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A REFEREED PAPER

METHODS FOR MEASURING INTERNAL GASES OF CITRUS FRUIT AND DETERMINING PEEL PERMEANCE

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Abstract. **A method for collection and 3-minute analysis of internal gas samples of citrus fruit is described in detail, including the handling of samples and analysis by gas chromatography with molecular sieve columns. A new method is presented for correcting internal O_2 concentrations of citrus fruit and apples for argon content. An internal-gas method is described for determining the barrier properties of fruit peel to movement of gases, including ethane and ethylene. Internal gas volume of fruit was measured by dilution of internal gases.**

It is well known that the quality of fresh citrus fruit, like that of many other fruits and vegetables postharvest, is much affected by the internal concentrations of CO_2 and O_2 (Ahmad and Khan, 1987; Hagenmaier, 2002). However, the measurement of internal gases is somewhat demanding in terms of proper technique, and no standard techniques are available. One of the goals of this paper is to present suitable techniques for measurement of internal gases of citrus fruit, and possibly other fruit as well. In addition, some other uses of internal gas measurements are presented.

Cameron and Yang (1982) developed a procedure for measuring the diffusion rate of ethane through tomato skin. This procedure consisted of holding the fruit in a container into which ethane is injected, then transferring the fruit to a second, ethane-free container and measuring the head space of that second container at different times. They found that ethane had 1000 times as much tendency, per unit of area, to pass through the stem scar than through the skin of tomatoes, which has few if any stomates. Their data analysis was based on Fick's law, which in general terms states that the rate of passage of a gas through a barrier is proportional to its partial pressure difference across that barrier.

It is well known that gas molecules pass through a fruit peel by two different mechanisms. One mechanism is diffusion (or effusion) through holes in the peel, such as lenticels, stomata, stem scars and injuries. The second mechanism is permeance, which consists of a gas dissolving into a barrier on its high-concentration side, diffusing through the barrier, and coming out of solution on the low-concentration side. The term 'permeability' sometimes means permeance through a barrier of unit thickness (Crank, 1956) although when used in reference to citrus peel the usage is not so strictly interpreted. The amount of gas *diffusing* through the peel is proportional to the open area × the coefficient of interdiffusion of that gas into air. The amount of gas permeating through a barrier is proportional to the peel area × gas solubility in the peel × the solid-state diffusion coefficient, which is very much less than the coefficient of interdiffusion, thus explaining why the amount hole area of peel (unknown) is much more important than its total area, which is relatively easy to measure.

Variations on the Cameron/Yang method were later developed by Banks (1985), Knee (1991) and Schotsmans et al. (2002), but the basic technique was similar: expose the fruit to gas in a first container and make periodic measurements with the fruit in a second container to determine release of the gas from the fruit. Much of the development work on the method involved mathematical treatment of data.

None of these techniques involved the analysis of samples of internal gas, which is the method developed in the present work. This method has a simplicity advantage over any used previously, for two reasons. First, experimentally, it involves only one step, namely uptake of gas by the fruit followed by direct measurement of that gas both inside and outside the fruit. Second, the calculation is much easier, because internal gas measurements are taken after only one exposure time.

Presented below is a simple version of Fick's law that does not include peel area, which postharvest scientists continue to use despite the current consensus that most gas exchange through fruit peel occurs by diffusion through holes (Amarante and Banks, 2001):

1.) $$dC_{in}/dt = K\,(C_{out} - C_{in})$$

where C_{out} is the gas concentration outside the fruit (but inside the container), C_{in} is the internal gas concentration, i.e., the gas concentration inside the fruit; t is exposure time (in min). The K value, which has units of t^{-1}, is not named, includes gas exchange by both diffusion and permeance, and is therefore dependent on peel area and hole area of that particular fruit. When C_{out} is constant the equation integrates to

2.) $$K = -\,[\ln((C_{out} - C_{in})/C_{out})]/t$$

Because the experiment as described involves direct measurement of C_{out}, C_{in} and t, this equation offers easy calculation of K.

