Chapter 2
Controlled Atmosphere Storage

Introduction

Clearly, the optimum temperature has an enormous effect on the postharvest like of fresh fruit and vegetables, but controlling the gaseous atmosphere in a store has been shown to improve the maintenance of their postharvest quality over and above the extensions gained by simply controlling the temperature and humidity. This chapter briefly reviews the effects of controlling the gases within the store and the technology that is used and puts the technology and effects in context with developments over time.

History

The effects of gases on harvested crops have been known for centuries. For example, Wang (1990) quotes a Tang dynasty eighth century poem that described how litchis were shown to keep better during long distance transport when they were sealed in the hollow centres of bamboo stems with some fresh leaves. The earliest documented scientific study of controlled atmosphere storage was by Berard (1821) who showed that fruit stored in atmospheres containing no O_2 did not ripen, but if they were held for only a short period and then placed in air they continued to ripen. In the 1850s and 1860s, a commercial cold storage company in the USA experimented with modifying the CO_2 and O_2 in an apple store by making it air tight. It was claimed that the apples were kept in good condition in the store for 11 months, but some fruit were injured; possibly by CO_2 toxicity (Dalrymple 1967). Some success was reported by Washington State University in the USA around 1903, and subsequently by others, on controlled atmosphere storage of apples, raspberries, blackberries, strawberries and loganberries. Sharples

A.K. Thompson, *Fruit and Vegetable Storage*, SpringerBriefs in Food, Health, and Nutrition, DOI 10.1007/978-3-319-23591-2_2

(1989) in his review in Classical Papers in Horticultural Science stated that "[Franklin] Kidd and [Cyril] West can be described as the founders of modern CA storage." Sharples described the background to their work and how it came about. Dalrymple (1967) in reviewing early work on the effects of gases on postharvest of fruit and vegetables stated "The real start of CA storage had to await the later work of two British scientists [Kidd and West], who started from quite a different vantage point". In 1918, the work being carried out at the Food Investigation Organisation in Cambridge was described as "a study of the normal physiology, at low temperatures, of those parts of plants which are used as food. The influence of the surrounding atmosphere, of its content of O_2, CO_2 and water vapour was the obvious point to begin at, and such work has been taken up by Dr. F. Kidd. The composition of the air in fruit stores has been suspected of being important and this calls for thorough elucidation. Interesting results in stopping sprouting of potatoes have been obtained, and a number of data with various fruits proving the importance of the composition of the air." (Anonymous 1919). Controlled atmosphere storage at low temperature of plums, apples and pears was described as "has been continuing" by Anonymous (1920) with large-scale gas storage tests on apples and pears. In 1920 a semi-commercial controlled atmosphere storage trial was set up at a farm at Histon in Cambridgeshire to test their laboratory findings in small scale commercial practice. In 1929 a commercial controlled atmosphere store for apples was built by a grower near Canterbury in Kent. Controlled atmosphere storage has continued to be used on an increasing scale, with an increasing variety of fruit and vegetables and with an increasing number of countries since that time (Thompson 2010).

Changes During Storage

The postharvest changes in fresh fruit and vegetables are affected by their postharvest environment as well as microorganism infection, the stage of their development or maturity at harvest and the conditions in which they have been grown. The changes also depend on the part of the plant or tree on which it has grown. Some vegetables are natural storage organs, for example potato tubers and onions bulbs, and their postharvest changes are different from say leaf vegetables, such as lettuce and cabbages. The postharvest requirements for fruit also can vary considerably. Fruits are often classified into climacteric and non-climacteric and, in some cases intermediate where their ripening metabolism is not clear. Climacteric fruits are those whose ripening is accompanied by an increase in respiration rate, called the climacteric rise, which is generally associated with increased ethylene production. Initiation of the climacteric rise in respiration rate is by ethylene biosynthesis and associated with other chemical and physical changes. There are more postharvest changes in climacteric fruit than in non-climacteric fruit or in vegetable. In non-climacteric fruit or vegetable, the chemical content remains similar during their postharvest life except for perhaps sugars which are utilised for metabolic

processes and therefore decrease. In climacteric fruit, there are considerable changes that we commonly refer to as ripening where the fruit develops typical flavour and aroma, changes colour (through loss of chlorophyll and synthesis of carotenoids and other pigments), changes of starch into sugars and changes in the cell wall constituents that probably contribute to softening. Cell walls are complex structures composed of cellulose and pectin, derived from hexoses including glucose, galactose, rhamnose and mannose, as well as pentoses including xylose and arabinose and some of their derivatives including glucuronic acid and galacturonic acid. The changes in aroma volatile chemicals are important since they affect the acceptability of fruit and vegetables. Controlled atmosphere storage has been shown to suppress aroma production in apples, for example the aroma levels decreased during long-term storage with those stored in 1 % O_2 having the lowest rate of aroma production compared to those stored in air (Villatoro et al. 2008). However, Fellman et al. (2000) reported that aroma levels rapidly returned to normal when they were removed from the controlled atmosphere store. There are also many changes in phytochemicals that can affect their nutritional and health promoting characteristics.

There is only limited direct evidence on the effects of hypobaric or hyperbaric storage on many chemical and nutritional changes in fruit and vegetables (these will be discussed in subsequent chapters) but the effects of controlled atmosphere storage on their quality has been more comprehensive studied. A few examples are given as follows: Van Der Sluis et al. (2001) found that controlled atmosphere storage of apples did not affect antioxidant activity differently from storage in air. Leja and Ben (2003) found that anthocyanin content of apples did not decrease during controlled atmosphere storage. There were some differences between cultivars on the effects of controlled atmosphere storage on the chemical content of the apples tested. Forney et al. (2003) compared storage of blueberries at 0 °C either in air or a range of controlled atmosphere conditions from 1 to 15 % O_2 combined with 0–15 % CO_2 and found that total phenolics decreased by 5–16 %, total anthocyanins by 8–18 % and antioxidant capacity by 4–14 % during 9 weeks storage depending on the atmosphere. Patil and Shellie (2004) found that when ultra-low O_2 levels in storage was used as a quarantine treatment for grapefruit that the levels of ascorbic acid, lycopene and β-carotene were higher than the controls. For avocado fruit Meyer et al. (2011) stated that here was no information available on the effects of controlled atmosphere storage on health-related compounds.

