

Some Factors Affecting the Activity of Carbon in Cigarette Filters

By J Walker and Dr M J Taylor

Filtrona Technology Centre, Jarrow, UK

Summary

Previous work indicates that the ability of activated carbon to reduce compounds in cigarette smoke is reduced upon storage with greater deactivation evident when stored as cigarettes rather than as filter rods. Filters stored at lower temperatures generally exhibit less deactivation over time. Higher storage temperatures of filters appear to accelerate the rate of triacetin hydrolysis to acetic acid. Initial studies suggest the role of triacetin in the deactivation of carbon may be less significant than both storage temperature & conditions i.e. exposure to tobacco volatiles. However, as levels of deactivation will depend on the initial capacity of the carbon, different weights of carbon may have a significant effect on levels and rates of deactivation.

This second study looks at the effect of age and conditions of storage on the activity of lower carbon weight in a cigarette filter. Carbon filter samples have been stored under four different conditions. These are -18°C at low water content, 4°C at low water content, 22°C at 60%RH and 35°C at 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. The rates of plasticiser hydrolysis as measured by the generation of acetic acid in the filters are also discussed.

Some Factors Affecting the Activity of Carbon in Cigarette Filters

The ability of activated carbon to reduce compounds in cigarette smoke is reduced upon storage with greater deactivation evident when stored as cigarettes rather than as filter rods. Generally filters stored at lower temperatures exhibit less deactivation over time. Higher filter storage temperatures accelerate the rate of triacetin hydrolysis to acetic acid. Initial studies suggest the role of triacetin in the deactivation of carbon may be less significant than both storage temperature & conditions i.e. exposure to tobacco volatiles. As levels of deactivation are likely to depend on the initial capacity of the carbon, different weights of carbon may have an effect on rates of deactivation.

This work was undertaken to study the effect of lower carbon weights in a filter. Filter samples were stored at four different temperatures & periodically sampled for measurement of vapour phase activity and acetic acid content. Previous work used a high carbon loading filter with 80 mg of carbon per filter tip; current work continued the study using a filter with 45 mg carbon tip. Both filter types were 25mm long dual filters of standard circumference with a 15 mm length segment of carbon on tow. The environmental conditions for storage are detailed in Figure 1.

Storage Location	Temp. (°C)	Water Content (g/m ³)
Freezer	-18	0.53
Fridge	4	3.2
Room Temp	22	11.6
Oven	35	28.2

With increasing temperature there is greater moisture content in the surrounding air. The role of water must be considered as a factor affecting the ageing process since this will affect hydrolysis.

Figure 1 – Sample Storage Conditions

The acetic acid & vapour phase measurements were carried out as follows. The method for acetic acid analysis in filter rods involves the extraction of 10 rods by shaking in 200mL of buffered mobile phase for 3 hours. Samples are filtered through PTFE (polytetrafluoroethylene) filter media before analysis by liquid chromatography (LC) with ultra-violet detection (UV). A typical chromatogram along with LC analysis parameters can be seen in Figure 2.

