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Sabbatical Report
1998-1999

on

Storage of Prunes Under Controlled Atmospheres for Quality Preservation and Insect Control

Shlomo Navarro

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ACKNOWLEDGMENTS:

Shlomo Navarro* thanks all those who helped to realize the work presented in this report; Pat Vail, Larry Zettler, Jim Leesch, Jane Tebbets, Richard Gill, Judy Johnson, Karen Valero, Shirley May, Vicki Yokoyama, Gina Miller, Charles Burks, David Brandl, Joel Siegel, Luis Aung, Joe Smilanick, David Obenland and Bas Kuenen of the HCRL, Gary Obenauf and Tom Jones of California DFA, Christopher Steggall and Krikor Y. Bedrosian, National Raisin Co., and Wayne Albrecht, Albrecht farms/ Dehydrator.

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Executive Summary

The major objective of the studies summarized in this report was to investigate economically feasible alternatives to methyl bromide for control of dried fruit insect pests in general and of prunes stored in California in particular. Laboratory studies included tests on the equilibrium relative humidity, the metabolic activity of prunes for modified atmosphere storage, and a demonstration of the critical limits of leakage rates on the effectiveness of modified atmosphere and conventional fumigation.

Experiments to determine moisture content of prunes showed that, even at extended drying times over 152 h, a constant weight could not be achieved. This indicates the difficulty in determining the absolute moisture content of prunes and that any reported values are highly variable depending on the test method.

The feasibility of using self-generated atmospheres based on the metabolic activity of prunes was investigated. However, prunes dried in commercial dehydrators at elevated temperatures are physiologically dead and do not respire. Respiration processes from the microorganism load and their particular composition on the fruit do occur when the water activity of the fruit is above 0.755. This water activity value, also known as the equilibrium relative humidity, is equivalent to a moisture content of 29% in the case of prunes.

Experiments determined that microorganisms on prunes would flourish and cause deterioration of the fruit if the water activity of the fruit is above 0.70 (moisture content of 24.6%). However, in sealed structures (like the Volcani Cube®) it was shown that prunes can be stored safely when water activity is as high as 0.65 (22% moisture content) without microorganism growth and deterioration of the fruit. Fruit samples taken from commercial storage bins showed that prunes are typically dried for 18 hours to a water activity of about 0.575 (15% moisture content) prior to storage. Samples taken during the drying process showed that prunes reached 0.65 water activity (22% moisture content = safe storage moisture content) after only 11.5 hours of drying. These experiments show that the drying process for prunes could be shortened significantly, with concomitant savings in dryer costs. These 'partially dried' prunes can then be safely stored in sealed structures like the Volcani Cube®, perhaps relying on the self-generated atmosphere or a modified atmosphere to prevent insect and microorganism deterioration. This strategy could eliminate the need for conventional fumigation.

Half-life pressure decay times, based on several different leak rates, were determined for fumigants and modified atmospheres contained in the Volcani Cube. Experiments showed that the following gas exchange rates were the critical values for maintaining a sufficiently gas tight chamber: N_2 atmosphere, 0.5% O_2/day infiltration rate with a 5 min half-life; CO_2, 2%/day loss with a 5 min half life; phosphine, 100 ppm/day loss with a 3 min half-life; and methyl bromide, 1.0 g/m3/day loss with a 4.5 min half-life. Gas exchange rates greater than these critical values would be too costly in gas maintenance or would likely result in control failures.

Finally, preliminary tests demonstrated the potential effectiveness of vacuum treatment in a flexible structure (to produce an oxygen deficient atmosphere) for pest control and quality preservation of fresh and dried commodities.

Foreword on the Sabbatical year

The Horticultural Crops Research Laboratory (HCRL) in Fresno is located in the central San Joaquin Valley of California. It is the heart of agricultural production for the state and represents a significant amount of the production in the United States. Major agricultural products include fresh fruit such as citrus, peaches, plums, pears, apples, apricots, grapes and durable products such as cereals, walnuts, almonds, pistachios, raisins and dried fruit. In communications prior to the Sabbatical of Shlomo Navarro interest on storage of dried fruit under controlled atmospheres for quality preservation and insect control was expressed by the HCRL.

During the Sabbatical, Shlomo Navarro has attended several professional meetings. Among them:

- Methyl Bromide Alternatives Outreach in Orlando, FL Nov. 1998.
- Prune Day, Visalia, CA, Dec. 1998.
- Annual meeting US-Israel Science and Technology Fund supported project on MB Alternatives, OSU, Stillwater, OK, Feb. 1999.
- Annual meeting of the ARO International Cooperation Committee, Bet Dagan, Israel, Mar. 1999,
- XIVth International Plant Protection Congress, Jerusalem, Jul. 1999.
- Demonstration trial in Boston of US-Israel Science and Technology Fund supported project on MB Alternatives, Boston, MA, Sept. 1999.
- Methyl Bromide Alternatives Outreach in San Diego, CA Nov. 1999.
- 19th ASEAN & 1st APEC Seminar on Postharvest Technology, HCMC, Vietnam, Nov. 1999.
- Training Course and Development of Cooperative Programs with Postharvest Authorities in China, Nanjing and Beijing, Nov. 1999.
- Prune Day, Sacramento, CA Dec. 1999.