The flavour of fruits is partly determined by their sugar and acid content. The sugar level in fully ripe apples is mainly determined by the proportion of starch to sugar at harvest since sugar losses due to fruit respiration is no more than 10 % (Knee and Sharples 1979). However, they found that acidity could fall by as much as 50 % during storage and that there was a good correlation between fruit acidity and sensory evaluation. Controlled atmosphere storage of apples in either 2 % O_2 + 98 % nitrogen or 2 % O_2 + 5 % CO_2 + 93 % nitrogen resulted in few organic volatile compounds being produced during the storage period (Hatfield and Patterson 1974). Even when the fruit were removed from storage, they did not synthesise normal amounts of esters during ripening and esters are

a major component of their aroma and flavour. In apples and pears, butyl ethanoate, 2-methyl butyl ethanoate and hexyl ethanoate are typical flavour and aroma compounds that are synthesised during ripening while terpenoid compounds such as linalool, epoxide and α-farnesene have been shown to be synthesised in some apple cultivars (Dimick and Hoskins 1983). Leja and Ben (2003) found a large increase in total phenolics in Jonagold and Sampion apples during storage for 120 days at 1 °C in air or 2 % O_2 + 2 % CO_2 followed by 7 days at 16 °C. They actually found a slight decrease in anthocyanins during storage in air but not in the controlled atmosphere. In contrast, MacLean et al. (2006) detected no change in total phenolics of Red Delicious apples during storage for 120 days at 0–1 °C followed by 8 days at room temperature, but there was an increase in chlorogenic acid and a decrease in anthocyanins. In 'Rocha', pears stored for 4 months in 2 % O_2 + 0–5 % CO_2 at 2 °C. Goodenough and Thomas (1981) showed that tomatoes ripened in 5 % CO_2 + 5 % O_2 had suppressed chlorophyll degradation and suppressed synthesis of the carotenoids lycopene and xanthophyll. In apples reducing the O_2 level predominantly inhibited chlorophyll degradation and TA was highest in 15 % O_2 + 10 % CO_2 and 5 % CO_2 + 3 % O_2 (Ben-Arie et al. 1993). Galvis-Sanchez et al. (2006) found no differences between storage atmospheres on the phytochemical content they measured in pears, but arbutin and flavan-3-ols increased while flavanols and hydroxycinnamic acid derivatives did not change in all atmospheres they studied. Martínez-Sánchez et al. (2006) found that the total flavonoid content of wild rocket (*Diplotaxis tenuifolia*) was approximately 100 mg 100 g^{-1} fresh weight and remained constant during storage or even increased at the end of the shelf-life in 5 % O_2 + 10 % CO_2. In contrast, it was degraded in those samples kept in air and the total content of vitamin C was higher in controlled atmosphere stored samples than those kept in air. A decrease in the total antioxidant capacity was observed during storage and it was particularly marked in samples stored in air.

Jeffery et al. (1984) showed that lycopene synthesis in tomatoes was suppressed during storage in 6 % CO_2 + 6 % O_2. Rogiers and Knowles (2000) stored four cultivars of Saskatoon Serviceberry (*Amelanchier alnifolia*) at 0.5 °C for 56 days in 2, 10 and 21 % O_2 factorially combined with 0.035 or 5 % CO_2. They found that the 5 % CO_2 atmosphere combined with either 21 or 10 % O_2 was most effective at minimising losses in fruit soluble solids, anthocyanin, firmness and weight. In blueberries, controlled atmosphere storage had little or no effect on phenolic content (Schotsmans et al. 2007). Zheng et al. (2003) found that total phenolics were increased in blueberries during storage at 5 °C in 60–100 % O_2 for 35 days to a greater extent than those stored in air or 40 % O_2. In grapes, anthocyanin levels were lower after storage at 0 °C for those that had been pre-treated for 3 days in 20 % CO_2 + 20 % O_2 compared to those that had not been pre-treated (Romero et al. 2008). Storage of snow pea pods in either 2.5 % O_2 with 5 % CO_2 or 10 % CO_2 with 5 % O_2 concentrations resulted in the development slight off-flavours, but this effect was reversible since it was partially alleviated after ventilation (Pariasca et al. 2001).

Damage

When the O_2 level in storage is too low or the CO_2 level too high, the crop can be damaged. Fidler et al. (1973) reported that the appearance of CO_2 injury symptoms is a function of concentration, exposure time and temperature. They describe external CO_2 injury in apples where "initially the damaged area is markedly sunken, deep green in colour and with sharply defined edges. Later in storage the damaged tissue turns brown and finally almost black". Injury caused as a result of low O_2 levels is due to fermentation resulting in the accumulation of toxic products usually alcohols and aldehydes, which can result in necrotic tissue that tends to begin at the centre of the fruit. The lower O_2 limit for apples was found to vary between cultivar from a low of about 0.8 % for Northern Spy and Law Rome to a high of about 1.0 % for McIntosh in cold storage. For blueberries, the lower O_2 limit increased with temperature and CO_2 level. Raising the temperature from 0 to 25 °C caused the lower O_2 limit to increase from about 1.8 % to approximately 4 %. Raising CO_2 levels from 5 to 60 % increased the lower O_2 limit for blueberry fruits from approximately 4.5 to >16 % (Beaudry and Gran 1993). Wardlaw (1938) showed that high CO_2 can cause surface-scald browning, pitting and excessive decay in aubergines and these symptoms are similar to those caused by chilling injury. Mencarelli et al. (1989) described CO_2 injury of aubergines as external browning without tissue softening and showed that susceptibility to CO_2 varied between cultivars. Gadalla (1997) showed that onions stored in 10 % CO_2 developed internal browning.

