Absorption kinetics of oxygen scavengers

Gaurav Tewari^{1,†}, Digvir S. Jayas^{1,*}, Lester E. Jeremiah² & Richard A. Holley³

- 1 Department of Biosystems Engineering, University of Manitoba, Winnipeg, Manitoba, Canada R3T 5V6
- 2 Agriculture and Agri-Food Canada, 6000 C & E Trail, Lacombe, Alberta, Canada T4L 1W1
- 3 Department of Food Science, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

(Received 23 February 2000; Accepted in revised form 6 January 2001)

Summary

The oxygen (O₂) absorption kinetics of six commercial O₂ scavengers were studied. The scavengers were placed in bags which were filled with 240 mL of air, 4.5 L N₂ + 15 mL of air, or 3.5 L CO₂ + 9 mL of air. The O₂ concentration in each bag was measured at hourly intervals for 8 h. The effects of variability among individual scavengers, initial O₂ concentrations of 20% or 500 ppm (0.05%), temperatures of 25, 12, 2 or -1.5 °C, and scavenger capacity on the O₂ absorption rate were determined. In addition, the effect of placing scavengers within over-wrapped trays within bags, was examined. Rates of O₂ absorption varied by factors of up to 2 between individual O₂ scavengers of the same type, but rates of absorption by groups of four scavengers of the same type were similar. Low temperatures gave longer O₂ half-life when compared with those at higher temperatures, e.g. O₂ half-lives of 7.1 and 1.0 h at -1.5 and 25 °C, respectively, were obtained for one scavenger type. Shorter O₂ half-lives were obtained in air than in N₂ atmospheres at the same temperature, e.g. O₂ half-lives of 1.0 and 3.3 h in air and N₂ at 25 °C, respectively, were obtained for one scavenger type. The O₂ absorption reactions were of first order for both high and low initial O₂ concentrations. However, O₂ concentration was the primary limiting factor for O2 absorption in atmospheres having O2 concentration of 500 ppm because of the dominance of diffusion. Scavengers, when placed within over-wrapped trays within bags had up to 12 times longer O₂ half-lives, indicating that the O₂ permeable film acts as an O₂ barrier when pack atmosphere has low O₂ concentrations. To obtain consistent and reproducible results, it is recommended that multiple scavengers be used in a packaging system. The appropriate number should be based on scavenger type, desired O₂ absorption rate, storage temperature, and pack atmosphere (air/N₂/CO₂).

Keywords

Arrhenius equation, food preservation, master packaging, meat, modified atmosphere packaging.

Introduction

Oxygen scavengers have been used for food preservation for the last 20 years. The purpose of O_2 scavengers is to create low O_2 atmosphere in sealed packs of products, thereby slowing or preventing deterioration because of the oxidation of product components and/or growth of microorganisms or survival of insects (Anonymous,

*Correspondent: Fax: +1 204 474 7512; e-mail: digvir jayas@umanitoba.ca

[†]Present address: ESL Global Inc., San Antonio, TX 78216, USA.

1998). Oxygen scavengers are extensively used in Japan to prevent discolouration of cured meats and tea, rancidity problems in high fat foods, and mould spoilage of intermediate and high moisture bakery products. In the USA, they are used to delay oxidative flavour changes in coffee, and to prevent mould growth, rancidity, and staling in bakery products (Smith *et al.*, 1995). Their use for the preservation of colour and flavour and the prevention of microbial spoilage in cooked, cured meats has also been reported (Smith *et al.*, 1995).

The current uses of O₂ scavengers generally involve packs in which the atmosphere contains

some substantial fraction of O₂, if not air, at the time of pack sealing and the inhibition of chemical reactions or proliferation of micro-organisms that proceed relatively slowly. Consequently, commercial O2 scavengers are designed to remove a specified amount of O₂ from a relative high O₂ atmosphere over periods of a day or more. The rate of O₂ absorption has then not been a principal concern in the design of commercial O₂ scavengers. However, there are applications for O₂ scavengers where the rate of O_2 absorption is of prime importance. For example, meat packed under O2depleted, controlled atmospheres discolours in the presence of the low O₂ concentrations in the initial atmospheres of such packs (Gill & Jones, 1994a,b). The discolouration resolves after 2 or 3 days, when the meat has stripped all O₂ from the pack atmosphere. However, such transient discolouration may be disadvantageous in some circumstances, such as in the use of controlled atmospheres to preserve centrally prepared masterpackaged retail-ready meat, some of which may have to be displayed a short time after master packaging (Gill & Jones, 1994a,b; Gill & McGinnis, 1995a). To prevent transient discolouration, the O2 concentration has to be reduced to < 10 ppm within 2 h when the storage temperature is -1.5 °C, and more rapidly at higher temperatures (Gill & McGinnis, 1995b), which might be possible with the appropriate O_2 scavenger.