From the professional and administrative aspect Shlomo Navarro has been instrumental in the early planning and preparations of the International Conference on Controlled Atmosphere (CAF) and Fumigation in Stored Products to be held in Fresno, Oct. 2000. He participated in all the meetings of the Local Organizing Committee and the Scientific Committee of the CAF Conference. Also in cooperation with Dr. J. Leesch and Dr. L. Zettler, he took active part in the preparation of the publication of the First and the Second Circular of the CAF Conference. Until the end of his Sabbatical Shlomo Navarro has continued to take active responsibilities as a member of the CAF Conference Scientific Committee.

Storage of Prunes under Controlled Atmospheres for Quality Preservation and Insect Control

INTRODUCTION

This report reflects the laboratory and field work carried out on "Storage of Prunes under Controlled Atmospheres for Quality Preservation and Insect Control" during the Sabbatical. To prepare a detailed plan of work that fits well within the work program of the USDA, ARS, HCRL in Fresno, a series of visits and meetings was held at different levels. The following is background information gathered on dried fruit storage in these meetings.

Background information

The plan of work on Controlled Atmospheres for Quality Preservation and Insect Control was prepared as a result of a series of visits and meetings that included:

1- Visit the National Raisin Company, Fowler, CA on December 21, 1998.
2- Information on the prune industry, meeting with Judy Johnson at the HCRL on December 28, 1998.
3- Meeting with Judy Johnson, David Brandl, Charles Burks and Joel Siegel, on January 25, 1999 at the HCRL.
4- Meeting with Pat Vail, Larry Zettler and Jim Leesch, on February 1, 1999 at the HCRL.
5- Meeting with Pat Vail, Larry Zettler, Jim Leesch, Gary Obenauf, Judy Johnson, Charles Burks and David Brandl, on February 12, 1999 at the HCRL.

1- Visit the National Raisin Company, Fowler CA.

1.1 Purpose of the visit : The visit was planned with the objective to study and identify the major postharvest problems or concerns of the dry fruit industry.

1.2. Persons met: The visit was organized by David Brandl, USDA, to meet Christopher Steggall, in charge of grower relations, and Krikor Y. Bedrosian, Vice President, National Raisin Co.

1.3.- Location and date: The visit took place in the Fowler, California facilities of National Raisin Co. on 12/21/98.

1.4.- Subjects discussed:
- The visited facilities are designated for processing principally raisins. A large portion of the raisins is received from the growers after sun drying. The U.S. standard for sun dried natural raisins is 16% MC, but for mechanically dried raisins, the MC is 14%. The mechanical drying is carried out on trays.

The plant processes organic raisins. They are stored in large stacks covered by craft paper and treated with N_2 to control insects.

- Prunes are also processed at National Raisin Co, except for pitting which is performed elsewhere. The two methods of drying prunes are:
a- Drying to 18 to 19 % MC and storing without turning the bins. This is termed the Co-op method which is energy intensive.
b- Drying prunes to 22 % MC and then turning the bins for conditioning, with the assumption that the prunes are at a wide range of MC, and the low MC will equilibrate with those at higher MC during storage. This is a preferred but labor intensive method.

To prevent mold damage the prunes and raisins are being treated with sorbates.

1.5 - Priorities:
- During the meeting two points of interest were discussed:
a- Selection of equilibrium MC values just below the critical limit to prevent mold development and to avoid the use of chemical preservatives. This subject will require further literature search and establishment of a drying/processing strategy that would enable proper storage without chemical preservatives. The industry is very interested in eliminating the possibility of using sorbates. In this context the importance of equilibrium MC was discussed.

b- The possibility of using smaller CA treatment chambers than those currently in use. In this context the use of the Volcani cube as an experimental storage structure, was discussed. The processors showed great interest in cooperating with the USDA to explore the potential of using the Volcani cube in CA treatments of organic raisins, particularly for the treatment of small lots.

1.6. CA treatment under kraft paper cover at the National Raisin Co. facilities: The installation was visited.

1.7 Analysis of the purge efficiency of the National Raisin Co. facilities:
Basic data were received. From this series of analysis based on assumptions, it would appear that the treatments have been applied in a professional manner and the results are comparable to those obtained from experimental trials. The gastightness of the treated structure falls within the standard recommended by Soderstrom and Brandl (1984) for performing application of CA using N2 (Table 1).