In order to calculate total quantity of gas passing through the peel, it is also necessary to know the internal volume of the fruit, since quantity = concentration × volume. Also presented here is a new method for measuring internal gas volume of fruit, also is based on analysis of internal gas concentration.

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Materials and Methods

Analysis of O_2, CO_2 and N_2 and Ar. The columns used for analysis of O_2, CO_2, Ar and N_2 were CTR columns (Alltech, Deerfield, Ill.), each comprised of two concentric packed stainless-steel tubes, 6 ft long, the outer tubing having ¼ inches outside diameter and packed with an activated molecular sieve packing that irreversibly absorbs CO_2. The packing of the inner column for the CTR I column was different from that for the CTR III column, as shown in Table 1. The CTR III column needed recharging periodically, when false values were found for standards, by flushing for 4 hours with a H_2 flow of 30 mL·min^{-1} at 135 °C. Either CTR column, after inadvertent injection of water, was heated 5 min at 150 °C, then 10 min at 220 °C, before being used again.

The gas samples were injected onto the column using an 8-port dual external sample injector (Valco Instruments Co., Inc., Houston, Tex.). Loop capacity was of 35-170 µL; bigger loops overloaded the detector. The inlet port of the injector was a female luer fitting. The detector and column temperatures were120 and 70 °C, respectively, the column flow rate was 70 ml min (at 30 psi), and sample volume at least 1 ml. The gas chromatogram was a Model 5890 from Agilent Technologies (Wilmington, Del.) or Model AutoSystemXL from Perkin Elmer (Norwalk, Conn.).

Syringes. Plastic syringes with black neoprene or rubber ends on the plungers were from Exel International, Culver City, Calif.; and from Becton Dickinson and Co., Franklin Lakes, N.J. Plastic syringes with plungers made of clear plastic were from Henke Sass Wolf GMBH, Tuttlingen, Germany. Glass syringes were Micromate from Popper and Sons, Inc., New Hyde Park, N.Y. The glass syringes with teflon plungers were from Hamilton and Agilent. The glass syringes with teflon plungers had 5 mL capacity and the others 10 mL capacity. The luer stopcock valves were either polycarbonate-high density polyethylene or metal, part Nos. 30800-01 and No. 31507-06, Cole Parmer, Vernon Hills, Ill.

Internal gas sampling. Internal gas samples were withdrawn by syringe, fitted with a stopcock-type on/off valve that was first flushed with N_2 (or other O_2 free gas) and kept filled with this gas until used to withdraw internal gas samples from fruit. A side-port needle, 18-22 gage, was attached to the valve and the syringe emptied of N_2. The tip of the needle was inserted into the fruit to avoid juice sacs, after having first dissecting two or three pieces of fruit to visually determine the approximate location of the internal cavity and the distribution of albedo. The needle was inserted to a depth of about 0.5 to 3 cm into the blossom end of the fruit, or it was inserted tangentially anywhere on the peel to a depth of about 1 cm, so that the tip was in the albedo (white portion of the peel) just below the flavedo (colored layer comprising approximately the outer 2 mm of the peel). The internal gas was withdrawn at a rate of roughly 1 mL/sec, with attention to whether excess backpressure developed, indicating that the tip of the needle had been inadvertently inserted into juice sacs rather than albedo or central cavity.

Table 1. Peak identification with CTR1 and CTR III columns.[z]

	CTR I		CTR III[y]	
Peak identification	Retention time (min)[z]	Gases	Retention time (min)	Gases
No. 1, inner	0.36	O_2, Ar, N_2	0.9	Ar
No. 2, inner	0.61	CO_2	1.2	N_2
No. 3, outer	1.75	O_2, Ar	2.0	O_2, Ar
No. 4, outer	2.52	N_2	3.0	N_2

[z]Column temperatures were 73 °C and 60 °C, respectively.

Injection of the sample into GC. The needle was removed and if there was no evidence of water inside the syringe or valve, the gas sample was injected into the loop with mild pressure on the plunger before opening the stopcock. A minimum of 1 mL gas was injected, followed by a 3-5 s pause before rotating the valve to inject the sample onto the column. In cases where water was evident, shaking or use of a second syringe was often sufficient to remove it from the exit pathway. When these measures were not successful, a 4 mm diameter filter, with PTFE membrane (0.45 µm pore size) was inserted between syringe and inlet; this blocked flow of gas into the injector if wetted. The sample could sometimes still be analyzed by closing the valve before releasing force on the plunger and replacing the filter. Duplicate analysis was performed for each sample.