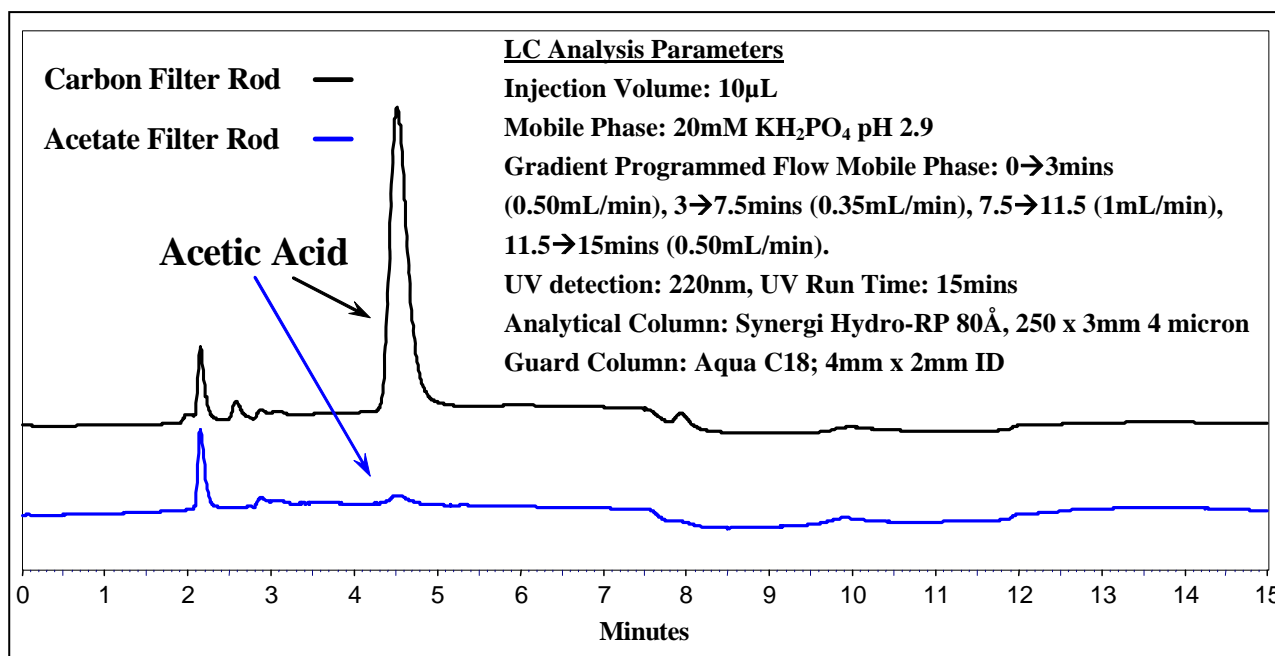


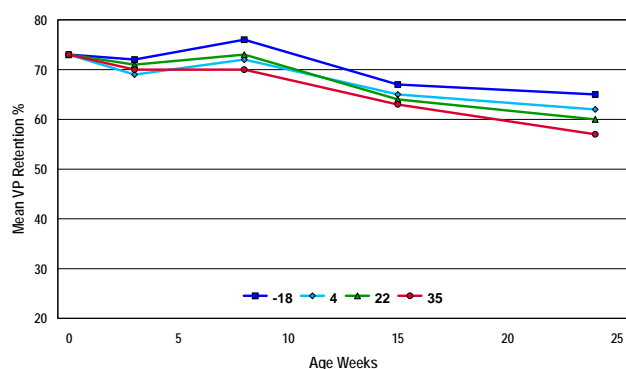
Figure 2 – Example Chromatogram & Analysis Parameters for Acetic Acid Analysis

The vapour phase analysis involved smoking 8 cigarettes with all tests performed in duplicate, thus a total of 16 cigarettes are smoked per determination. Particulate phase matter is trapped on a

cambridge filter pad with vapour phase collected in a tedlar bag & injected directly into GC. The method detects 12 compounds under the following conditions:

- GC column 25M x 0.25mm ID Poraplot Q with an 8 um film.
- Oven temperature programmed; 50 (hold 1 minute) to 90 at 50°C per minute then to 185 at 3°C/min then to 235 at 50°C/min (hold for 5 minutes)
- Carrier Gas Hydrogen column flow 2 ml/min
- Injection – split, split flow 10 ml/min
- Valve temperature 120°C, Injector temperature 200°C, Detector Temperature 250°C.

A mean is taken of the 12 smoke components listed, that is acetaldehyde, 1,3-butadiene, propionaldehyde, acrolein, acetone, acrylonitrile, isoprene, butyraldehyde, methyl ethyl ketone, crotonaldehyde, benzene & toluene. This represents the mean vapour phase retention calculated against a monoacetate control filter rod. For a more highly loaded carbon filter with 80 mg of carbon per tip a plot of mean vapour phase retention against storage time at different temperatures can be seen in Figure 3.



Distribution over the range of storage conditions can be seen with the lower temperatures displaying less reduction in retention over ageing. However, overall there appears to be little reduction in the retention of vapour phase when 80mg carbon is present in a filter.