1.8. Conclusions:
From this series of analysis based on assumptions, it would appear that the treatments have been applied in a professional manner and the results are comparable to those obtained from experimental trials. The gastightness of the treated structure falls within the standard recommended by Soderstrom and Brandl (1984) for performing application of CA using N_2 (Table 1).

2- Information on the prune industry, meeting with Judy Johnson, HCRL on December 28, 1998:

2.1 Objective of the meeting: To discuss subjects of priority for the dried prune industry in California.

2.2- Excerpt of the meeting held on 12/28/98:

Judy has been in professional contacts with Mariani, one of the large processors of prunes in California. This processor receives from the growers 70% of the prunes already dried from the growers. There are dozens of growers who supply the prunes to Mariani, there may be a small portion sun dried and the rest dried mechanically. Mariani dries the remainder (some 30%) of the prunes using mechanical dryers.

The preferred industry storage MC for prunes is 17 to 19 %.

The principal storage pest is the Indian Meal Moth (*Plodia interpunctella*). Other pests like the Saw-toothed grain beetle (*Oryzaephilus surinamensis*) and the Dried fruit beetles (*Carpophilus hemipterus)* could also be present.

The University of California at Davis has studied prune drying processes. One of the Ag. Eng. involved in this development is Jim Thompson.

It is suspected that most of the infestations occurred in those prunes previously dried by the growers and brought into the Mariani facilities. Because Mariani uses mechanical drying, the general understanding has been that the elevated temperatures used during the process (at about 55°C for 48 h) have a sterilizing effect on insects. Thus, prunes supplied by the growers are probably reinfested after the drying process because of the infested facilities in use.

The prunes are stored in large stacks of up to 4 bins high (4 x 4 ft = 16 ft 4.88 m) and in rows of 24 by 10 to 15 bins length. Each standard storage bin is 4 x 4 x 4 ft (= 64 cf. 1.81 m^3) to contain 2,000 lb (908 kg). This results in a typical stack of 960 bins (24 x 4 x 10) containing 872 tonnes of prunes.

Prune fumigation using MB is carried out up to three times a year, once in the beginning of the season (November) and up to twice in March through July, before the weather gets warm.

The phase out of MB and the restrictions proposed by EPA upon the use of phosphine has caused an alarming situation in treatments related to the control of insect pests.

During the meeting with Judy two possible treatments were considered:

a- Treatment by sealing each individual bin: Since much of the infestation is suspected to be caused through the prunes supplied by the growers, the possibility of treating each individual bin was discussed. These bins could be treated upon receipt in the Mariani

facilities and stored for convenience according to required storage period in the yards of the plant.

b- Treatment by sealing of stacks: In case that large portions can be treated, the use of large sealed bags to contain 1,725 bins was discussed. This technology is available and it may be more economically feasible than the sealing of individual bins.

In both cases, in view of the restrictions and limitations of conventional fumigants, the possibility of using CO_2 was envisaged.

The prune industry, although reluctant in changing their fumigation practices, has not rejected the idea of using CA treatments. It may accept the strategy that by using one of the above mentioned treatments, and keeping the commodity in sealed conditions, a secondary or third fumigation treatment (from March to July) would not be necessary.

3 - Minutes of the meeting with HCRL staff on January 25, 1999

Possibilities of using MA by the dry fruit industry in CA:

- Efficacy of the MA applied at National Raisins Co. (NRC):

The dried fruit industry has been using modified atmospheres (MA) for organic raisins. The results of the visit at National Raisins Co. demonstrated that the technique has been applied in a professional manner and that N_2 usages are comparable to those obtained from experimental trials carried out by Soderstrom and Brandl (1984).

- The gastightness of the treated structure covered with kraft paper, was found to be within the standard recommended by Soderstrom and Brandl (1984) for performing application of CA using N_2.

- Tests for the evaluation of gastightness of the structures used by National Raisins Co. and the fumigation chambers used by the Blue Diamond were considered.

- A cost comparison of the use of CO_2 and N_2 was made using prices obtained from the industry, and they are summarized in the following Table 2:

According to this table it would appear that CO_2 is twice as expensive as N_2 when the supply in large quantities is considered in Fresno, CA area. However, CO_2 has the advantage that even in empty structures gas purge would not exceed 1m3 CO_2/ m^3 of treated storage volume. This compared to the N_2 purge volume of 3.8 m^3/ m^3 of treated storage volume (Table 1).

- Purge time (2.5 weeks) and exposure time (4 weeks) applied by the NRC are extended time treatments, and suit most prolonged storage of organic raisins. Using the combination of CO_2 at elevated temperatures (39°- 45°C) it would be possible to reduce the treatment time. For example, using CO_2 an approximate 0.5 day purge and a 4 h

exposure may be sufficient for a structure of 1800 m3 for controlling the codling moth at 43°C. For this MA, the time necessary to increase the temperature of the raisins remains an aspect that needs further investigation.

- In case that phosphine would not be re registered, CO_2 could be used for periodic treatments in long term storage of prunes and raisins.