Calibration. Standard gases were injected before and after analysis of samples. The most useful standard gas contained 10% CO_2, 5% O_2 and 85% N_2 (Fisher Scientific, Pittsburgh, Pa.). A pressure regulator was installed on the gas tank, with a septum in the outlet of the regulator. A needle was inserted into the septum, connected by tubing to the loop injector. Samples of room air were also analyzed regularly during the day, about every 10 samples of internal gas, in order to a) check the performance of the column and b) get values of environmental gas for use in the described calculations. The Ar content of standards needed checking. A standard gas labeled as 1.00% each CO_2 and O_2, balance N_2, actually contained 0.095% Ar, which would have led to about 10% error in calculation of O_2 content. Instability of analysis was most often corrected by heating the column at about 180-220 °C for 30-60 min. Columns were used regularly for 1-2 years.

Diffusion procedure. The sample containers were paint cans of 4 liters capacity, connected to diaphram pumps for recirculation of headspace gas at 2 L·min^{-1}. Five oranges were put into the can, the pump started and sufficient hydrocarbon indicator gas (normally ethane, see Discussion) was injected into the can to bring the headspace concentration to about 300 ppm (0.03 kPa). Samples of the circulating gas were withdrawn at 5-min intervals for analysis. The can was opened, the exposure time recorded, and the fruits withdrawn immediately (within 5 sec) to be submerged in water, and kept there for 1-4 min each until samples of internal gas were withdrawn.

Hydrocarbon analysis. Samples of circulating gas and internal gas, in duplicate, were injected via a 50 µL loop onto a Unibeads 2S 68/80, 6 ft × 1/8 inch column operated at head pressure of 30 psi and column flow of 60 m·min^{-1}. A Perkin-Elmer Auto-System gas chromatograph was used with injection, oven, and FID detector temperatures of 250 °C, 115 °C, and 250°, respectively. The syringe used for hydrocarbon analysis was the glass syringe with metal stopcock; plastic syringes tended to absorb enough hydrocarbons that the composition of later samples depended on the history of the syringe. Diffusivity was calculated with equation 2) with C_{out} calculated as the mean circulating gas concentration during 30 min exposure time.

Internal gas volume. A partial vacuum was created inside submerged fruit by removing about 1 mL of internal gas by sy-

ringe. A measured amount (50-100 µL) of a N_2-ethane was injected under the flavedo and permitted to diffuse throughout the fruit while submerged for about 20 min, after which an internal gas sample was taken for analysis of ethane concentration. The same amount of ethane was injected into 33.5 mL-capacity glass vials. The gas volume was calculated as the 1 mL volume withdrawn before injection plus:

3.) $$Vol^{fruit} = Vol^{vial} \times Conc^{vial}/Conc^{fruit},$$

where Vol^{fruit} and Vol^{vial} are the internal gas volumes of fruit and vial; $Conc^{fruit}$ and $Conc^{vial}$ are the gas concentrations of fruit and vial, respectively. In the case where ethane was previously used for determination of diffusivity, propane was used. Alternatively, neon might be used as the dilution gas, and its concentration determined with the CTR I column at 83 °C.

Vacuum withdrawal. An individual fruit was placed in a beaker containing 2 L of recently He-purged water, positioned in an inverted 2-L plastic bottle with the bottom removed and closed at the neck with a rubber stopper fitted with a stopcock valve. After removal of gas from the inverted bottle the stopcock was closed and a vacuum applied (0.1 ± 0.03 atm for 90 sec). The gas captured under the bottle was removed within 2 minutes after release of the vacuum.