Residual Effects

There is considerable evidence in the literature that storing fruits and vegetables in CA storage can affect their subsequent shelf or marketable life (Thompson 2010). For example, Bell peppers exposed to 1.5 % O_2 for 1 day exhibited suppressed respiration rate for at least 24 h after transfer to air (Rahman et al. 1993). Burdon et al. (2008) showed that avocados that had been stored in controlled atmospheres had a longer shelf-life than those that had been stored in air for a similar period. Khanbari and Thompson (1996) showed that potatoes in controlled atmosphere storage did not sprout either during storage or when they had been removed. Wills et al. (1982) showed that pre-climacteric bananas exposed to low O_2 took longer to ripen when subsequently exposed to air than fruits kept in air for the whole period.

Measurement and Control Technology

Temperature and humidity are controlled in controlled atmosphere stores in the same as those described in Chap. 1. This section therefore deals only with O_2, CO_2 and ethylene.

Carbon Dioxide and Oxygen

The original way, and one that is still in common use, to control the CO_2 and O_2 levels in a controlled atmosphere store was by constant analysis. In many systems, the level of O_2 was allowed to reduce by sealing the room and allowing O_2 level to reduce by the respiration of the fruit. When the required level was reached, it was maintained at that level by frequently introducing fresh air from outside of the store. Usually tolerance limits were set at, say, plus or minus 0.1 % so that, if say 1 % O_2 was required, when the O_2 level went down to 0.9 % air was vented until it reached 1.1 %. CO_2 level in a store will increase, again through fruit respiration, and when it reaches the required level it is removed by passing the store air through or past a chemical that will remove the CO_2 and return the air back into the store. This method of CO_2 removal is called 'active scrubbing'. Alternatively, the CO_2 removing chemical may be placed inside the store where it can keep the level generally at low levels (usually about 1 %). This method is called 'passive scrubbing'. These methods of controlling O_2 and CO_2 in controlled atmosphere stores are referred to as 'product generated', since the gas levels are produced by the crops' respiration. The time taken for the levels of these two gases to reach the optimum (especially for the O_2 to fall from the 21 % in normal air) can reduce the maximum storage life of the crop. It is common therefore to fill the store with the crop, seal the store and inject nitrogen gas until the O_2 has reached the required level and then maintain it in the way described above. Scrubbers to control CO_2 are generally classified according to the mode of absorption (i.e. chemical or physical), or to the mode of air passage through the absorbing agent. Material used in chemical removal systems includes calcium hydroxide, sodium hydroxide, zeolites (alumino-silicate minerals) and activated charcoal. Hydroxides react irreversibly with the CO_2 producing carbonates. These must be replaced by fresh hydroxides when the reaction is complete. Bishop (1990) calculated that 1 kg of calcium hydroxide will adsorb 0.59 kg of CO_2 before it needs to be replaced. Koelet (1992) calculated that for one tonne of apples, 7.5 kg of calcium hydroxide was needed every 6–10 weeks depending on which cultivar was stored. Gas removal using zeolites and activated charcoal is based on the fixing of CO_2 in a particular way, and then releasing it again on contact with the outside air. So for this method, two stage systems have been developed where store air is passed through one part of the equipment while the other part is being ventilated by fresh air. The system is then reversed and so on.

The atmosphere in many modern controlled atmosphere stores is constantly analysed for CO_2 and O_2 levels using an infra-red gas analyser to measure CO_2 and a paramagnetic analyser for O_2. The analysers are monitored and controlled by a computer. In early controlled atmosphere stores, an Orsat gas analyser was used. This ingenious analyser was patented around 1873 by H Orsat and was used by taking a sample of gas through a valve in the store wall, which was then pumped to consecutive absorption bottles where CO_2 and O_2 were absorbed separately. After absorption of the CO_2 and O_2, the volume of the remaining gas

mixture was verified, thus allowing determination of volumes. The Orsat gas analyser consists of a calibrated water-jacketed gas burette connected by glass capillary tubing to two absorption pipettes, one containing potassium hydroxide solution to absorb CO_2 and the other potassium pyrogallate solution to absorb O_2. By means of a rubber tubing arrangement, the gas to be analysed was drawn into the burette and flushed through several times. Typically, 100 ml was withdrawn for ease of calculation. Using the stopcocks that isolate the absorption burettes, the level of gas in the levelling bottle and the burette was adjusted to the zero point of the burette. The gas was then passed into the potassium hydroxide burette, left to stand for about two minutes and then withdrawn, isolating the remaining gas via the stopcock arrangements. The process was repeated to ensure full absorption. After levelling the liquid in the bottle and burette, the remaining volume of gas in the burette indicates the percentage of CO_2 absorbed. The same technique was repeated for O_2, using the potassium pyrogallate. A 100 ml gas sample will give about 0.1 % resolution. The volume of a gas, of course, varies with temperature and pressure and therefore these variables are need to be corrected. Some considerable skill was involved in making accurate measurement and in the 1970s, one of the Experimental Officers at the Tropical Products Institute in London (the late Peter Crowther) was very skilled with an Orsat and could achieve a much higher resolution then the rest of us.

The benefits of O_2 levels as low as 1 %, or even less, have been shown in extending the storage of some fruits; for example Table 2.1 shows the progressive extension in the storage life of apples over the years mainly due to lower O_2 levels in store. Very accurate control of O_2 level at these very low concentrations is vital in order not to damage the fruit. Methods that have been developed are based on approaches to the physiology of the fruit. There are three main approaches: one based on respiratory quotient (RQ) one based on ethanol biosynthesis and one based on chlorophyll fluorescence. Wollin et al. (1985) discussed the possibility that RQ may be used to calculate the lowest oxygen level that can be tolerated in fruit storage to be incorporated in an automated system. International Controlled Atmosphere Limited developed a system called 'Safepod' to measure the CO_2 and O_2 and calculate RQ within a sample chamber. The Safepod sits in the controlled atmosphere storage room and thus has the same temperature, humidity, pressure

Table 2.1 Changes in the recommended storage conditions for cox's orange pippin apples all at 3.5 °C (Bishop 1994)

O_2 %	CO_2 %	Approximate storage time in weeks	Approximate date of implementation
21	0	13	–
16	5	16	1920
3	5	21	1935
2	<1	27	1965
1¼	<1	31	1980
1	<1	33	1986

and atmosphere as the store. Periodically the valves are closed and the CO_2 and O_2 and RQ are measured. The Van Amerongen/AgroFresh uses RQ by measuring O_2 and CO_2 in stores feeding the data into a computer, which initiates an alarm at a pre-determined RQ level.