- For long term storage of raisins, the possibility of using a partition wall inside the kraft paper covered storages to divide the structure into interconnected cells was considered. There would be benefits in having access to a portion of the stack while maintaining the atmosphere integrity of the remainder of the stack and likely in increasing purge efficiency.

- For the increase of temperature, preliminary experiments using heat were carried out on prunes and raisins (Judy Johnson). Increase of heat using steam was found to be a slow process due to the low conductivity of the product (2 days to attain 48°C at 18" depth of raisins).

- The possibilities of integrating MA created from the metabolic activity of the commodity and its associated microflora was discussed. Such information could form the basis for independent treatments without the use of fumigants or MAs for long term storage of prunes and raisins.

4 - Meeting with Pat Vail, Larry Zettler and Jim Leesch, on February 1, 1999 at the HCRL

Background information on post-harvest respiration and energy metabolism in preservation of prunes and raisins:

Pat raised the possibility of studying the physiological state of prunes in post-harvest situations. This subject may be analyzed from different perspectives. Most storage fungi are inhibited by atmospheres with less than 1%O_2, while CO_2 concentrations greater than 80% may be required to prevent fungal growth and subsequent product deterioration. Mycotoxin production is even more sensitive than fungal growth to low O_2 and high CO_2. Concentrations of CO_2 between 20 and 60% have been shown to prevent or significantly reduce mycotoxin production by some *Fusarium, Aspergillus,* and *Penicillium* species. Likewise, production of T-2 toxin by *Fusarium sporotrichioides* was totally inhibited under 60% CO_2, 20%O_2.

The hypothesis has been that at moisture contents below the level permitting bacterial growth, namely at water activity (A_w) <0.87, most storage fungi are fully inhibited in atmospheres containing less than 1% oxygen (O_2). In addition, risks of mycotoxin production are nullified at reduced O_2 concentrations.

The objective of preventing losses using the aspects of microfloral and atmospheric gas composition interactions has not yet been addressed to the preservation of dried fruits, particularly raisins and prunes. In particular, the subject of storage at high initial moisture contents in airtight conditions, requires fuller investigation.

In this study, the equilibrium relative humidity (ERH) values for the common prune and raisin varieties in California will serve as basis for determining the range of moisture contents equivalent to the A_W to be studied.

5 - Meeting with Pat Vail, Larry Zettler, Jim Leesch, Gary Obenauf, Judy Johnson, Charles Burks and David Brandl, on February 12, 1999 at the HCRL

In this meeting the plan of work for the research to be carried out by Shlomo Navarro was set as in the following:

Plan of work during the Sabbatical of Shlomo in Fresno

A- OBJECTIVES

Major objective:

To investigate the economically feasible MB alternatives for the control of dried fruit insect pests in California.

1- Field studies:

1.1 - Demonstration of phosphine gas containment in sealed structures. A series of fumigations will be carried out using controlled leak sizes to demonstrate the relationship between the ventilation rate and level of gas containment..

1.2 - Demonstration tests on controlled atmospheres (CAs): The objective of these studies is to provide the dried fruit industry with information on the economical feasibility of using CAs in structures with improved gas tightness, CO_2 instead of N_2, and the CAs as an alternative treatment to methyl bromide (MB). For this purpose three series of tests will be carried out:

1.2.1 - Demonstration tests on retention of CAs in sealed structures. A series of treatments will be carried out using controlled leak sizes to demonstrate the relationship between ventilation rate and level of gas containment.

1.2.2 - Comparative demonstration studies on retention of CO_2 and N_2 in sealed structures. In this series the objective will be to evaluate the feasibility of using CO_2 instead of N_2 on a basis of cost comparison and on speed of effectiveness in shortening treatment exposure times.

1.2.3 - Demonstration studies on increasing CAs effectiveness in sealed structures. In this series the objective will be to evaluate the feasibility of using CO_2 at elevated temperatures with the attempt in shortening treatment exposure times.

2- Laboratory studies:

Demonstration of the feasibility of using self-generated modified atmospheres relying on the metabolic activity of moist prunes.

2.1 - Demonstration of the moisture distribution of prunes at the initial phase of storage. A literature search accompanied by a laboratory study will concentrate on determining the equilibrium relative humidity values for the most common prune varieties in California at the time they are received to the processing plants.

2.2- Determining the metabolic activity of prunes at different levels of ERH. The respiration rates of prunes at different ERH levels will be determined. This study will be accompanied by microflora counts to determine the role of microfloral load and fungi populations on the respiration rates of the tested prunes.