Results and Discussion

Use of syringes. When using syringes to collect gas samples from fruit it was very helpful to be able to detect by feel whether the tip of the needle was properly positioned so that gas entered the syringe when the plunger was withdrawn. When the needle tip was inadvertently positioned in a juice sac so that little or no gas was withdrawn, the plungers of the glass and the plastic syringes popped back to the fully inserted position when released. However, for syringes with teflon plungers it was not apparent whether gas was being withdrawn from the fruit, and therefore these are less suitable.

Errors in measurement of internal O_2 syringes due to mixing with air could be kept below about 0.2% with some precautions. These consisted of flushing syringes with N_2 or He before they were used to load samples (Table 2) and keeping samples in plastic syringes for a maximum of about 2 hr after withdrawal from the fruit (Table 3). Glass syringes, if used, needed to be wetted to prevent uptake of air because of the partial vacuum (about 0.2 atm) created in the syringe during withdrawal of samples from the fruit.

Syringe and valve recommendations. The syringes most suitable for CO_2, O_2, and N_2 analysis were leur-lock syringes made of plastic (Bectin Dickinson, Excel or Henke). The polypropylene-polyethylene stopcocks worked better than the metal stopcock with these because of the tighter fit. However, most suitable for the hydrocarbon analysis are glass syringes with metal stopcocks.

Table 2. O_2 content of N_2 gas samples held in Excel plastic syringes with polypropylene valves for about 1 min.

	%O_2
Syringe preparation	Mean
None	0.77 a
Flushed twice	0.03 c

[z]Mean values not with the same letter are significantly different ($p < 0.05$, Tukey), n = 5.

Table 3. Oxygen gain (kPa) of gas in syringes from storage or reduced pressure.[z]

	Valve type	2 hr storage	18 hr storage	0.5 atm, 10 sec
Exel 10 mL	plastic	0.0 b	0.6 a	0.2 b
BD 10 mL	plastic	0.0 b	0.7 a	0.1 b
Henke 10 mL	plastic	0.1 b	0.7 a	0.2 b
Glass 10 mL, dry[y]	metal	2.7 a	nv	0.8 a
Glass 10 mL, wet	metal	0.0 b	0.7 a	0.4 b
Agilent 5 mL, wet	metal	0.0 b	0.6 a	0.2 b
Hamilton 5 mL, wet	metal	nv	nv	0.2 b
Hamilton 5 mL, dry	metal	0.0 b	0.2 a	0.7 a

[z]Mean values in a column not with the same letter are significantly different ($p < 0.05$, Tukey), n = 5.
[y]Dry or wet refers to absence or presence of water between barrel and plunger.

Determination of O_2. The chromatographs from the CTR I column had 4 peaks (Table 1), but only peaks 2, 3 and 4 were useful for analytical purposes. At column temperatures above about 90 °C the peak resolution was less than 2 for the separation of peaks 1 and 2, and/or peaks 3 and 4 (Table 4) indicating that the retention times were insufficiently different (Grob, 1995).

At no column temperature was O_2 separated from Ar by the CTR I column. In trials with pure gases at temperatures of 40, 60, 80 °C the Ar retention time was only 0.02 min less than that of O_2, and the mean peak widths were 0.13 min for both components. The area ratios, O_2/Ar were 0.89, 0.90 and 0.93 at temperatures of 40, 60 and 80 °C, respectively (data not shown elsewhere). Therefore, in order to calculate O_2 concentration with data from the CTR I column, it is necessary to know the Ar concentration, and a method will be shown for calculating that.

For internal gas samples from citrus fruit and apples the internal gas concentrations were determined with both CTR I and CTR III columns (Figs. 1a, b). These data show that concentration ratio of Ar inside and outside the fruit was virtually the same the N_2 ratio, that is

4.) $$(\text{Internal Ar})/(\text{atmospheric Ar}) = (\text{Internal } N_2)/(\text{atmospheric } N_2)$$

where all gas Internal Ar and N_2 are gas concentrations inside the fruit. Atmospheric Ar and N_2 are a gas concentrations in

Table 4. Peak resolution on the CTR I column.