Where these very low O_2 levels were used in commercial controlled atmosphere stores in the 1990s an alcohol detector was fitted which sounded an alarm if ethanol fumes were detected as a result of fermentation in the fruit. Fermentation in fruit occurs when the O_2 level is insufficient to support the oxidative chemical processes in fruit and vegetables. Where fermentation (anaerobic respiration) begins, it is called the anaerobic compensation point. This anaerobic compensation point varies with type and cultivar of fruit as well as their physiological maturity and storage conditions. When the detector alarm sounded the store operator could increase the O_2 level and, where this was done quickly, no damage was done to the fruit. This technology was subsequently developed and Schouten et al. (1997) described a system which he called "dynamic control of ultra-low oxygen storage" based on headspace analysis of ethanol levels that were maintained at less than 1 ppm. With an alarm in place O_2 levels as low as 0.3–0.7 % could be maintained in the store. Computer controls were subsequently developed for this system. Schouten et al. (1997) described storage of the apple cultivar Elstar with the ethanol level in the store maintained below 1 ppm in an atmosphere of 0.3–0.7 % O_2 + < 0.5 % CO_2 that retained fruit quality better than those stored in 1.2 % O_2 + 2.5 % CO_2.

Recently, other stresses associated with metabolic responses of fruit and vegetables to low O_2 levels have been developed, called dynamic controlled atmosphere (DCA) or dynamic controlled atmosphere-chlorophyll fluorescence (DCA-CF). A link between the minimum fluorescence (*Fo*) and a metabolic shift from predominantly aerobic to fermentative metabolism (the lower O_2 limit) is the foundation of DCA (Wright et al. 2012). One method has been developed and was patented in Canada in 2001 as HarvestWatch™ (Prange et al. 2002; DeLong et al. 2004). HarvestWatch™ uses a computer programme that can automatically adjust the O_2 level when stress, based on chlorophyll fluorescence measurement, is detected. DCA storage requires leak-proof capacity of 0.1 m^2 100 m^{-3} or less. Prange et al. (2014) used DCA-CF to calculate the lower oxygen limit for apples and showed that this reduced considerably during storage for three of the cultivars tested (Table 2.2). They also found that this DCA-CF system was sensitive to other stresses that can occur in fruit during storage including CO_2 toxicity, chilling injury, 1-methylcyclopropene treatment, toxic ammonia refrigeration gas and desiccation as well as lower oxygen limit.

Various commercial systems have been developed including Isolcell and Storex. The Isolcell system is a commercial application of the Harvest Watch™ chlorophyll fluorescence method incorporated into Isolcell's atmosphere control equipment and installed in some 2000 commercial CA stores since 2003. Fruit samples are placed in 'kennels' within the CA store where the chlorophyll fluorescence is closely monitored by the computerised control system which enables corrective action to be taken when low O_2 levels are detected in the fruit. The first large-scale DCA installation was completed in the UK in 2013 by Isolcell in conjunction with UKCA Ltd. The Storex (DCS) system is based on ethanol

Table 2.2 The effects of time in storage on the lower oxygen limit detected by Dynamic Controlled Atmosphere-Chlorophyll Fluorescence (DCA-CF) on four apple cultivars (Prange et al. 2014)

Apple cultivar	Lower oxygen limit	
	10–19 October (%)	1–4 December (%)
Delicious	0.85	0.47
Golden delicious	0.92	0.45
Honeycrisp	0.90	0.50
Empire	0.90	0.88

production in fruit and uses smaller sample chambers integrated into the main store enabling low level measurements of ethanol from the fruit samples when the anaerobic compensation point is reached. Storex have installed their DCS system in commercial stores in Holland (http://www.ukcaltd.com/ accessed April 2015).

Ethylene

The measurement of ethylene in the laboratory can be carried out using a gas chromatograph fitted with a flame ionisation detector. Detector tubes are used in packhouses and stores. These are filled with molybdate palladium reagent and the most sensitive will indicate 0.5–10 μL L^{-1} ethylene concentration. Ethylene can be measured successfully with a portable gas chromatograph fitted with a photo ionisation detector capable of measuring ethylene to a concentration below 0.01 uL L^{-1}. EASI-1 uses a proprietary 'nanoporous gold sensor technology' for "accurate real-time measurement of ethylene gas concentrations". This is licensed from Fluid Analytics in USA, which offers a claimed sensitivity to ethylene in the air at levels as low as 10 ppb. Levels of ethylene in the atmosphere due to pollution were measured by Lawton (1991), which showed that levels were very low with a maximum of 0.038 μL L^{-1} (Table 2.3). Ethylene levels measured in a packhouse were higher than in a store for kiwifruit due to the engines in the forklifts, while in stores levels were considerably higher, especially in CA stores (Table 2.4).

Table 2.3 Ethylene levels in ambient air in μL L^{-1}. Modified from Lawton 1991

Sample locations	Ethylene concentration
Australian terminals	0–0.015
New Zealand terminals	0–0.026
New Zealand fruit terminals	0.002–0.038
Belgium fruit terminals	0.003–0.015
Pacific ocean	0–0.009
Atlantic ocean	0–0.010

Table 2.4 Ethylene concentrations in fruit stores μL L^{-1}. Modified from Lawton 1991

Sample locations	Ethylene concentration	Source of ethylene
Kiwifruit packhouse	0–0.070	Forklifts
Kiwifruit stores	0.005–0.055	Fruit
Air apple stores	1–30	Fruit
Air pear stores	2–25	Fruit
CA pear store	11–118	Fruit
CA apple store	27–243	Fruit

As will be described later, one of the additional benefits of hypobaric storage is the removal of ethylene from the store and even from individual fruit or vegetable cells. Ethylene is naturally produced by plant cells and for climacteric fruit it is responsible for initiating the ripening process. Exposure to ethylene can also cause negative effects, for example chlorophyll breakdown resulting in degreening and leaf abscission of leafy vegetables. Another negative effect can occur in mushrooms where exposure to ethylene can stimulate the stalk to elongate and the cap to expand and kiwifruit soften significantly during storage at 0 °C in response to ethylene concentrations as low as 10 nl L^{-1} (Retamales and Campos 1997). The major effect of ethylene removal in apple stores was shown to delay in the onset of softening and also slow softening once it has started (Dover and Stow 1993). In persimmons, exposure to 1 and 10 μl L^{-1} ethylene at 20 °C also accelerated softening and limited their marketability therefore ethylene removal or exclusion during transport and storage was recommended by Crisosto et al. (1995).