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Table 1 - Comparison of National Raisin Company CA Efficiency to Soderstrom et al. (1984)

		Soderstrom et al.	National Raisin	
Storage Data:				
Bins	high	8	10	
	wide	10	7	
	long	20	16	
Feet	high (x2.3)	18.6	23.3	
	wide (x4)	40	28	
	long (x4)	80	64	
Bin volume	ft^3	59648	41754	
Head space	height	3.97	2.5	
	width	40	28	
	length	80	64	
Head space volume	ft^3	6352	2240	
Total storage volume (SV)	ft^3	66000	43994	
	m^3	1869	1246	
Estimated tonnes of raisins	metric tonnes	726	508.5	
CA Data:				
Purge rate	m^3/h	283	14	
Purge time	hours	24	336	
Purge volume liquid N2	gal	--	1800	
Purge volume (PV)	m^3	6792	4746	
Maintenance rate	m^3/h	17	4.4	
Maintenance time	days	30	30	
Maintenance volume liquid N2	gal	--	1200	
Maintenance volume (MV)	m^3	12240	3164	
[O2]	%	<0.5	<1	Ratio Sodest./Nation.
Purge Vol/Storage Vol ratio:		**3.6**	**3.8**	1.0
Purge Vol/Storage Mass ratio:		**9.4**	**9.3**	1.0
Maint. Vol/Storage Vol ratio:		**6.5**	**2.5**	2.6
Maint. Vol/Storage Mass ratio:		**16.9**	**6.2**	2.7

Table 2- Cost comparison of liquid CO_2 vs. liquid N_2 in Fresno, CA area.

	Gas	Container (lb)	Conversion factor (SCF/lb)	SCF	Cost ($US)	Cost ($/lb)	Cost ($/SCF)
Supply in small containers	CO_2	384	8.741	3356.54	203	0.5286	0.0605
	N_2	263	13.803	3630.19	178	0.6768	0.0490
Supply in large containers	CO_2				0.2	0.2002	0.0229
	N_2				1.0	0.0874	0.0100

STORAGE OF PRUNES UNDER CONTROLLED ATMOSPHERES FOR QUALITY PRESERVATION AND INSECT CONTROL

I - EQUILIBRIUM MOISTURE CONTENT OF CALIFORNIA PRUNES

INTRODUCTION

Moisture content of food is an important parameter that determines storage stability and its susceptibility to microflora spoilage, and it influences texture. The moisture content of food products has been used as a marketing standard, assuming that the product would be free from microbial spoilage below a certain moisture level.

The relationship between water activity (a_w) and moisture content of foods at a state of equilibrium has been termed "equilibrium moisture content" and can be expressed by moisture or water sorption isotherms. These isotherms also reveal information about the sorption mechanism and interaction of food biopolymers with water. They are important in design and optimization of unit operations such as preservation, drying, storing, packaging, and mixing.

Water activity (a_w) of a product is a criterion that determines a product's susceptibility to microbial growth more accurately than moisture content. Most microorganisms have a specific a_w below which they will not grow. Non enzymatic browning rate is also affected by a_w with a maximum occurring between 0.3-0.7. Also, the rates of enzymatic browning and fatty acid oxidation reactions vary with a_w. Some grading standards stipulate a_w instead of moisture content (Federal Register, 1976).

Most of the sorption data in the literature were obtained at only one temperature, representing the normal storage conditions. However, sorption properties over a wide temperature range are essential for modeling dehydration or rehydration processes and storage stability of dehydrated foods. Savaracos and Stinchfield (1965) found that temperature had an entirely different effect on the adsorption isotherms of glucose-containing starch gels, compared to simple starch gels. Iglesias and Chirife (1975) determined the sorption isotherms of sugar beet root. Roman et al. (1982) measured the desorption isotherms of apples between 20° and 60°C and they interpreted the data in terms of thermodynamic and structural changes. The effect of temperature on the sorption isotherms of dehydrated corn meal and fish meal and a thermodynamic analysis of the data was presented by Labuza et al. (1985). Weisser et al. (1982) determined the sorption isotherms of sugar substitutes (sorbitol, mannitol, xylitol, and palatinit) between 25° and 80°C. Vagenas et al. (1986) reported the adsorption isotherms of Sultana raisins at 30°C, and Saravacos et al. (1986) measured the adsorption isotherms of Sultana raisins in the temperature range 20-35°C. Abdelhag and Labuza (1987) reported results for apricots, and Maroulis et al. (1988) presented data for raisins, figs, prunes, and apricots.

Due to the complex food composition, theoretical prediction of the isotherms is not possible and experimental measurements are necessary. Reliable sorption data are also needed for the prediction of food quality of stored foods (Labuza and Kamman, 1983). Formulation of an analytical relation for prediction of sorption behavior of foods presents difficulties due to complexity of their structure. The addition or removal of water changes the composition and size of the material and can cause phase transitions (dissolution, sugar crystallization, etc.). The change in moisture content as a function of water activity (a_w), is determined by a combination of factors, each of which is predominant in a specific region of the isotherm (Iglesias and Chirife, 1976).