	Resolution[z]	
Column temperature (°C)	Peaks 1 & 2	Peaks 3 & 4
25	7.6	4.8
50	4.9	3.4
70	3.4	2.6
80	2.9	2.3
90	2.4	2.0
100	2.1	1.8
110	1.8	1.5

[z]Resolution = (delta retention time)/(sum of peak widths), n = 2.

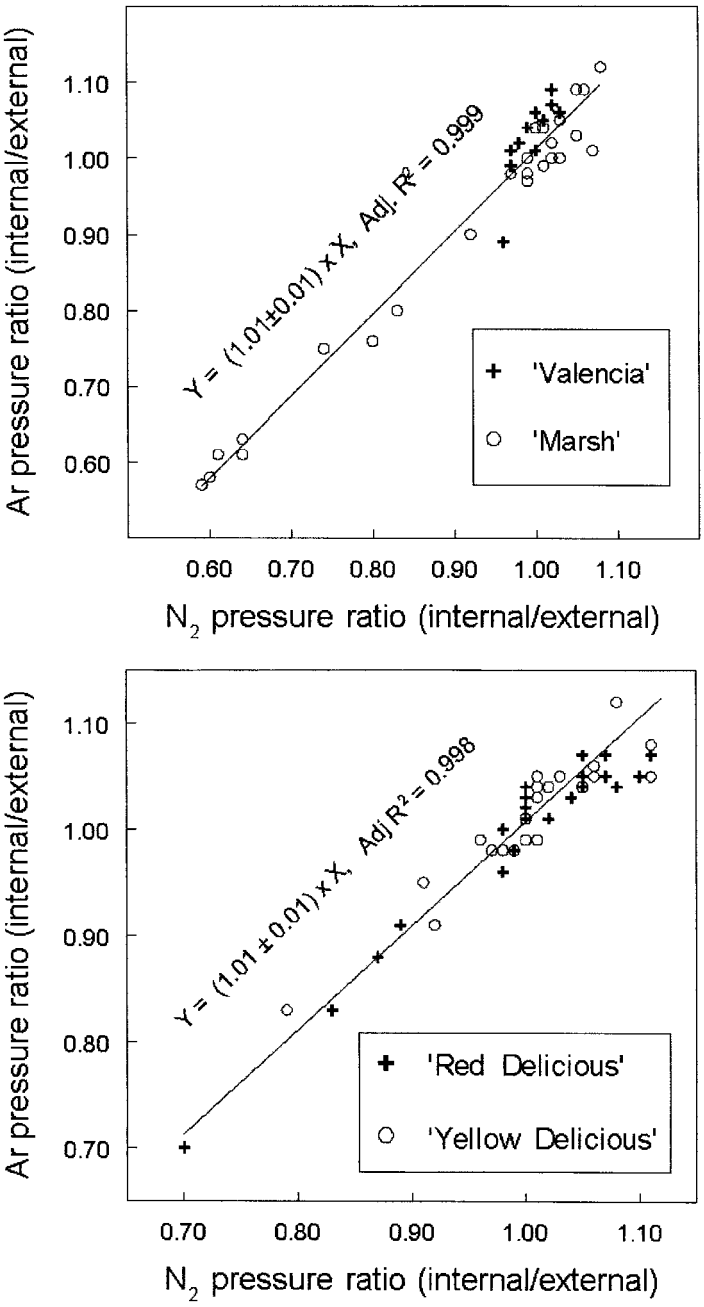

Fig. 1. Concentration ratio (internal/external) of Ar plotted against same ratio for N_2 in individual fruits. A: citrus fruit, B: apples.

the environmental air, which were 0.93 and 78 kPa, respectively at 20 °C, 50% (Weast, 1976). The Internal N_2 was measured, and therefore Internal Ar can readily be calculated.

In practice, whether calculated from equation 4) or measured directly, the internal Ar was 0.9 to 1.1 kPa whenever internal CO_2 was < 25 kPa, which included virtually all fruit not obviously spoiled. Estimation of Ar with the formula seems preferable to making a separate analysis for each sample with the CTR III to save time, and also because of the regular maintenance that column needed to replenish the oxygen-absorbing ability of its inner column.