The O_2 absorption rates of O_2 scavengers may vary with the nature of their reactants and other materials used in their construction. Rates of absorption may also be affected by factors such as temperature and the compositions of the atmospheres to which they are exposed. Therefore, the objective of this study was to determine the O_2 absorption kinetics of six commercial O_2 scavengers. The effects of initial O_2 concentrations, temperature, and scavenger capacity on O_2 absorption rates were also quantified.

Materials and methods

O₂ scavengers

The O₂ scavengers, which were studied were Ageless[®] FX-100 (Mitsubishi Gas Chemical Co. Inc., Tokyo, Japan), FreshPax[®] M-100, R-300, and R-2000 (Multisorb Technologies, Buffalo,

NY, USA) and Bioka® S-75 and S-100 (Bioka Ltd, Kantvik, Finland). Their characteristics are described in Table 1.

Absorption of O2 by scavengers

Oxygen scavengers were placed in bags composed of a laminate of polyester, oriented nylon, and an EVOH/EVA co-extrusion (ESOPAEV2E 121575 R, WinPak, Winnipeg, Manitoba, Canada), with an O₂ transmission rate of 0.55 mL m⁻² 24 h⁻¹ at atmospheric pressure, 23 °C and 70% r.h. The bag size was 550×440 mm. Bags containing scavengers were either emptied of air by flattening each bag around the scavengers it contained or were evacuated then filled with a known volume of N₂ or CO₂, using a controlled atmosphere packaging (CAP) machine (CAPTRON Model # ZR897, Securefresh Pacific Limited, Auckland, New Zealand), before being sealed. Then, a quantity of air was injected into each bag using a gas-tight syringe (Model # 8881-114030, Sherwood Medical, Bally Money, North Ireland) inserted through a stick-on septum (Modern Controls Inc., Minneapolis, MN, USA). Immediately after the injection of air, the puncture-point was sealed using a hot iron. Each filled bag was stored at room or a constant temperature. Samples (8 mL) of the atmosphere in each bag were obtained every hour for 8 h by means of a gas-tight syringe inserted through a stick-on septum. If no substantial O2 absorption was noticed within 8 h, samples were taken after every 12 h for up to 96 h. Immediately after each sampling, the O₂ concentration in the sample was determined using an O₂ analyser (Mocon MS-750, Modern Controls Inc., Minneapolis, MN, USA) with a zirconium oxide sensor, and the puncturepoint was then sealed using a hot iron. The O₂ analyser had an accuracy of ± 5 ppm in the 0-1000 ppm range, $\pm 0.05\%$ in the 0.1-10%range, and $\pm 1\%$ in the 10–100% range for O₂ concentrations. The resolution of the analyser was smaller than the accuracy, i.e. in the 0-1000 ppm O_2 concentration range the resolution was 1 ppm. Residual air in the emptied bag was measured as the volume of water displaced by the emptied bag, and was used in the calculation (see data analysis).

To examine the effect of variability among individual O_2 scavengers on rates of O_2 absorption, an Ageless® FX-100 scavenger on a moist

Table 1 Manufacturers' specifications for O2 scavengers*

Name	Scavenging reaction	Capacity (mL O ₂)	Features & suggested applications	Atmosphere (CO ₂ /Air/N ₂)	Activating agent
Bioka [®] S-100	Enzyme mediated oxidation	100	-	Air/N ₂	Self-activated
Bioka® S-75	Enzyme mediated oxidation	75	-	Air/N ₂	Self-activated
Ageless [®] FX-100	Iron oxidation	100	For moist food; stable in air before use; excellent water resistance	Air/N ₂	Moisture
FreshPax [®] M-100	Iron oxidation	100	For refrigerated applications; designed for modified atmosphere packaging of moist product	CO ₂	Moisture
FreshPax [®] R-300	Iron oxidation	300	For refrigerated and frozen application; recommended for cases where rapid removal of O_2 is required	Air/N ₂	Self-activated
FreshPax [®] R-2000	Iron oxidation	2000	For refrigerated and frozen application; recommended for cases where rapid removal of O_2 is required	Air/N ₂	Self-activated