Figure 3 - Mean Vapour Phase Retention Filter Storage 80mg Carbon

To investigate the relationship between weight of carbon and ageing for vapour phase retention this study was carried out at 45mg carbon per filter tip. Filters were tested for vapour phase retention after storage under the four conditions as assembled cigarettes & filter rods. To simplify the expression of results as well as mean values, 4 compounds were chosen from the vapour phase to represent a range of boiling points and these are shown in figure 4.

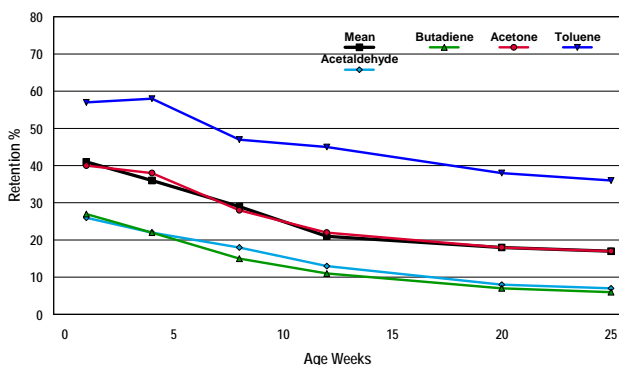
Compound	Boiling Point (°C)
1, 3-Butadiene	- 4.5
Acetaldehyde	21
Acetone	56
Toluene	111

In the plots of retention versus storage age that follow the behaviour of the mean values and these four compounds will be discussed.

Figure 4 – Compounds chosen from vapour phase for further discussion.

For storage at room temperature, as assembled

cigarettes, the mean vapour phase decreases by half from 40% retention to less than 20% after 25 weeks ageing. Figure 5 shows how acetone performs very similarly to the mean whereas toluene with greater initial retention, still follows a similar order of magnitude in reduction of retention on ageing.



The vapour phase activity of carbon towards 1,3-butadiene & acetaldehyde also undergo a very similar ageing profile (figure 5), again losing over half their initial retention after 25 weeks.

Figure 5 – Vapour Phase Retention Aged as Cigarettes

45mg Carbon

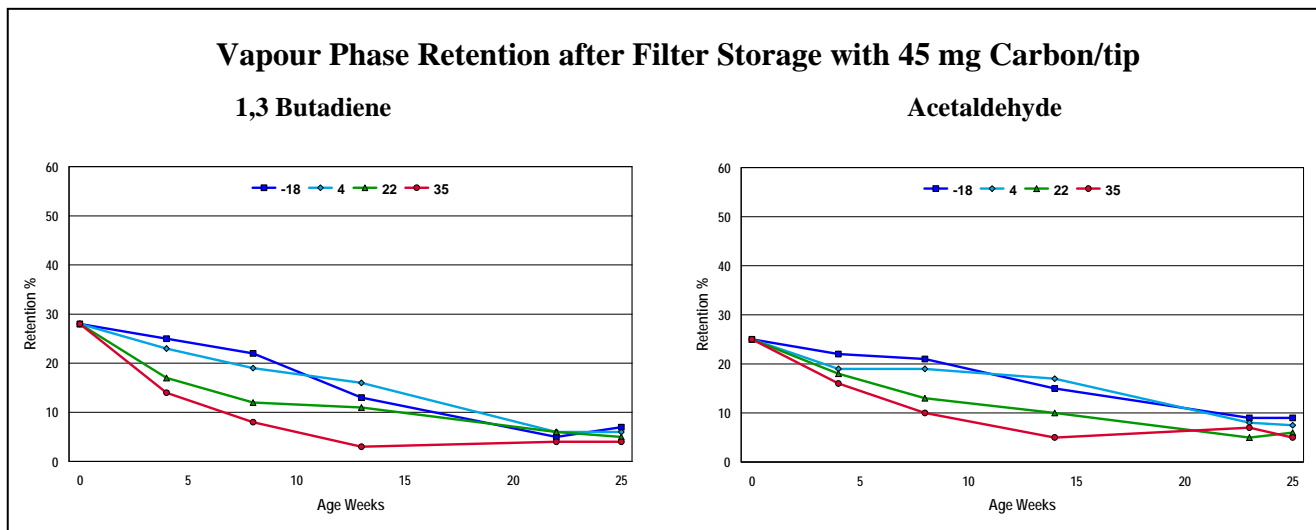


Figure 6 – 1,3 Butadiene & Acetaldehyde Retention Aged as Filters 45mg Carbon/tip

When stored as filters, as shown in figure 6, the ageing profiles of 1,3-butadiene & acetaldehyde are again very similar with lower temperature storage conditions showing greater retentions up to 13 weeks. The higher temperature storage conditions display a step initial loss of retention ability of around a half after just 4 weeks ageing. After 23 weeks ageing it appears storage temperature is no longer a significant factor and the carbon has aged to an average retention.