Internal CO_2 and N_2. The internal CO_2, like internal O_2, is very important to fruit quality during storage. The methods here described are sufficiently reproducible to show a big difference between fruit subjected to different coating treatments (Table 5). An added advantage (besides calculation of the Ar concentration) for recording the N_2 contents was to enable calculation of the sum ($N_2 + O_2 + CO_2 + Ar$), which was typically 97.5 ± 2.5 kPa (Table 5), about as expected, considering that 2.3 kPa is the water vapor content of saturated air at 20°C.

The concentrations of CO_2 and O_2 in internal gases withdrawn by syringe were compared to those of gas samples extracted by vacuum from the same fruits (Table 6). The concentration similarities seem remarkable, considering the changes in gas composition likely to occur during vacuum extraction, especially the release of CO_2 and O_2 dissolved in the juice or adsorbed on the peel, and the re-solution of these gases in the 2 L of water used in the apparatus.

Concentration gradients. Two different experiments indicated that ethane gradients inside citrus fruit are minimal about 10 minutes after exposure or injection. Ethane concentration gradients inside 'Valencia' oranges were minimal within 10 min after injecting gas under the peel of 'Valencia' oranges (Fig. 2). The ratio of concentration in samples taken from peel and was near unity after 8 min exposure (Table 7). For determination of diffusivity, the fruit was exposed to gas for about 30 min, which is more than sufficient time for uniform distribution of ethane throughout the fruit. Low gas gradients, reflected by concentration differences within about 5% for samples taken from different locations inside fruit have been reported by Burg and Burg (1965) for ethylene in red delicious apples and by Rajapakse et al. (1990) for O_2 in apples, nectarines, and pears.

Internal volume by dilution of gas. The internal gas volumes of 'Valencia' oranges was about 28 to 45 mL, and the values were about the same whether determined by dilution or by vacuum withdrawal (Table 8).

Fruit diffusivity. With 5 oranges in a 4-L container (total weight about 1.5 kg), the value of C_{out}, the concentration of 'outside' gas, decreased by an average of about 5% during 30 min exposure (data not shown), which is about what would be expected from the measurements of internal gas volume. Thus, the value of C_{out} was not constant, as assumed in the derivation of equation 2). Smaller decreases would be expected with less fruit. However, that amount of change during an experiment would cause only about 3% error in calculation of K when the experiment is terminated when $C_{in}/C_{out} < 0.5$,

Table 5. Internal gas concentrations of Valencia oranges with different coatings.[z]

Coating[y]	CO_2	O_2	Ar	N_2	Total
HS 590	12.8 a	1.9 c	0.99 a	81.9 a	97.2 a
PE	5.4 c	8.7 b	1.00 a	82.5 a	97.6 a
B155	13.5 a	2.2 c	0.97 a	80.6 a	97.4 a
Carnauba	8.2 b	6.3 b	0.99 b	81.5 a	97.5 a
Washed	3.3 cd	18.0 a	0.93 b	77.2 b	98.2 a
Field run	2.0 d	16.5 a	0.93 b	77.3 b	98.0 a

[z]Numbers in a column not with the same letter are significantly different ($p < 0.05$, Tukey), n = 12.

[y]The treatments for washed fruit consisted of Stay-Fresh 590HS (FMC, Lakeland, FL), a polyethylene microemulsion, Brogdex 555 (Brogdex, Pomona, CA), or a carnauba wax microemulsion (Brilliance, CH2O, Inc., Olympia, WA), washed with no coating. Field run was fruit not washed and not coated.

Table 6. Comparison of internal gases withdrawn by syringe and vacuum from 'Valencia' oranges with high-gloss coatings.[z]

	Internal CO_2 (kPa)		Internal O_2 (kPa)	
Fruit no.	Syringe	Vacuum	Syringe	Vacuum
1	16.3 a	20.7 b	0.8 a	1.5 b
2	24.2 a	29.9 b	0.6 a	1.1 b
3	33.6 a	35.8 a	0.8 a	2.0 b
4	28.8 a	36.3 b	0.7 a	2.0 b
5	14.2 a	19.0 b	2.2 a	1.6 a

[z]Numbers for CO_2 not with the same letter are significantly different ($p < 0.05$, Tukey), n = 2. Likewise for O_2.

and therefore, that restriction is advised (analysis not shown). In applying this test, it is useful to know that 0.693/K is the time required for C_{in}/C_{out} to reach the 0.5 mark.