^{*}All of the scavengers are designed for products with a water activity ≥0.85.

absorbent pad (MP-30620, Paper Pak® Corp., La Verne, CA, USA), was placed in each of the five bags. Each bag was emptied of air and sealed, then 240 mL of air was injected into each bag. The bags were stored at room temperature. Five bags each with a FreshPax® R-300 scavenger, five bags each with a Bioka® S-100 scavenger, and five bags each with a FreshPax® R-2000 scavenger, were similarly prepared.

To examine the effects of temperature and initial O₂ concentrations on O₂ absorption rates, groups of four scavengers were placed in bags after the scavengers, in their original sealed package, had been held overnight at the temperature at which O₂ absorption was to be measured. For each type of scavenger at each temperature, six bags were prepared. Three of the bags were emptied of air, and sealed, then 240 mL of air was injected into each. The other three bags were each filled with 4.5 L of N₂ before being sealed, then 15 mL of air was injected into each. For each of the scavenger types, Ageless[®] FX-100, Bioka[®] S-100, FreshPax[®] R-300, or FreshPax[®] M-100 scavengers, four sets

of six bags were prepared, with one set being stored at each of the following temperatures: 25, 12, 2 or -1.5 °C. Three sets of six bags, with each bag containing four FreshPax® R-2000 scavengers, were similarly prepared and stored at 25, 2 or -1.5 °C. One set of six bags, with each bag containing four Bioka® S-75 scavengers, was prepared and stored at 25 °C. In addition, four sets of three bags, with each bag containing four FreshPax® M-100 scavengers, were prepared. Each bag was filled with 3.5 L of CO₂, sealed and 9 mL of air was injected. A set of bags was stored at each of the following temperatures: 25, 12, 2 or -1.5 °C. Placing two scavengers in bags was also tried; however, substantial differences in O₂ absorption were observed among replicates. Hence, placing four scavengers in bags, which gave similar O₂ absorption rates with no significant difference (P > 0.05), was chosen as the standard format for conducting the present study.

To characterize O_2 absorption when O_2 scavengers were placed inside over-wrapped retail trays within master packs, a $216 \times 133 \times 25$ mm

^{-,} Not given.

 $(L \times W \times H)$ retail tray (clear plastic tray no. 2D, Western Paper & Food Distributors (Int.) Ltd, Calgary, Alberta, Canada) over-wrapped with a film of O2 with a transmission rate of 8000 mL m⁻² 24 h⁻¹ at atmospheric pressure, 23 °C and 70% r.h. (Vitafilm 'Choice Wrap', Goodyear Canada Ltd, Red Deer, Alberta, Canada), containing four FreshPax® R-300 scavengers was placed in each of six bags. A 5 mm hole was made at one corner of the over-wrapped film to allow free exchange of atmospheres during gas flushing. Three bags were emptied of air and sealed, then 240 mL of air was injected into each. The other three bags were each filled with 4.5 L of N_2 to which 15 mL of air was added by injection. The bags were stored at 25 °C. Similarly, three bags, each containing a retail tray with four Ageless® FX-100 scavengers on a moist absorbent pad and 240 mL of air, were prepared and stored at 25 °C. Residual air in the retail tray was assumed to be negligible, and thus was not taken into consideration while performing calculations.