Controlled atmosphere storage can reduce or eliminate detrimental effects of ethylene accumulation possibly by the increased levels of CO_2 competing for sites of ethylene action within the cells of the fruit. Stow et al. (2000) studied the effects of ethylene in controlled atmosphere apple stores and concluded that to obtain a benefit from ethylene removal, internal ethylene concentrations must be kept below about 4 μl m^{-3} (0.1 ppm). The control of internal concentrations of ethylene in crops may be ultimately limited by the resistance of the crop to diffusion rather than its removal from the atmosphere surrounding the crop (Dover and Stow 1993). Tubamet AG reported that when they placed their Swingtherm ethylene absorber in cold stores the levels of ethylene were reduced. These reductions varied but were measured as 0.05 ± 0.1 ppm ethylene in citrus, pear and vegetable cells and <0.02 ppm ethylene for kiwifruit cells. Scald, a physiological storage disorder of apples and pears, has been associated with ethylene levels in the store atmosphere. Scald can be controlled by a pre-storage treatment with a suitable chemical antioxidant such as 1,2-dihydro-2,2,4-trimethylquinoline-6-yl ether or diphenylamine but there is consumer pressure to reduce postharvest chemical treatment and reducing ethylene in store may be an effective alternative to these chemical treatments. Coquinot and Richard (1991) stored apples in an atmosphere containing 1.2 % O_2 and 1 % CO_2 with or without removal of ethylene and found that in this atmosphere scald was controlled and ethylene removal was not necessary.

Baumann (1989) described a simple scrubber system which could be used in stores to remove both CO_2 and ethylene using activated charcoal. He gave a chart that showed the amount of activated charcoal required in relation to the CO_2 levels required and ethylene output of the fruit in the store. Molecular sieves and activated carbon can hold CO_2 and organic molecules such as ethylene. When fresh air is passed through these substances, the molecules are released. This means that they can be used in a two stage system where the store air is being passed through the substance to absorb the ethylene, while the other stage is being cleared by the passage of fresh air. After an appropriate period, the two stages are reversed. Hydrated aluminium silicate or aluminium calcium silicate are used. The regeneration of the molecular sieve beds can be achieved when they are warmed to 100 °C to drive off the CO_2 and ethylene. This system of regeneration is referred to as 'temperature swing' where the gases are absorbed at low temperature and released at high temperature. Two types of ethylene scrubber are marketed by UKCA Ltd where the store air is passed through a chamber either containing a hot metal catalyst (manufactured by Absoger, France) or alternatively relatively high concentrations of Ozone (Bioturbo^{TM} manufactured by Miatech, USA). Both systems are also reported to kill airborne pathogens and it has been claimed that they can kill over 99.5 % of airborne bacteria and fungal spores thus contributing to the control of postharvest diseases on the fruit or vegetables. (http://www.ukcaltd.com/ accessed April 2015). However, ozone is hazardous to human health and is highly corrosive which can result in damage to storage facilities. The Bioturbo^{TM} system overcomes these two problems by containing the whole process inside a discrete unit so that ozone is contained in the unit and is never released into the store atmosphere. This also means that it can be used at higher concentrations, which greatly increases effectiveness. Both these systems process the returning air so that it is fit to reintroduce to the storage chamber or packhouse.

Catalytic converters remove ethylene by chemical reaction. Air from the store is passed through a device where it is heated to over 200 °C in the presence of an appropriate catalyst, usually platinum (Wojciechowski 1989). Under these conditions, the ethylene in the air is oxidised to carbon dioxide and water. It requires an energy input of 30–80 watts per cubic metre of purified air, so it is a high energy consuming method. However, with suitable heat exchanges it is possible to make the method more energy efficient. One such device, called 'Swingtherm', reduced energy consumption to 7–14 W m^{-3}. Another ethylene converting device was marketed by Tubamet AG of Vaduz in Liechtenstein in 1993 and called "Swingcat". They took out a patent (Serial Number: 74095681) for a heated catalyst scrubber for the elimination of organic air pollutants. Portable ethylene scrubbers are available that can be placed in a store or packhouse (Fig. 2.1).

Chemicals can be used to remove or absorb ethylene. Proprietary products, including Ethysorb®, Purafil®, Consever-21 and Bi-On 4 are available which are basically made by impregnating an active alumina or zeolite clay carrier with a saturated solution of potassium permanganate and then drying it. Any molecule of ethylene in the atmosphere that comes into contact with the granule will be oxidised, therefore they are formed into small granules; the smaller the granules, the