The published data on the relationship between moisture content and water activity in prunes is very limited. Bolin (1980) measured ad- and desorption isotherms for raisins and prunes at 25° and 35°C, Maroulis et al. (1988) presented data for raisins, figs, prunes, and apricots, Tsami et al., (1990) for raisins, currants, figs, prunes and apricots at 15°, 30°, 45° and 60°C, Stencl et al. (1998) for prunes in the range of 15° to 45°C. However comparison of these data revealed a large variation in equilibrium moisture content values.

The original plan of work was to demonstrate the moisture distribution of prunes by sampling prunes immediately after they are received at the processing plant and then to determine the distribution of their moisture content during storage. This objective was partially achieved. Since the available literature data were not consistent, more emphasis was placed in determining the relationship between moisture content and water activity in California prunes.

MATERIALS AND METHODS

Origin of prune samples:

The samples of prunes used in this study were from two different crops; from the 1998 and the 1999 crop.

Moisturized samples

The National Raisin Company, Fowler, California, supplied the samples of commercial prunes from the 1998 crop. These samples were in commercial storage for about four months (late August - early September to late December) after they were dried and had an initial moisture content of about 16% (wet basis) tested by the vacuum oven method (detailed later).

To raise the moisture content, a rapid method of spraying atomized distilled water directly on the prunes was used. The total quantity of water needed to attain a given moisture content was calculated and applied in successive small aliquots each of which was divided equally between all the prunes in the sample. For this treatment the prunes were spread out in a single layer on the inside of a 1-gallon jar placed on its side. The

upper surface of each layer was sprayed so that it was thoroughly wetted but none of the water ran off on to the wall of the jar. About an hour later, when the water had been absorbed, the prunes were turned and the other side was sprayed in the same way. Once again time was allowed for the added water to be absorbed. This procedure was repeated until the calculated amount of water had been added and absorbed. The intervals between sprayings increased of necessity because the rate of absorption decelerated as the moisture content of the prunes increased.

Twelve samples, each of 2.5 kg, were taken and the moisture content of each was raised by spraying with the calculated amounts of water. These amounts were intended to give moisture contents of approximately 18%, 20%, 22%, 24%, 26%, 28%, 30%, 32%, 34%, 36% and 38%. After moisture adjustment these samples were allowed to equilibrate in 1 gallon jars for at least 4 weeks at 0°±2°C. These samples will be termed "**moisturized samples**".

Dryer samples

Albrecht Farms Dehydrator, Del Ray, California supplied the commercial samples of French regular variety of prunes from the 1999 crop.

The samples were obtained by stopping the drying process and sampling from the dryer on September 1, 1999. The drier tunnel is designed to accommodate 12 wagons. The drying wagons, about 2 m wide, are equipped with trays of 1.5 m long. The trays are stacked to a 2 m high on wagons that enable rolling the trays into the tunnel. Each tray permits lateral ventilation and is exposed to a temperature of 55°C for 18 h. Each wagon is removed from the tunnel after 18 h drying, so after the first drying batch a new wagon is added to the tunnel, from the start point, at each successive 1.5 h. Samples were taken from the following drying hours: 7.5 h, 9 h, 10.5 h, 12 h, 13.5 h, 15 h, 16.5 h and 18 h of drying. One sample each of one gallon capacity using zip-lock bags was taken from the trays at a height of about 1.75 m. These samples were brought to the HCRL and were kept for 2 h at 0°C. After then they were transferred to – 35°C. These samples will be termed "**dryer samples**".

Determination of moisture content:

Moisture content can be expressed in several ways but most often, particularly in stored product technology, a "wet basis" percentage is used. Mathematically the wet basis percentage is the weight of the water in sample as percent of the total weight of sample (includes the weight of dry matter and the water before it was removed). In food technology and drying processes the "dry basis" percentage is used. The moisture content "dry basis" is the percentage of the water of the dry matter of sample. In the following report for moisture content a "wet basis" percentage is used.

The method recommended by the Association of Official Analytical Chemists for moisture determination in dried fruits (method 934.06, 1990) is based on mixing the prune sample with finely divided asbestos and hot water, and evaporate almost to dryness

on a steam bath. It is then transferred to a vacuum oven and dried for 6 h, at 70°C, under the reduced pressure of less than 100 mm Hg. However, Pixton and Warburton (1973; 1976) modified the AOAC method to a more convenient method for sultana raisins and figs. For this method samples of about 5-g were macerated and dried at 70°C under reduced pressure of less than 5 mm Hg for 18 h, followed by two 3-h drying periods.

All drying methods for moisture determination are based on the assumption that when the samples have reached constant weight all free water has been removed (constant weight is defined as a change of less than 0.005 g between two successive weighings of a sample initially weighing 3-5 g). For raisin and fig samples tested according to Pixton and Warburton (1973; 1976) seldom was constant weight achieved in 24 h; generally it was achieved in 30 h when the moisture contents averaged 0.2% higher than those calculated after 24 h. This enabled a comparison of figs to sultana raisins.