Data analysis

The half-life of O2 in a pack atmosphere was calculated as the time required for the O2 concentration in the pack atmosphere to be reduced to half the initial value. The half-life was calculated from the volumes of O₂ at successive time intervals during the storage of the pack. In calculating the volumes of O₂ absorbed from each atmosphere of air by the scavenger, the initial volume of air was taken to be the 240 mL added to the pack plus the measured volume of residual air. The volume of O₂ in a pack at the end of any period was calculated as the volume of atmosphere at the end of the period multiplied by the concentration of O₂ in the atmosphere at that time. The volume of atmosphere at the beginning of each period was taken to be the volume of atmosphere at the beginning of the previous period less the volume of the atmosphere removed as a sample at the end of the period and the volume of O2 calculated to have been absorbed during the previous period. The volume of O₂ absorbed during a period was calculated as the volume of atmosphere at the start of the previous period multiplied by the concentration of O₂ in the atmosphere at the beginning of the period less the volume of atmosphere at the start of the period multiplied by the concentration of O_2 at the end of the period. In calculating the volumes of O_2 remaining in the pack in atmospheres of N_2 or CO_2 to which air was added, the volumes of the atmosphere removed during sampling and the volumes of O_2 absorbed during a period were neglected.

To determine the order of reaction, plots were prepared of the natural logs (\log_n) and the reciprocals of the volumes of O_2 remaining in the pack atmosphere against time. If the \log_n plot approximated a straight line, the reaction was regarded as first order. If the reciprocal plot approximated a straight line, the reaction was regarded as second order. Rate-constants were calculated using the following equations (Brown et al., 1994):

$$\ln[\mathbf{A}]_t = -kt + \ln[\mathbf{A}]_0$$

for first-order reactions and

$$\frac{1}{[\mathbf{A}]_t} = kt + \frac{1}{[\mathbf{A}]_0},$$

for second-order reactions, where $[A]_t$ is the amount of reactant A at time t (h), k the rate constant (h⁻¹), and $[A]_0$ the initial amount of reactant.

Frequency factors and activation energies were calculated from the Arrhenius equation of the form (Brown *et al.*, 1994):

$$\ln(k) = \left(\frac{-E_{a}}{R}\right) \left(\frac{1}{T}\right) + \ln(A)$$

where A is the frequency factor (frequency of collisions), E_a the activation energy (J mol⁻¹), R the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T the temperature (K).

Validation of constants for Arrhenius equation

For validation of the experimentally determined constants for the Arrhenius equation, four Fresh-Pax $^{\otimes}$ R-300 scavengers were placed in each of the six bags. Three bags were each emptied of air and sealed, then 240 mL of air was injected into each. The other three bags were each filled with 4.5 L of N₂ to which 15 mL of air was added. The bags were stored at 7 °C, and the O₂ concentrations were measured at hourly intervals for 8 h.

Results

The residual O_2 in each bag previously emptied of air was 1.5 ± 0.5 mL. With a single scavenger in each bag, the half-lives of O_2 in bags containing air ranged from 2.8 to 4.6 h and were significantly (P < 0.05) different. Whereas when four scavengers were placed in each bag, the differences in half-lives of O_2 were negligible, i.e. non-significant (P > 0.05) at 25 °C (Table 2).

Using four Ageless® FX-100 scavengers in bags containing air, the O_2 half-life was four times longer at -1.5 °C than at 25 °C, but with a N_2 atmosphere, the O_2 half-life at -1.5 °C was only double that at 25 °C (Table 3). The O_2 half-life in bags containing air and four Bioka® S-100 scavengers was seven times longer at -1.5 °C than at

Table 2 Variability in O_2 half-life among single vs. four O_2 scavengers of the same type in air at 25 °C

	Half-life of O ₂ (h)				
Scavenger-type	Single O ₂ scavenger	Four O ₂ scavengers			
Ageless® FX-100	1.8–2.5	0.6–0.7			
Bioka® S-100	2.8-4.6	0.9-1.0			
FreshPax® R-300	2.0-2.8	0.8-0.9			
FreshPax® R-2000	0.9–1.6	0.6-0.7			

25 °C, but was only two and a half times longer at -1.5 °C than at 25 °C with a N_2 atmosphere. With four FreshPax® R-300 scavengers in bags containing air, there were no significant (P > 0.05) differences between O_2 half-lives at different temperatures, but with N_2 atmospheres the O_2 half-life was two and a half times longer at -1.5 °C than at 25 °C. With four FreshPax® M-100 scavengers in bags containing air or N_2 , the O_2 half-lives were longer than with other scavenger types. However, in bags containing four scavengers and a CO_2 atmosphere, the O_2 half-lives were shorter than for other atmospheres (air or N_2), but still longer than for other scavenger types at 2 and -1.5 °C.