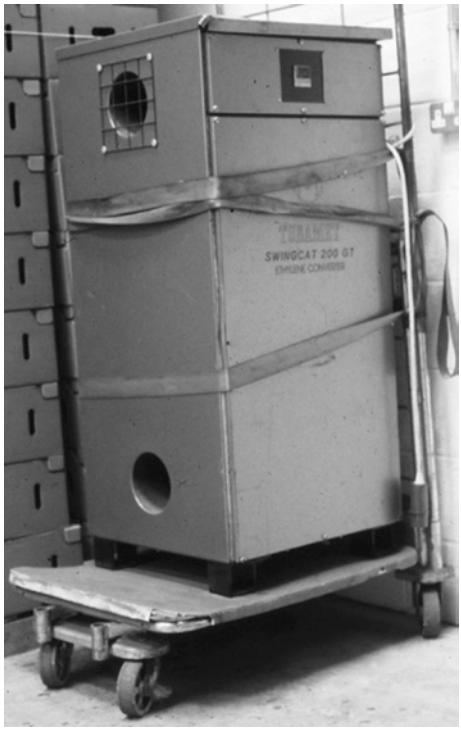

Fig. 2.1 Tubamet AG Swingcat portable ethylene scrubber installed in a cold store in UK

larger the surface area and therefore quicker their absorbing characteristics. The oxidising reaction is not reversible and the granules change colour from purple to brown which indicates that they need replacing. Strop (1992) studied the effects of storing broccoli in PE film bags with and without Ethysorb. She found that the ethylene content in the bags after 10 days at 0 °C was 0.423 $\mu l\ L^{-1}$ for those without Ethysorb and 0.198 $\mu l\ L^{-1}$ for those with Ethysorb. However, Scott et al. (1971) showed that the inclusion of potassium permanganate in sealed packages reduced the mean level of ethylene from 395 to 1.5 $\mu l\ L^{-1}$. Where potassium permanganate was included in the bags containing bananas the increase in storage life was 3–4 times compared to non-wrapped fruit and could be stored for 6 weeks at 20 or 28 °C and 16 weeks at 13 °C (Satyan et al. 1992). Kiwifruit are very susceptible to ethylene in the storage atmosphere. Ben-Arie and Sonego (1985) found that kiwifruit stored in sealed polyethylene film bags containing Ethysorb had less than 0.01 $\mu l\ L^{-1}$ ethylene resulting in a slower rate of softening and improved keeping compared to those with no ethylene absorbent. Terry et al. (2007) described a palladium-impregnated zeolite giving finely dispersed palladium particles that was far superior to potassium permanganate-based scavengers when used in low amounts.

Lawton (1991) evaluated four techniques for the removal of ethylene in ambient air and cargoes prior to and during refrigerated transport from the southern hemisphere to Europe. The methods were: ventilation with air, potassium

permanganate, platinum catalyst heated to approximately 250 °C and ultraviolet radiation at 184 and 254 nm. He concluded that ventilation with air was the best method for the removal of ethylene gas. In the holds of a ship recently loaded with New Zealand kiwifruit, ethylene gas concentrations were found to be low, between 0.001 and 0.008 μl L^{-1} (Lawton 1991). In an extensive review Keller et al. (2013) concluded that photo-catalysis offered the greatest potential for removing ethylene. Photo-catalytic oxidation is a combination of a catalyst (usually titanium dioxide, but other catalysts have been used) and light that breaks down volatile organic compounds such as ethylene into carbon dioxide and water. Lin et al. (2013) reported that intermediates have been detected in some photo-catalytic oxidation processes that can poison the active sites resulting in deactivation of catalysts as well as being more toxic to human health. These should be removed or further oxidised to CO_2.

As indicated above, ethylene reduction or removal from fruit and vegetable stores is beneficial. However, with papaya Broughton et al. (1977) showed that scrubbing ethylene from a cold store had no effects on their storage life. In a study of ethylene on pears, Retamales et al. (1998) found little benefit in removing ethylene from pears during storage at −0.5 °C and Bower et al. (2003) concluded that although it is desirable to minimise ethylene in the storage atmosphere for pears, benefits are likely to be minor compared with the potential gains from good temperature management.

References

Anonymous 1919. Food Investigation Board. Department of Scientific and Industrial Research Report for the Year, 1918.

Anonymous 1920. Food Investigation Board. Department of Scientific and Industrial Research Report for the Year, 1920, 16–25.

Baumann, H. 1989. Adsorption of ethylene and CO_2 by activated carbon scrubbers. *Acta Horticulturae* 258: 125–129.

Beaudry, R.M., and C.D. Gran. 1993. Using a modified-atmosphere packaging approach to answer some post-harvest questions: Factors influencing the lower O_2 limit. *Acta Hortciulturae* 326: 203–212.

Ben-Arie, R., and L. Sonego. 1985. Modified-atmosphere storage of kiwifruit (*Actinidia chinensis* Planch) with ethylene removal. *Scientia Horticulturae* 27: 263–273.

Ben-Arie, R., A. Levine, L. Sonego, and Y. Zutkhi. 1993. Differential effects of CO_2 at low and high O_2 on the storage quality of two apple cultivars. *Acta Horticulturae* 326: 165–174.

Berard, J.E. 1821. Memoire sur la maturation des fruits. *Annales de Chimie et de Physique* 16: 152–183.

Bishop, D. 1990. Controlled atmosphere storage. In *Cold and Chilled Storage Technology*, ed. C.J.V. Dellino, 66–98. London, UK: Blackie.

Bishop, D.J. 1994. Application of new techniques to CA storage. *Commissions C2, D1, D2/3 of the International Institute of Refrigeration International Symposium* June 8–10 Istanbul Turkey, 323–329.

Bower, J.H., W.V. Biasi, and E.J. Mitcham. 2003. Effect of ethylene in the storage environment on quality of 'Bartlett pears'. *Postharvest Biology and Technology* 28: 371–379.

Broughton, W.J., A.W. Hashim, T.C. Shen, and I.K.P. Tan. 1977. Maturation of Malaysian fruits. I. Storage conditions and ripening of papaya *Carica papaya* L. cv. Sunrise Solo. *Malaysian Agricultural Research and Development Institute Research Bulletin* 5: 59–72.

Burdon, J., N. Lallu, G. Haynes, K. McDermott, and D. Billing. 2008. The effect of delays in establishment of a static or dynamic controlled atmosphere on the quality of 'Hass' avocado fruit. *Postharvest Biology and Technology* 49: 61–68.

Coquinot, J.P., and L. Richard. 1991. Methods of controlling scald in the apple Granny Smith without chemicals. Methodes de controle de l'echaudure de la pomme Granny Smith sans adjuvants chimiques. *Neuvieme colloque sur les recherches fruitieres, 'La maitrise de la qualite des fruits frais', Avignon*, 4–5–6 Decembre 1990, 373–380.