Diffusion constants for ethane, propane, butane and ethylene were proportional to one another for fruits exposed simultaneously to more than one gas (Table 9, Fig. 3a, 3b). This observation expands the utility of the method. As mentioned it is important to measure gas volume when measuring diffusivity. Thus, ethane can be used to measure diffusivity and propane to measure the volume. Another example of flexibility is to use ethane to determine ethylene diffusivity, without incurring the change in physiology likely to be incurred by exposing the fruit to ethylene. Finally, should any fruit containing a natural substance that passes through the chromatography column at the same retention time as ethane, another gas can be used.

Non-destructive. The methods here described are non-destructive, providing some precautions are taken. First, it is useful to weigh the fruit periodically to detect any water entering the fruit during withdrawal of internal gas samples.

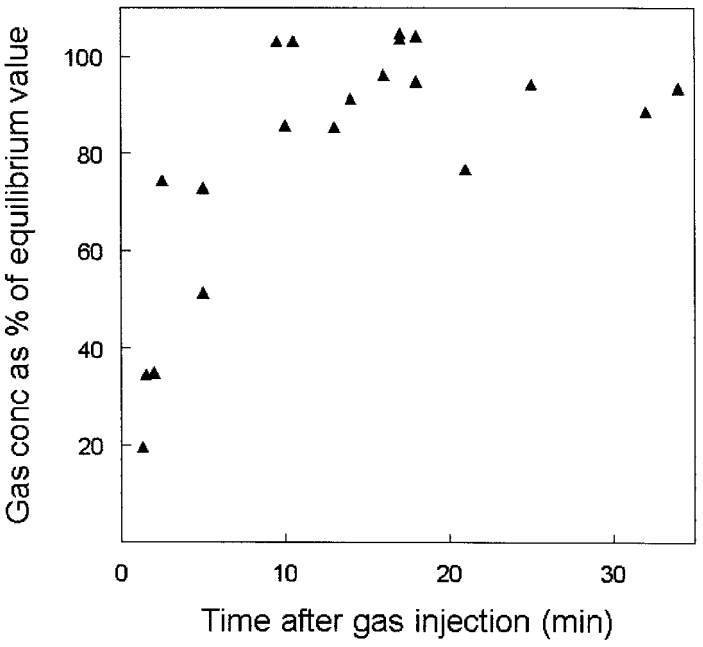

Fig. 2. The concentration of ethane gas at the propane injection site as % of value expected from knowledge of the amounts injected ('Valencia' oranges).

Table 7. Ratio between ethane concentrations of 3 ml gas samples removed from both periphery and center of seven non-coated grapefruit.

	Relative concentrations[z] peel/center	
Duration of gas exposure (min)	Ethane	Propane
8	0.96	
8	0.94	No results
10	0.94	
18	1.08	
10	0.97	0.93
10	1.02	0.97
11	1.07	1.10
Means	1.00	1.00

[z]Ratio of mean concentrations, each measured twice for each sample.

Second, water can be blotted from the fruit surface and the fruit dried after submersion to prevent the water from acting as a second coating or to damage any coating that was applied. Finally, puncture wounds may be plugged with a boiled toothpick after withdrawal of internal gas samples.

Conclusions

Procedures are herein described for rapid and non-destructive measurement of internal CO_2, internal O_2 corrected for Ar, internal N_2, diffusivity and internal gas volume. Internal gas concentrations of citrus fruit reached steady-state values within 10 min after injection of gases, were virtually the same whether taken from the peel or the core. Internal gas volumes were about the same whether collected under a vacuum or withdrawn by syringe.

Table 8. Comparison of internal gas volume (ml) of 'Valencia' oranges determined by dilution and vacuum withdrawal.