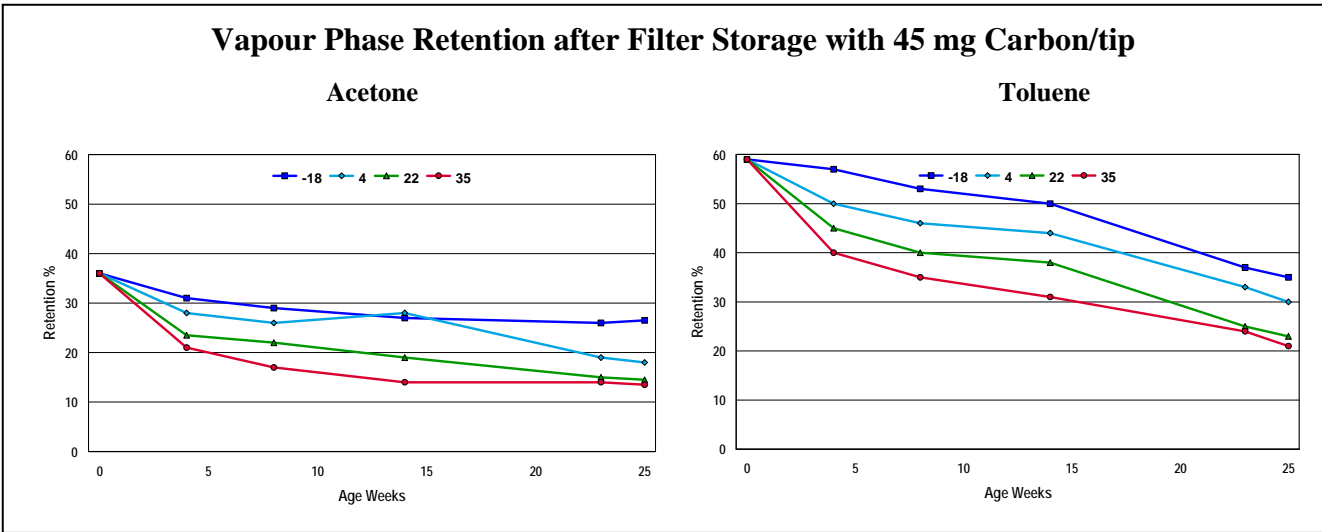
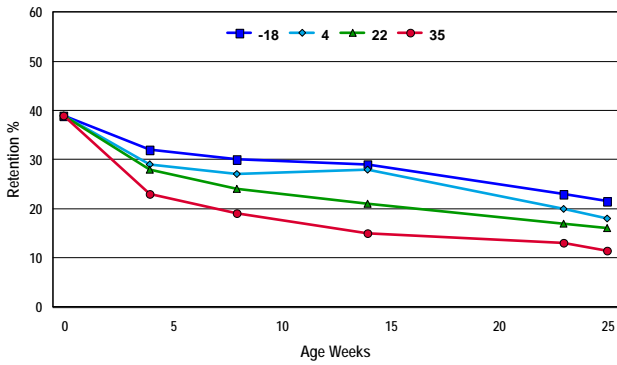