Crisosto, C.H., Mitcham, E.J., and A.A. Kader. 1995. Produce facts: Persimmons. *Perishables Handling* 84: 19–20. http://postharvest.ucdavis.edu/produce/producefacts/index.html.

Dalrymple, D.G. 1967. The development of controlled atmosphere storage of fruit. Division of Marketing and Utilization Sciences, Federal extension Service, U.S. Department of Agriculture.

DeLong, J.M., R.K. Prange, J.C. Leyte, and P.A. Harrison. 2004. A new technology that determines low-oxygen thresholds in controlled-atmosphere-stored apples. *HortTechnology* 14: 262–266.

Dimick, P.S., and J.C. Hoskins. 1983. Review of apple flavour. State of the Art. *CRC Critical Review, Food Science and Nutrition* 18: 387–409.

Dover, C.J., and J.R. Stow. 1993. The effects of ethylene removal rate and period in a low ethylene atmosphere on ethylene production and softening of Cox apples. *Sixth Annual Controlled Atmosphere Research Conference, Cornell University, Ithica, New York*.

Fellman, J.K., T.W. Miller, D.S. Mattinson, and J.P. Mattheis. 2000. Factors that influence biosynthesis of volatile flavour compounds in apple fruits. *HortScience* 35: 1026–1033.

Fidler, J.C., B.G. Wilkinson, K.L. Edney, and R.O. Sharples. 1973. The biology of apple and pear storage. *Commonwealth Agricultural Bureaux Research Review 3*.

Forney, C.F., M.A. Jordan, and K.U.K.G. Nicholas. 2003. Effect of CO_2 on physical, chemical, and quality changes in 'Burlington' blueberries. *Acta Horticulturae* 600: 587–593.

Gadalla, S.O. 1997. Inhibition of sprouting of onions during storage and marketing. *PhD thesis, Cranfield University, UK.*

Galvis-Sanchez, A.C., F.C. Fonseca, A. Gil-Izquierdo, M.I. Gil, and F.X. Malcata. 2006. Effect of different levels of CO_2 on the antioxidant content and the polyphenol oxidase activity of 'Rocha' pears during cold storage. *Journal of the Science of Food and Agriculture* 86: 509–517.

Goodenough, P.W., and T.H. Thomas. 1981. Biochemical changes in tomatoes stored in modified gas atmospheres. I. sugars and acids. *Annals of Applied Biology* 98: 507.

Hatfield, S.G.S., and B.D. Patterson. 1974. Abnormal volatile production by apples during ripening after controlled atmosphere storage. In: *Facteurs and Regulation de la Maturation des Fruits. Colleques Internationaux, CNRS, Paris*, 57–64.

Jeffery, D., C. Smith, P.W. Goodenough, T. Prosser, and D. Grierson. 1984. Ethylene independent and ethylene dependent biochemical changes in ripening tomatoes. *Plant Physiology* 74: 32.

Keller, N., M.N. Ducamp, D. Robert, and V. Keller. 2013. Ethylene removal and fresh product storage: A challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation. *Chemical Review* 113: 5029–5070.

Khanbari, O.S., and A.K. Thompson. 1996. Effect of controlled atmosphere, temperature and cultivar on sprouting and processing quality of stored potatoes. *Potato Research* 39: 523–531.

Knee, M., and R.O. Sharples. 1979. Influence of CA storage on apples. In: Quality in stored and processed vegetables and fruit, *Proceedings of a Symposium at Long Ashton Research Station, University of Bristol 8–12 April 1979*, 341–352.

Koelet, P.C. 1992. *Industrial Refrigeration*. London, UK: MacMillan.

Lawton, A.R. 1991. Measurement of ethylene gas prior to and during transport. *19th International Congress of Refrigeration, IIR/IIF, Montreal*, 1–11.

Leja, M., and J. Ben. 2003. Antioxidant properties of two apple cultivars during long term storage. *Food Chemistry* 80: 303–307.

Lin, Lin, Yuchao Chai, Bin Zhao, Wei Wei, Dannong He, Belin He, and Qunwei Tang. 2013. Photocatalytic oxidation for degradation of Volatile organic compounds. *Open Journal of Inorganic Chemistry* 3: 14–25.

MacLean, D.D., D.P. Murr, J.R. DeEll, and C.R. Horvath. 2006. Postharvest variation in apple (*Malus* × *domestica* Borkh.) flavonoids following harvest, storage, and 1-MCP treatment. *Journal of Agriculture and Food Chemistry* 54: 870–878.

Martínez-Sánchez, A., A. Allende, R. Bennett, F. Ferreres, and M. Gil. 2006. Microbial, nutritional and sensory quality of rocket leaves as affected by different sanitizers. *Postharvest Biology and Technology* 42: 86–97.

Mencarelli, F., Fontana, F., and R. Massantini. 1989. Postharvest practices to reduce chilling injury CI on eggplants. Proceedings of the fifth international controlled atmosphere research conference, Wenatchee, Washington, USA, 14–16 June, 1989. Vol. 2, Pullman, Washington, USA, Washington State University, pp. 49–55.

Meyer, M.D., S. Landahl, M. Donetti, and L.A. Terry. 2011. Avocado. In *Health-promoting properties of fruit and vegetables*, ed. L.A. Terry, 27–50. Oxford, UK: CAB International.

Pariasca, J.A.T., T. Miyazaki, H. Hisaka, H. Nakagawa, and T. Sato. 2001. Effect of modified atmosphere packaging (MAP) and controlled atmosphere (CA) storage on the quality of snow pea pods (*Pisum sativum* L. var. *saccharatum*). *Postharvest Biology and Technology* 21: 213–223.

Patil, B.S., and K. Shellie. 2004. Carotenoids and vitamin C changes by semi-commercial ultra-low oxygen storage in grapefruit. *Acta Horticulturae* 632: 321–328.

Prange, R.K., J.M. Delong, J.C. Leyte, and P.A. Harrison. 2002. Oxygen concentration affects chlorophyll fluorescence in chlorophyll-containing fruit. *Postharvest Biology and Technology* 24: 201–205.