With four FreshPax® R-2000 or Bioka® S-75 scavengers in each bag containing air or N_2 , the O_2 half-lives were significantly (P < 0.05) shorter and longer than FreshPax® R-300 or Bioka® S-100, respectively (Table 3). When four Ageless® FX-100 scavengers were placed in an over-wrapped tray which was placed in a bag containing air, at 25 °C, the O_2 half-life was significantly (P < 0.05) longer than when four such scavengers were placed directly in a bag containing air (Table 3). In a similar fashion, significantly (P < 0.05) longer O_2 half-lives were obtained when four FreshPax® R-300 scavengers were placed in over-wrapped trays than

Table 3 Half-life of O_2 in bags containing four scavengers and air, N_2 , or CO_2 atmosphere

		O ₂ half-life (h)			
Scavenger-type	Atmosphere	25 °C	12 °C	2 °C	−1.5 °C
Ageless [®] FX-100	Air	0.6 (0.04)*	0.7 (0.02)	1.0 (0.03)	2.5 (0.04)
	N ₂ + air	1.3 (0.03)	1.5 (0.04)	2.2 (0.05)	2.3 (0.05)
Bioka® S-100	Air	1.0 (0.03)	1.6 (0.02)	4.0 (0.02)	7.1 (0.04)
	N ₂ + air	3.3 (0.02)	7.1 (0.03)	12.0 (0.03)	8.4 (0.03)
FreshPax [®] R-300	Air	0.9 (0.03)	0.9 (0.02)	0.9 (0.02)	1.2 (0.02)
	N ₂ + air	2.5 (0.04)	3.1 (0.02)	4.4 (0.04)	6.1 (0.04)
FreshPax [®] M-100	Air	7.5 (0.04)	12.1 (0.06)	38.8 (0.2)	40.0 (0.5)
	N ₂ + air	6.1 (0.05)	12.8 (0.1)	29.5 (0.5)	37.3 (0.8)
	CO ₂ + air	5.0 (0.1)	12.0 (0.5)	18.0 (0.8)	21.8 (0.6)
FreshPax® R-2000	Air	0.6 (0.04)	_	0.8 (0.05)	0.8 (0.04)
	N ₂ + air	0.9 (0.02)	-	0.9 (0.04)	1.3 (0.04)
Bioka® S-75	Air	1.6 (0.02)	_	_	-
	N ₂ + air	6.5 (0.06)	-	-	-
Ageless® FX-100 (in over-wrapped tray)	Air	7.5 (0.08)	_	_	-
FreshPax [®] R-300 (in over-wrapped tray)	Air	4.5 (0.08)	_	_	_
	N ₂ + air	5.0 (0.08)	_	_	-

^{*}e d

^{-,} An experiment was not performed under this condition.

when four such scavengers were placed directly in a bag containing air or N_2 atmosphere at 25 °C.

The O_2 absorption reaction was first order for all the commercial O_2 scavengers. Rate constants were therefore calculated from the first-order kinetics equations, and generally increased with increasing temperature (Table 4). For Ageless[®] FX-100, Bioka[®] S-100, and FreshPax[®] R-300 scavengers, the rate constants for O_2 absorption reaction were higher for air than for N_2 atmos-

pheres at any temperature, and the rate constants tended to decrease with decreasing temperature (Table 4). However, for FreshPax $^{\otimes}$ M-100, k was generally less for air than for N₂ or CO₂ atmospheres at the same temperature, although A₀ for air was generally larger. In most cases, the calculated (Table 4) and observed (Table 3) O₂ half-lives were comparable.

Constants for the Arrhenius equation for the various types of scavenger were obtained using the