	From dilution[z]		
Fruit weight (g)	Ethane	Propane	Vacuum
226	27.7	28.1	27.3
267	26.5	27.9	29.1
280	38.8	39.5	37.1
286	44.7	46.0	41.4
309	38.0	35.4	34.8

[z]Measured 25 min after injection, n = 2.

Table 9. Diffusion constants for fruit exposed to ethane and another gas simultaneously.[z]

		K gas/K ethane	
	Gas	Mean	Std D
Flame Red grapefruit	butane	0.67	0.06
Flame Red grapefruit	propane	0.78	0.05
Valencia oranges	propane	0.81	0.02
Valencia oranges	ethylene	1.06	0.09

[z]Exposure time was 25-35 minutes, n = 12.

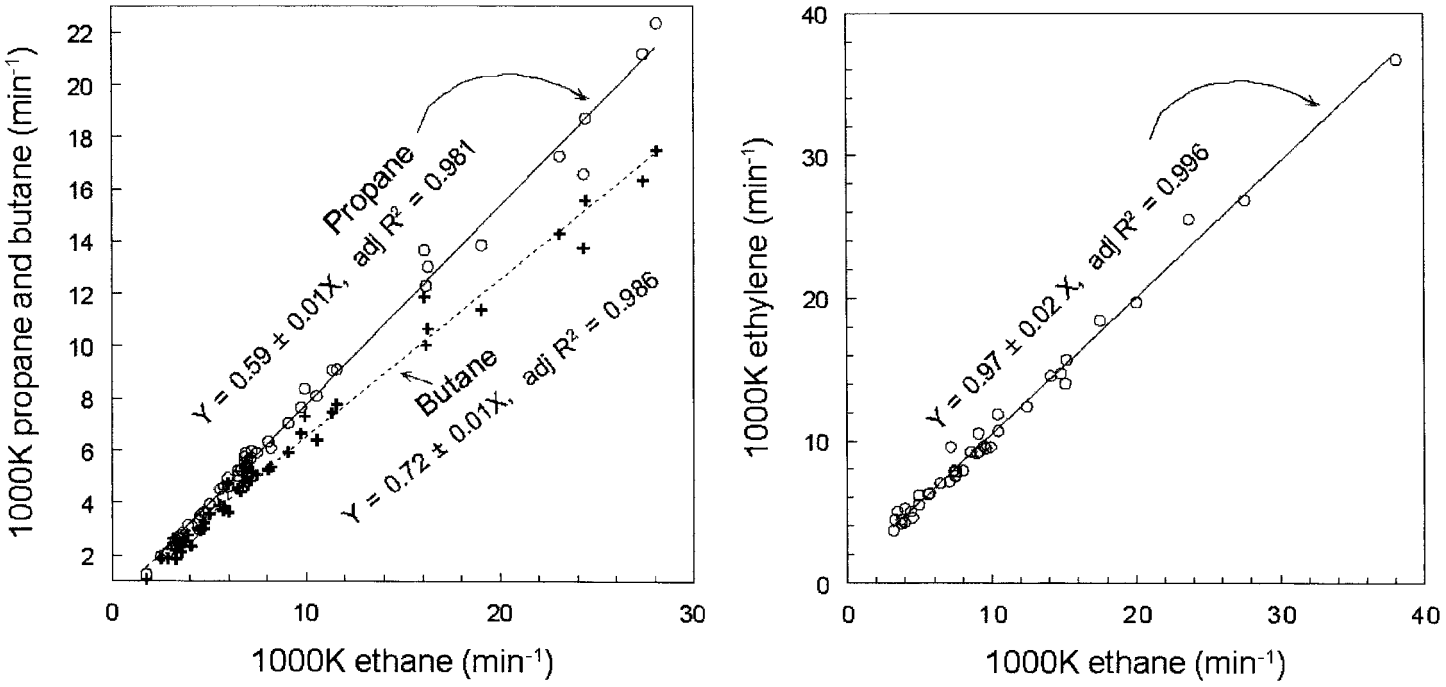

Fig. 3. The relationship between diffusion constants measured simultaneously in the same fruit. A: propane, butane and ethane of 'Flame' grapefruit. B: ethylene and ethane of 'Valencia oranges'.

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