In preliminary tests carried out for moisture content determination on prunes the test method of Pixton and Warburton (1973; 1976) was adopted for 6 h drying period and compared with longer drying times with an attempt to reach constant weight. Thin slices of prunes, approximately 1 mm thick, were cut from a representative sample to facilitate drying in the vacuum oven. Samples were than placed in lidded tins of 56 mm i.d. and 18 mm height. A standardized procedure was employed for weighing the samples on a Mettler analytical balance. Afterwards samples were removed from the oven and each tin was covered with a tight-fitting lid, cooled in a desiccator for 1 h and weighed.

It was observed that the longer the drying of a sample continued the more weight, or "apparent water" was lost. Even after 180 h "water" continued to be removed. Most probably, breakdown of the chemical constituents of the prunes occurred. The curve was plotted showing weight against drying time starting from 6 h and onwards for up to 152 h. In the present experiments for moisture content determination, the constant weight could not be achieved for prunes. Therefore it was decided to present the data obtained for different drying times and base the reports on 6 h and 24 h drying times.

Determination of the moisture content/equilibrium relative humidity (ERH):

The ERH was determined using Novasina ms1, Defensor with a "enMBRK-3" sensor and RH equilibration chamber of 68-mm i.d. and 100 mm length (363 mL) (Fig. 1.1 and 1.2). A sample of 25-28 prunes weighing about 150 g was taken from the selected sub-sample and placed in the ERH apparatus. After equilibrating to the set temperature for 24 h, the samples were left in the apparatus for another 2 h to equilibrate before the relative humidity was determined.

Sugar content:

The liquid chromatographic method of AOAC (1995) was used by the DFA of California for the determination of sugar content in prunes.

RESULTS and DISCUSSION

Determination of moisture content:

Fig. 1.3 and 1.4 show the weight loss attributed to moisture content of prunes exposed to 70°C in a vacuum drying oven in relation to time. Results were obtained for **"moisturized samples"** of prunes in the intended range of 16% to 38% moisture content. Fig. 1.3 shows that for the intended moisture content range of 16% to 26%, constant weight was not achieved even after 152 h of drying. Therefore, it was decided to test the change in weight for the upper range of intended moisture content of 28% to 38%. Fig. 1.4 shows a similar pattern in change in weight but this time the drying in the vacuum oven was continued up to 80 h.

In comparison to "**moisturized samples**" the prune samples taken from the dryer and named as "**dryer samples**" were also tested for their response to weight loss over extended drying times in the vacuum oven at 70°C. In these samples also, constant weight was not reached even after 117 h of drying (Fig. 1.5).

In all the moisture content determination tests for "**moisturized samples**" and "**dryer samples**", the curve fit was with the measured data statistically highly significant. For most of the tests the exponential curves resulted in r^2 values no less than 0.9. From the equations attached to Figures 1.3, 1.4 and 1.5 it is possible to calculate the specific rate of weight loss by using the coefficient and the exponential values.

Because a constant weight was not reached within the extended drying times, it was not possible to determine the specific drying time that would precisely indicate the moisture content of the prunes. In their work on figs, Pixton and Warburton (1976) could not achieve constant weight within 24 h. However, to enable comparison to their earlier work on raisins (Pixton and Warburton, 1973), the 24 h vacuum drying time was adopted. In the following results also, two drying times will be reported; a 6 h drying time to compare data with AOAC method and/or a 24 h drying time to compare data with raisins and figs (Pixton and Warburton, 1973; 1976).

Moisture content of prunes at different stages of drying in commercial dryers:

It was interesting to observe the actual moisture content values achieved in the commercial drying process. For this purpose Fig. 1.6 was prepared based on the "**dryer samples**". There is a sharp decrease in the moisture content of those prunes dried for over 12 h. The samples taken between 7.5 h and 12 h show a particularly marked decrease in moisture content. However, those samples taken after 12 h showed a decreased drying rate. The approximate drying rate between 7.5 h and 12 h is 2.8 percentage points (pp)/h, whereas that between 13.5 h and 18 h is only 0.3 pp/h.

Moisture content/equilibrium relative humidity relationship of "moisturized samples" of prunes at 25°C:

The moisture content/equilibrium relative humidity (MC/ERH) relationship isotherms for the "**moisturized samples**" at 25°C are shown in Fig. 1.7. Since it was not possible to determine a drying time that would indicate the actual moisture content of prunes, I preferred to use values obtained in the vacuum oven after drying for 6 h and 24 h.

The moisture content of the commercially stored prunes was about 15% when the drying time in the vacuum oven was 6 h and 16% for drying time of 24 h. However both determinations were carried out on the same sample that had an equilibrium relative humidity value of 57.5%. The 70% equilibrium relative humidity value was equivalent to 22.8% and 24.7% moisture content for 6 h and 24 h drying times, respectively.