Figure 7 – Acetone & Toluene Retention Aged as Filters 45mg Carbon/tip

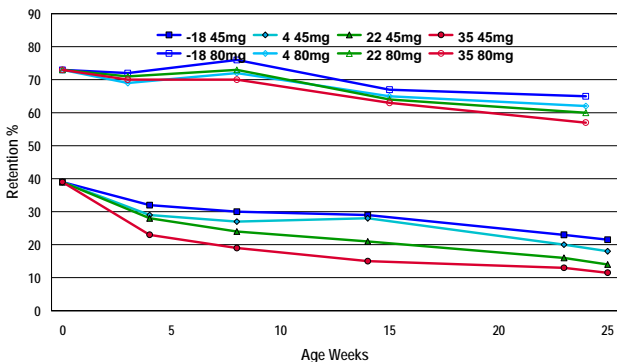
From figure 7 toluene & acetone still appear to show some difference in filter retention after 25 weeks. Acetone shows only around a 10% drop in absolute retention when stored at -18°C compared to the 20% drop when stored at 35°C . For toluene the initial retention was almost 60% which fell to 35% after 25 weeks ageing at -18°C freezer conditions compared to 22% when stored in an oven at 35°C . These two compounds remain of interest as their ageing appears to be affected by storage temperature even after prolonged periods.



The mean vapour phase retention after 25 weeks ageing indicates prolonged but diminishing effects of storage temperature on activity of 45mg carbon in a filter.

Figure 8 - Mean Vapour Phase Retention Filter Storage

45 mg Carbon/tip



A comparison between 45 & 80mg carbon per tip in figure 9 shows the more pronounced effects of storage temperature on retention when less carbon is present.

Figure 9 - Mean Vapour Phase Retention for Filter Storage 45mg vs. 80mg Carbon/tip

Vapour Phase Retention after Filter Storage 45mg vs. 80mg Carbon/tip

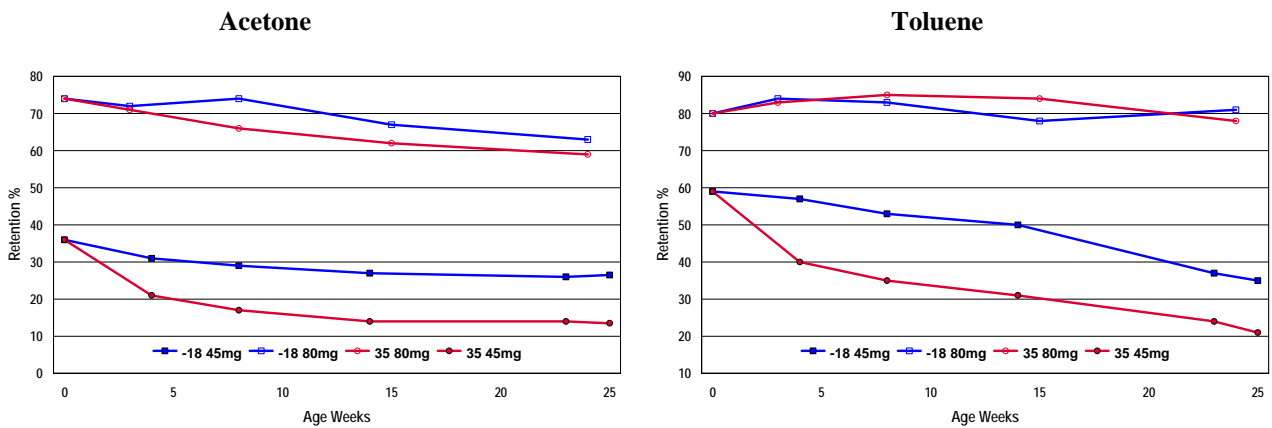


Figure 10 – Acetone & Toluene Retention for Filter Storage 45mg vs. 80mg Carbon/tip

When comparing the extremes of storage conditions in figure 10, it can be seen that there is little difference for both acetone & toluene retention after 25 weeks with 80mg/tip carbon whereas 45mg/tip indicates a lower storage temperature immediately reduces & prolongs the effects of ageing towards these compounds. For storage at room temperature, figure 11 gives a comparison of the ageing for the two carbon weights 45mg & 80mg stored as both filter rods & assembled cigarettes. The 80 mg carbon filter appears to undergo greater loss of activity when stored as an assembled cigarette. However at 45mg/tip carbon loading there appears to be no difference between filter & cigarette storage.