Prange, R.K., Wright, A.H., DeLong, J.M., and A. Zanella. 2014. History, current situation and future prospects for dynamic controlled atmosphere (DCA) storage of fruits and vegetables, using chlorophyll fluorescence. http://www.harvestwatch.net/history.html. Accessed December 2014.

Rahman, A.S.A., D. Huber, and J.K. Brecht. 1993. Respiratory activity and mitochondrial oxidative capacity of bell pepper fruit following storage under low O_2 atmosphere. *Journal of the American Society for Horticultural Science* 118: 470–475.

Retamales, J., and R. Campos. 1997. Extremely low ethylene levels in ambient air are still critical for kiwifruit storage. *Acta Horticulturae* 444: 573–578.

Retamales, J., R. Campos, and D. Castro. 1998. Ethylene control and ripening in Packham's Triumph and Beurre Bosc pears. *Acta Horticulturae* 475: 559–566.

Rogiers, S.Y., and N.R. Knowles. 2000. Efficacy of low O_2 and high CO_2 atmospheres in maintaining the postharvest quality of saskatoon fruit (*Amelanchier alnifolia* Nutt.). *Canadian Journal of Plant Science* 80: 623–630.

Romero, I., M.T. Sanchez-Ballesta, R. Maldonado, M.I. Escribano, and C. Merodio. 2008. Anthocyanin, antioxidant activity and stress-induced gene expression in high CO_2-treated table grapes stored at low temperature. *Journal of Plant Physiology* 165: 522–530.

Satyan, S., K.J. Scott, and D. Graham. 1992. Storage of banana bunches in sealed polyethylene tubes. *Journal of Horticultural Science* 67: 283–287.

Schotsmans, W., A. Molan, and B. MacKay. 2007. Controlled atmosphere storage of Rabbiteye blueberries enhances postharvest quality aspects. *Postharvest Biology and Technology* 44: 277–285.

Schouten S.P., Prange R.K., and T.R. Lammers. 1997. Quality aspects of apples and cabbages during anoxia. *Proceedings of the7th international controlled atmosphere research conference* Davis CA. USA, vol. 2, 189–192.

Scott, K.J., J.R. Blake, G. Strachan, B.L. Tugwell, and W.B. McGlasson. 1971. Transport of bananas at ambient temperatures using polyethylene bags. *Tropical Agriculture Trinidad* 48: 245–253.

Sharples, R.O. 1989. Kidd, F., and West, C. In *Classical papers in horticultural science*, ed. J. Janick, 213–219. New Jersey: Prentice Hall.

Stow, J.R., C.J. Dover, and P.M. Genge. 2000. Control of ethylene biosynthesis and softening in 'Cox's Orange Pippin' apples during low-ethylene, low-oxygen storage. *Postharvest Biology and Technology* 18: 215–225.

Strop, I. 1992. *Effects of plastic film wraps on the marketable life of asparagus and broccoli*. MSc thesis, Silsoe College, Cranfield Institute of Technology, UK.

Terry, L.A., T. Ilkenhans, S. Poulston, L. Rowsell, and A.W.J. Smith. 2007. Development of new palladium-promoted ethylene scavenger. *Postharvest Biology and Technology* 45: 214–220.

Thompson, A.K., 2010. *Controlled atmosphere storage of fruits and vegetables*. Second edition. CAB International, Oxford, UK.

Van Der Sluis, A.A., M. Dekker, A. De Jager, and W.M.F. Jongen. 2001. Activity and concentration of polyphenolic antioxidants in apple: Effect of cultivar, harvest year, and storage conditions. *Journal of Agricultural and Food Chemistry* 49: 3606–3613.

Villatoro, C., G. Echeverria, J. Graell, M.L. Lopez, and I. Lara. 2008. Long-term storage of pink lady apples modifies volatile-involved enzyme activities: Consequences on production of volatile esters. *Journal of Agricultural and Food Chemistry* 56: 9166–9174.

Wang, C.Y. 1990. Physiological and biochemical effects of controlled atmosphere on fruit and vegetables. In *Food preservation by modified atmospheres*, eds. Calderon, M., and R. Barkai-Golan, 197–223. Boca Raton, Ann Arbor, Boston, USA: CRC Press.

Wardlaw, C.W. 1938. Tropical fruits and vegetables: An account of their storage and transport *Low Temperature Research Station, Trinidad Memoir* 7, Reprinted from *Tropical Agriculture Trinidad* 14.

Wills, R.B.H., S. Pitakserikul, and K.J. Scott. 1982. Effects of pre-storage in low O_2 or high CO_2 concentrations on delaying the ripening of bananas. *Australian Journal of Agricultural Research* 33: 1029–1036.

Wojciechowski, J. 1989. Ethylene removal from gases by means of catalytic combustion. *Acta Horticulturae* 258: 131–142.

Wollin, A.S., Little, C.R., and J.S. Packer. 1985. Dynamic control of storage atmospheres. In: *Controlled atmospheres for storage and transport of perishable agricultural commodities*, ed. S. Blankenship, 308–315. Proceedings of the 4th National Controlled Atmosphere Research Conference, Raleigh, North Carolina, USA.

Wright, A.H., J.M. DeLong, A.H.L.A.N. Gunawardena, and R.K. Prange. 2012. Dynamic controlled atmosphere (DCA): Does fluorescence reflect physiology in storage? *Postharvest Biology and Technology* 64: 19–30.

Zheng, Y.H., C.Y. Wang, S.Y. Wang, and W. Zheng. 2003. Effect of high-oxygen atmospheres on blueberry phenolics, anthocyanins, and antioxidant capacity. *Journal of Agricultural and Food Chemistry* 51: 7162–7169.

http://www.springer.com/978-3-319-23590-5

Fruit and Vegetable Storage
Hypobaric, Hyperbaric and Controlled Atmosphere
Thompson, A.K.
2016, XIII, 126 p. 9 illus., Softcover
ISBN: 978-3-319-23590-5