Table 4 Constants of first-order kinetics equation for different scavengers

	Temp. (°C)	Atmosphere	Initial O ₂ concentration (ppm)	Constants of first-order kinetics equation*			
Scavenger-type				k (h ⁻¹)	A ₀	Calculated O ₂ half-life [†] (h)	Correlation coefficient (r ²)
Ageless® FX-100	25	Air	200 000	2.46	3.94	0.3	0.98
•	25	N ₂ + air	500	0.35	0.51	1.8	0.92
	12	Air	200 000	1.82	3.96	0.4	0.96
	12	N ₂ + air	500	0.36	0.61	1.9	0.98
	2	Air	200 000	0.69	3.61	1.0	0.99
	2	N ₂ + air	500	0.25	0.79	2.7	0.99
	-1.5	Air	200 000	0.31	3.54	2.3	0.92
	-1.5	N ₂ + air	500	0.26	0.76	2.7	0.99
Bioka [®] S-100	25	Air	200 000	0.56	3.34	1.2	0.99
	25	N ₂ + air	500	0.20	0.88	3.5	0.99
	12	Air	200 000	0.40	3.62	1.7	0.99
	12	N ₂ + air	500	0.09	0.84	7.7	0.99
	2	Air	200 000	0.20	3.45	3.5	0.99
	2	N ₂ + air	500	0.06	0.80	11.5	0.96
	-1.5	Air	200 000	0.08	3.72	8.7	0.98
	-1.5	N ₂ + air	500	0.08	0.84	8.7	0.99
FreshPax [®] R-300	25	Air	200 000	1.04	3.60	0.7	0.99
	25	N ₂ + air	500	0.35	0.94	2.0	0.95
	12	Air	200 000	0.99	3.60	0.7	0.99
	12	N ₂ + air	500	0.23	0.87	3.1	0.99
	2	Air	200 000	0.91	3.80	0.8	0.98
	2	N ₂ + air	500	0.18	0.82	3.9	0.99
	-1.5	Air	200 000	0.74	3.60	1.0	0.99
	-1.5	N ₂ + air	500	0.15	0.86	4.7	0.99
FreshPax [®] M-100	25	Air	200 000	0.09	3.88	7.7	0.88
	25	N ₂ + air	500	0.15	1.10	4.6	0.82
	25	CO ₂ + air	500	0.18	0.73	3.9	0.82
	12	Air	200 000	0.08	3.87	8.7	0.88
	12	N ₂ + air	500	0.05	0.90	13.9	0.92
	12	CO ₂ + air	500	0.08	0.68	8.7	0.88
	2	Air	200 000	0.02	3.68	33.7	0.91
	2	N ₂ + air	500	0.02	0.87	34.5	0.88
	2	CO ₂ + air	500	0.05	0.72	14.0	0.82
	-1.5	Air	200 000	0.02	3.70	35.9	0.89
	-1.5	N ₂ + air	500	0.01	0.90	47.5	0.94
	-1.5	CO ₂ + air	500	0.03	0.71	23.1	0.98

^{*}In[O_2]_t = $-kt + A_0 = -kt + In[O_2]_0$; [O_2]_t is volume (mL) of O_2 in the pack atmosphere at time t (h) and [O_2]₀ is volume (mL) of O_2 in the pack atmosphere at t = 0 h.

 $^{^{\}dagger}$ Calculated half-life (h) = 0.693/k; observed half-life in Table 3.

Table 5 Arrhenius equation for different O₂ scavengers

Scavenger-type	Atmosphere	Arrhenius equation*
Ageless® FX-100	Air N ₂ + air	$k = 484077.4e^{(-6004.03/T)}$ $k = 0.005e^{(-1118.23/T)}$
Bioka® S-100	Air N ₂ + air	$k = 13082.1e^{(-5379.43/T)}$ $k = 2.04e^{(-3169.74/T)}$
FreshPax® M-100	Air N ₂ + air CO ₂ + air	$k = 1636e^{(-5301.5/T)}$ $k = 7404511.2e^{(-7703.6/T)}$ $k = 1480.3e^{(-5129.87/T)}$
FreshPax® R-300	Air N ₂ + air	$k = 0.006e^{(-881.25/T)}$ $k = 0.41e^{(-2487.72/T)}$

^{*}k: rate constant (s⁻¹); T: temperature (K).

rate constants at different temperatures for each type of scavenger (Table 5). During validation of these constants for FreshPax $^{\otimes}$ R-300 scavengers at 7 $^{\circ}$ C, observed and calculated O_2 half-lives were 0.8, 0.9 h and 3.9, 3.8 h in bags containing air and N_2 atmospheres, respectively.