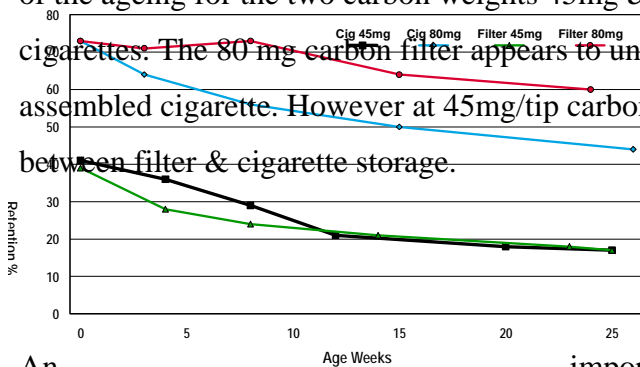


Figure 11 – Mean Vapour Phase Retention for Storage at 22°C

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. Carbon filters stored at room temperature show substantially elevated acetic acid levels compared to monoacetate filters, as seen in figure 12. Time 0 is that of filter manufacture with acetic acid extraction commencing immediately. The carbon filter has a high carbon loading with both filters containing typical triacetin levels of around 7% for the monoacetate and 5-6% for the carbon filter rods. As yet it is undetermined what proportion of acetic acid extracted from filters would be available to migrate to the rod surface & atmosphere to generate an odour.

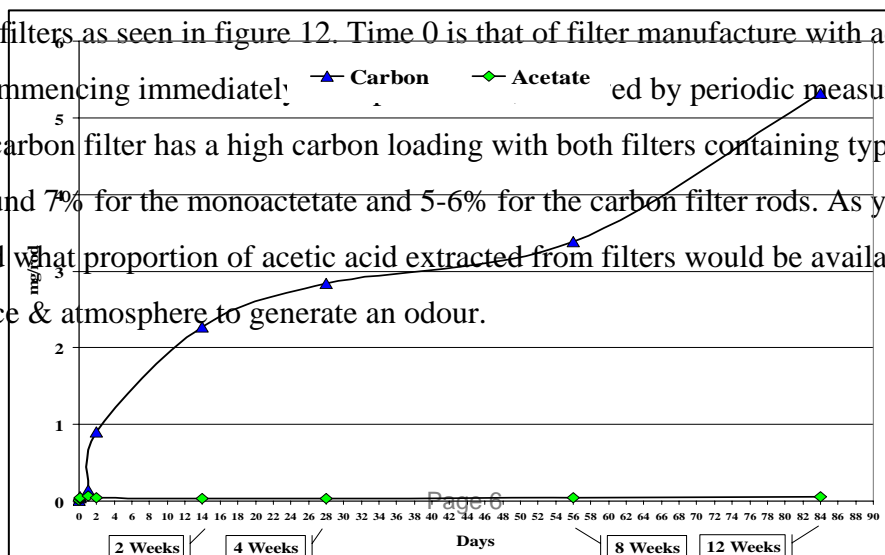


Figure 12 - Effects of Ageing on Acetic Acid in Filter Rods Stored at Room Temperature

Generation of acetic acid in filter rods and cigarettes is slowed with lower storage temperatures. Previous study data shown in figure 14, illustrates that after 24 weeks ageing filter rods with 80mg carbon stored at elevated temperatures have significantly higher levels of acetic acid than if stored under cooler conditions. The level of acetic acid in rods stored at 35°C is about 4 times higher than those stored at – 18°C after 24 weeks of storage.

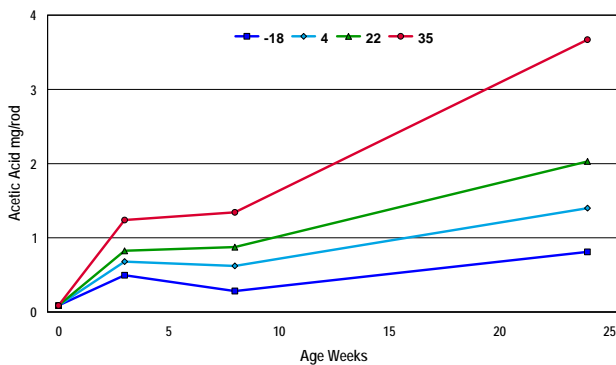


Figure 13 – Acetic Acid Content 80 mg Carbon

Filters with 80mg carbon stored at 4°C for 23 weeks show comparable acetic acid levels to storage for only 3 weeks at 35°C. It appears elevated temperatures significantly increase triacetin degradation to acetic acid.

