water content around 0.53 $mg/m^3$, in a refrigerator temperature 4C with water content of 3.2 $mg/m^3$, room temperature of 22C water content 11.6 $mg/m^3$ and in an oven at temperature 35C water content 28.2 $mg/m^3$. A further sample of rods was assembled into cigarettes for initial vapour phase testing. A sample of acetate filters were also made to act as a control for the vapour phase measurements. These cigarettes were conditioned for 48 hours at 22C and 60% RH before vapour phase retention testing.

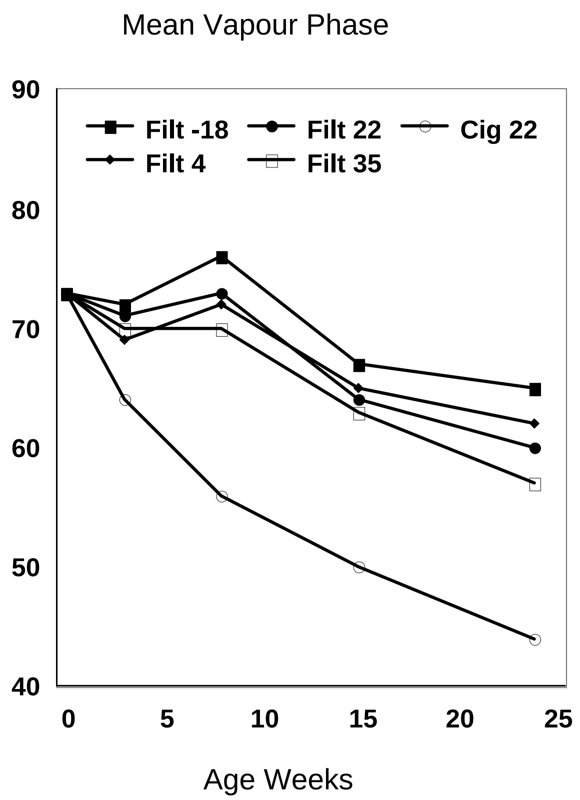
The filter rods were stored under the four different atmospheres and sampled periodically for testing. Testing was carried out after 0, 3, 8, 14 and 24 weeks storage. For each test the filters were removed from storage and allowed to come to room temperature and assembled into cigarettes. These were conditioned for 48 hours before testing. So at each age the filters were tested using cigarettes that were only 2 days old.

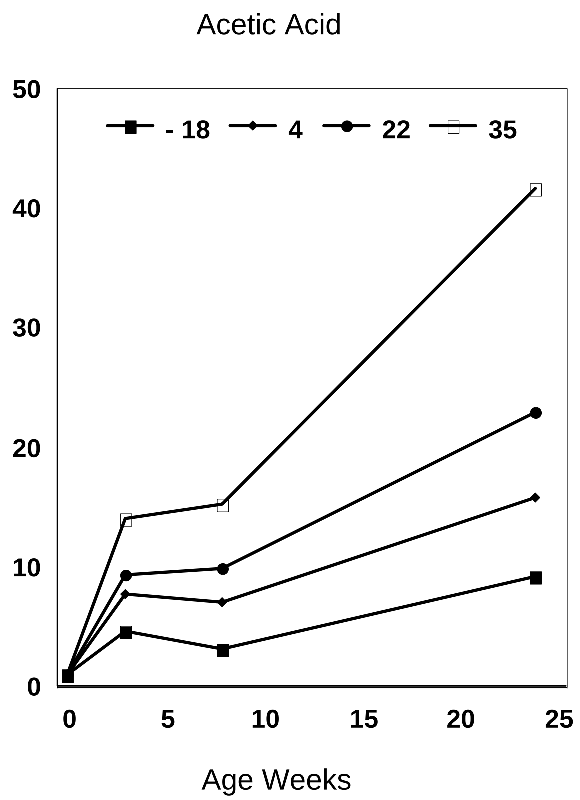
To illustrate the effect of filter storage we have plotted the retention of various compounds (Y axis percentage retention) as a function of time (x axis age in weeks) and temperature of storage. These plots are shown below. For Acetaldehyde a fall in retention as the filters age is clearly seen. It can also be seen the higher the temperature of storage of the filters the greater the decline in retention. A similar trend is seen for 1, 3 Butadiene with a similar level of retention fall for each of these two compounds. For storage at 22 C the decline in retention is less than that seen earlier for cigarette storage. Both of these compounds are relatively volatile and if we look at less volatile compounds a smaller fall in retention is seen. The first of these is Acetone where the fall in retention is quite small and again it can be seen the lower the storage temperature the smaller the effect. For compounds with higher boiling points such as Toluene the effects are negligible. Allowing for some experimental error in the results the lines for storage at -18 and 4 C could be considered to show no change and those for the higher storage temperatures only a very slight fall over the 24 week period.




Taking the average of all 12 compounds measured, as shown in the plot below again of age in weeks (x axis) against percentage retention (y axis) a small overall decline in vapour phase retention can be seen with the largest fall for the highest storage temperature and the smallest for the lowest storage temperature. At 22 C the mean vapour phase retention has fallen from 73 to 60 %. The previous data for cigarettes stored at 22 C is also shown on this plot and it can be seen that a mean vapour phase retention fall from a similar starting value to 44 % over the same time period is given. It would appear therefore that the fall in carbon activity with storage is greater for cigarette storage than for filter storage.

An important aspect of filter storage is the possible hydrolysis of the Triacetin plasticiser, initially to Glycerol Diacetate and Acetic Acid. Acetic acid of course in extreme cases can produce a characteristic vinegar smell on the filters. In theory the rate of hydrolysis is temperature dependant so that higher storage temperatures should produce higher levels of Acetic acid. The Acetic acid content of the filter rods has been measured during this experiment using a solvent extraction followed by GC analysis. The data is also shown in the plot below. The plot shows the filter age in weeks (X axis) plotted against an increase factor of Acetic acid content (Y axis) which is the value at the age of testing divided by the initial very small value. As perhaps expected it has shown that the temperature of storage has a very large effect on the Acetic acid content of the rods. The level of Acetic acid in the rods stored at 35 C is about 4.5 times higher than those stored at – 18 C after 24 weeks of storage.




Considering filter rod storage purely from the Acetic acid point of view, it can be seen that the filter should be stored at as cool a temperature as possible.

Although the complexity of this subject means that definitive conclusions cannot be drawn from a single study it appears that for carbon filters, storage as assembled cigarettes seems to give greater deactivation than storage as filters. This may mean that Triacetin is not the major factor in carbon deactivation. Which would support the hypothesis that the increased availability of more volatile compounds when carbon is in the presence of tobacco is the major factor in carbon deactivation. As levels of deactivation will depend on the initial capacity of the carbon, lower carbon weights will almost certainly deactivate to a greater degree with perhaps a higher contribution from Triacetin. In general filters stored at lower temperatures show lower deactivation on storage. As expected the higher the temperature of storage the more rapid the rate of Triacetin hydrolysis leading to higher levels of Acetic acid in the filters. To achieve minimum deactivation and Triacetin hydrolysis in storage filter rods should be stored under cool dry conditions.

Filtrona's filter performance results shown here were obtained under controlled laboratory conditions, in accordance with ISO or Filtrona test methods (details available upon request) and are stated for Filtrona's illustrative purposes only and should not be relied upon by any other person for any reason.

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