Discussion

Commercial O2 scavengers are composed of powders in sachets of plastic coated paper which is perforated to allow the ingress of O_2 . The powder contains particles of non-uniform sizes, and materials placed in the pouches are mixed rapidly immediately before each sachet is filled, to limit O₂ absorption before pouch formation, which might reduce O₂ absorbing capacities of the scavengers. As mixing is likely to be imperfect and the film perforation is variable, consistent performance by non-homogenous mixtures in the sachets is unlikely. Considerable variability in the O2 absorption rates among individual O₂ scavengers must be expected (Gill & McGinnis, 1995b). Therefore, results are likely to be reproducible only when multiple scavengers are used for each test, and generalizations from previous studies which involved systems where single scavengers were used must be treated with caution (Rousset & Renerre, 1990; Sorheim et al., 1995a,b; Allen et al., 1996; Doherty & Allen, 1998; Isdell et al., 1999).

The O_2 concentrations affected the O_2 half-lives substantially for any scavenger type resulting in longer O_2 half-lives for the low initial O_2 concentration of 500 ppm in N_2 atmospheres than for the

high initial O₂ concentration of 200 000 ppm in air at the same temperature. The magnitude of this effect varied for different scavenger types, depending upon their formulation. FreshPax[®] M-100 are designed for high CO₂ atmospheres; hence, generally longer O₂ half-lives were obtained in air and N₂ atmospheres than in CO₂ atmospheres.

Lower O2 absorption rates at low O2 concentrations (<1%) were reported by Gill & McGinnis (1995b). They argued that at low O₂ concentrations, rate of absorption becomes directly proportional to the O2 concentration so that the O2 concentration in the pack atmosphere declined exponentially with time, i.e. it followed a firstorder kinetic reaction. This behaviour is supported by the kinetic data of the present study which showed that the O2 absorption reaction was firstorder at both high (20%) and low (500 ppm) initial O2 concentrations and included O2 concentration as a limiting factor. At high initial O₂ concentration, other factors, such as the scavenger surface area and environment, may also affect the O₂ absorption rates. However, at low initial O₂ concentrations a diffusion phenomenon, which is a derivative of O2 concentration, was the dominant influence and resulted in low O2 absorption. A threshold O2 concentration existed where there was a dramatic decrease in O2 absorption rate and O₂ concentration became the primary limiting factor for the O₂ absorption rate. Consequently, different rate constants were observed for the same O₂ absorption curve at the same temperature, depending upon the initial O_2 concentration. Therefore, the overall O₂ absorption curve produced by the scavenger was bi-phasic. This supports the results of Gill & McGinnis (1995b) who found that at concentrations of <1%, O_2 concentration is the limiting factor for O2 absorption

Higher temperatures gave shorter O_2 half-lives. Generally, the rate constants increased with increasing temperature, as expected. However, the magnitude of the temperature effect was dependent upon the scavenger types because of the differences in their formulations. For some scavengers, the temperature effects on both O_2 half-lives and rate constants were more dramatic in air than in N_2 or CO_2 atmospheres. For others the reverse occurred, which may be because of differences in their formulations.

The Arrhenius equation for different scavengers may find its application in the computer simulation of varying O_2 concentrations in a package atmosphere at specific temperatures and at known initial O_2 concentrations. Such computer models may further be modified to predict possible deterioration of food products as related to O_2 absorption rate of the scavenger. This area requires further research.

Oxygen scavengers with more capacity also tended to absorb O_2 at a higher rate than scavengers with less capacity, which may be because of an increase in the surface area for O_2 absorption. It is interesting to note that although scavengers with greater capacity have a lower formula weight per square centimetre than scavengers with less capacity, they may undergo faster reactions, because of higher collision-frequency of the reactant, generating more heat, which may have resulted in high O_2 absorption rates. However, measurements of heat generated were not done in the present study. This area also requires further research.

The effect of the positioning of scavengers within packs was also substantial and significant (P < 0.05), which suggests that despite its high O_2 permeability, the barrier film acted as an O_2 barrier at low O_2 concentrations. Additionally, its barrier effect may increase with decreasing temperature. Consequently, the size of the hole in the lidding film is likely to be the limiting factor for O_2 absorption when retail trays were placed in a bag.