With 45mg/tip carbon the effect of storage temperature on acetic acid levels remains significant as seen in figure 14. It does appear that between 23 to 31 weeks there is a stabilisation of acetic acid production. Filters stored at -18°C show little change from initial acetic acid levels after 31 weeks ageing whereas after 31 weeks at 35°C around 4 times more acetic acid is present. Again as storage temperature increases so does acetic acid content.

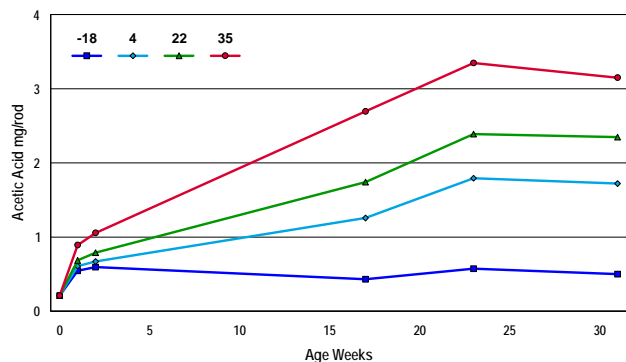
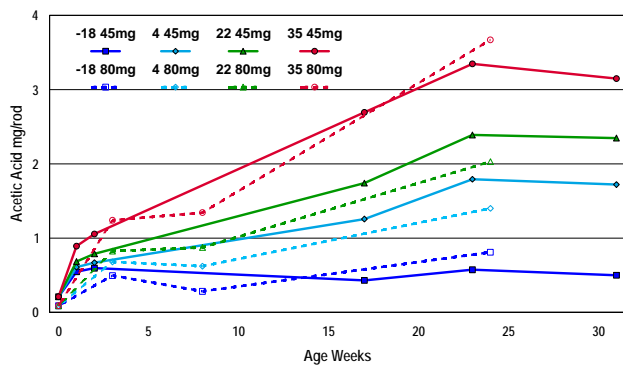


Figure 14 – Acetic Acid Content 45 mg Carbon



When acetic acid data from both lower & higher carbon weight filters is compared in figure 15 there appears little difference between carbon loadings at the individual storage conditions.

Figure 15 – Acetic Acid Content 45mg and 80 mg

Carbon

After 23 weeks there are similar levels of acetic acid generated with either 45mg or 80mg carbon per filter tip. This indicates that the weight of carbon present is not a limiting factor for hydrolysis of triacetin to acetic acid. Storage conditions appear to have the most significant effect on acetic acid generation with elevated temperatures & moisture contents being associated with increased rate of triacetin hydrolysis to acetic acid.

The effects of storage conditions on deactivation of carbon, as measured by vapour phase retention, is more pronounced when less carbon is present in a filter. For carbon filters with high loadings storage as assembled cigarettes seems to give greater deactivation than storage as filters although this effect is not evident with lower carbon loadings. This may mean that triacetin is not a major factor in carbon deactivation when there is a low ratio of triacetin to carbon. However, when the ratio of triacetin to carbon is higher the retention of vapour phase compounds can be influenced by storage conditions. It appears levels of deactivation depend on initial capacity of the carbon, lower carbon weights producing more rapid deactivation with perhaps a higher contribution from triacetin. To achieve minimum deactivation and acetic acid generation during storage, filter rods should be stored under cool dry conditions. It can be hypothesised that the excess presence of acetic acid at greater temperature storage conditions could lead to either surface chemistry modifications or salt formation due to interaction with the alkaline surface of carbon. Both these effects could reduce the ability of carbon to retain these compounds in smoke. Further work will be carried out to investigate the effects of direct exposure of tobacco volatiles and triacetin to varying weights of carbon.

REFERENCES;

1. TAYLOR M.J.; WALKER J. CORESTA Meet. Smoke Sci.–Prod. Techno. Groups, Stratford-upon-Avon, 2005. The influence of age and storage conditions on the activity of carbon in cigarette filters.

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