Because of significant variation in O2 absorption rates of commercial O2 scavengers, their appropriate selection is of importance in situations where high O₂ absorption is initially required, as in prevention of transient discolouration of ground beef. It is important to recognize that while manufacturers normally provide information and recommendations on application environments and O2 absorption capacity, rates of O_2 absorption are not readily available. At most temperatures, absorption rate characteristics can be as essential in making successful O_2 scavenger selections as O_2 capacity. Ageless[®] FX-100 or FreshPax® R-2000 scavengers had the highest O₂ absorption rates among the commercial scavengers used in the present study and may be used in situations where rapid removal of residual O2 is required. However,

because of significant positioning effects in our experiments, we found that they should be placed either inside the retail trays containing O₂ sensitive products or inside the retail trays as well as in the surrounding gas-impermeable bags. Multiple O₂ scavengers should also be placed in the retail package to obtain a consistent and reproducible O2 absorption rate. While this may add to the cost of the food product it is probable that the increased cost may be compensated by better quality product with longer shelf-life. Furthermore, the determination of the appropriate number of scavengers should be based upon O₂ scavenger type, initial O₂ amount, storage temperature, and desired O₂ absorption rate. The present study should serve as a guide for possible application of O₂ scavengers in situations where the rate of O₂ absorption is of primary importance.

Acknowledgments

The authors thank the Natural Sciences and Engineering Research Council of Canada for partial funding of this study, Dr C.O. Gill for technical advice and review of this manuscript, and Ms L.L. Gibson for technical assistance.

References

Allen, P., Doherty, A.M., Buckley, D.J., Kerry, J., O'Grady, M.N. & Monahan, F.J. (1996). Effect of oxygen scavengers and vitamin E supplementation on color stability of MAP beef. 42nd International Conference on Meat Science and Technology. Pp. 88–89. The Hague, Netherlands: ICoMST.

Anonymous (1998). Ageless®. Technical Literature. New York: Mitsubishi Gas Chemical America Inc.

Brown, T.L., Lemay, H.E. Jr & Busten, B.E. (1994). Chemistry: the Central Science. Pp. 496–506. Englewood Cliffs, NJ: Prentice Hall.

Doherty, A.M. & Allen, P. (1998). The effect of oxygen scavengers on the color stability and shelf life of CO₂ packaged pork. *Journal of Muscle Foods*, **9**, 351–363.

Gill, C.O. & Jones, T. (1994a). The display life of retail-packaged beef steaks after their storage in master packs under various atmospheres. *Meat Science*, 38, 385–396.

Gill, C.O. & Jones, T. (1994b). The display life of retail packs of ground beef after their storage in master packages under various atmospheres. *Meat Science*, 37, 281–295.

Gill, C.O. & McGinnis, J.C. (1995a). The effects of residual oxygen concentration and temperature on the

- degradation of the color of beef packaged under oxygendepleted atmospheres. *Meat Science*, **39**, 387–394.
- Gill, C.O. & McGinnis, J.C. (1995b). The use of oxygen scavengers to prevent the transient discoloration of ground beef packaged under controlled, oxygen-depleted atmospheres. *Meat Science*, **41**, 19–27.
- Isdell, E., Allen, P., Doherty, A.M. & Butler, F. (1999).
 Color stability of six beef muscles stored in modified atmosphere mother pack system with oxygen scavengers.
 International Journal of Food Science and Technology, 34, 71–80.
- Rousset, S. & Renerre, M. (1990). Comparison of different packaging systems for the storage of fresh beef meat in carbon dioxide atmosphere with or without residual oxygen. *Sciences Des Aliments*, **10**, 737–747.
- Smith, J.P., Abe, Y. & Hoshino, J. (1995). Modified atmosphere packaging-present and future uses of gas absorbents and generators. In: *Principles of Modified Atmosphere and Sous-Vide Product Packaging* (edited by J.M. Farber & K.L. Dodds). Pp. 287–323. Lancaster, PA: Technomic Publishing.
- Sorheim, O., Grini, J.A., Nissen, H., Anderson, H.J. & Lea, P. (1995a). Pork loins stored in carbon dioxide: color and microbiological shelf life. *Fleischwirtschaft*, 75, 679–681.
- Sorheim, O., Lea, P., Arnesen, A.K., Haugdal, J. (1995b). Color of beef loins stored in carbon dioxide with oxygen scavengers. In: *Foods and Packaging Materials Chemical Interactions* (edited by P. Ackermann, M. Jägerstad & T. Ohlsson). Pp. 217–221. Lund, Sweden: The Royal Society of Chemistry.