The curves that represent the moisture content/equilibrium relative humidity relationship were almost parallel for 6h and 24 h drying times. Data used to represent these curves resulted in exponential equations with highly significant fit at r^2 values above 0.97.

Moisture content/equilibrium relative humidity relationship of "moisturized samples" of prunes at three different temperatures:

The equilibrium relative humidity values were determined at three temperatures; 25°, 30° and 35°C. However, the change in temperature had no significant effect on the MC/ERH relationship (Fig. 1.8). Therefore, only the isotherm values obtained for 25°C and 24 h vacuum drying time are shown in Fig. 1.8.

Previous work with sultana raisins tested at 15°, 25° and 35°C also demonstrated that temperature had no effect on MC/ERH relationship (Pixton and Warburton (1973). To reveal if such an effect exists with figs, tests were carried out by Pixton and Warburton (1976). But in their tests also a change in temperature did not result in a consistent effect on MC/ERH relationship with figs. Therefore all their results with figs and sultana raisins were based on means of the ERH's measured at three temperatures.

MC/ERH relationship of "dryer samples" of prunes at 25°C:

The MC/ERH relationship isotherms for the "**dryer samples**" of prunes at 25°C are shown in Fig. 1.9. These isotherms also are similar to those obtained from "**moisturized samples**" and were based on values obtained in vacuum oven after drying for 6 h and 24 h.

The moisture content of the commercially dried prunes after 18 h was about 14.5% when the drying time in the vacuum oven was 24 h. The 70% equilibrium relative humidity values were equivalent to 22.4% and 24.5% moisture content for 6 h and 24 h drying times, respectively. The isotherm values in these tests were very close to those obtained with "**moisturized samples**" for which the 70% equilibrium relative humidity values were equivalent to 22.8% and 24.7% for 6 h and 24 h drying times, respectively.

The curves that represent the moisture content/equilibrium relative humidity relationship were almost parallel for 6h and 24 h drying times. Data used to represent these curves resulted in exponential equations with highly significant fit at r^2 values above 0.98.

MC/ERH relationship of "dryer samples"" of prunes at three different temperatures:

The equilibrium relative humidity values for **"dryer samples"**" also were determined at three temperatures; 25°, 30° and 35°C. The change in temperature had no significant effect on the MC/ERH relationship (Fig. 1.10). Therefore, only the isotherm values obtained at 25°C and 24 h vacuum drying time are shown in Fig. 1.10.

Sugar content:

Table 1.1 summarizes results obtained on determination of sugar content of prune samples. The highest moisture content range of "**moisturized samples**" was selected for sugar content determination. Although only four samples were tested, they were considered sufficient to indicate the range of moisture content. The sugar content is the principal factor in reducing the water activity in dried fruits in general and in prunes in particular. In comparing water activity values, it is essential to refer to sugar content values since prunes with different maturation levels or deriving from different varieties may have different water activity values. The individual samples at different moisture content levels were not sufficient to establish a statistical analysis for determining the variations in relation to their moisture content.

Table 1.1 – Sugar content expressed as fructose, glucose and total sugars for four samples of prunes with the highest moisture contents used in the tests to determine prunes water activity.

Nominal moisture content (%)	Fructose (%)	Glucose (%)	Total sugars (%)
32	8.4	18.2	26.6
34	7.4	17.1	24.5
36	7.6	18	25.6
38	8.3	16.8	25.1

Equilbrium moisture content, equilibrium relative humidity (ERH) and water activity:

In stored products these are commonly used terms to define the relationship between commodity moisture content and air relative humidity. If the commodity equilibrates with air maintained at a relatively constant environmental condition, the commodity moisture

content is referred to as the equilibrium moisture content (EMC) corresponding to the existing air conditions. On the other hand, if the commodity is surrounded by a limited amount of air (such as occurs in the interstitial spaces of a commodity mass in a storage bin), the air will reach moisture equilibrium with the commodity without any significant change in the commodity moisture content. The relative humidity of the air in this situation is referred to as the equilibrium relative humidity (ERH) corresponding to the existing commodity moisture content at the prevailing temperature. All equilibrium moisture properties are a function of temperature and therefore the properties change with changes in temperature. However, this effect of temperature may not be significantly detectable for all commodities at relatively narrow temperature differences. For example ERH values obtained between two temperatures 5°C apart would hardly show any significant difference. But for some commodities a 10°C change would yield a marked difference.

Stored product aeration and drying technologies have adopted the terms EMC and ERH. Food technologists and microbiologists have used the term of water activity (A_w) or (a_w) to define the state in which an organism responds to the availability of water in the atmosphere that surrounds it. Water deficiency in the organism in relation to the partial pressure of water in the atmosphere greatly determines the survival of microorganisms. As for the food products, their water content in relation of the partial pressure of water in the atmosphere would indicate the direction of water flow from the commodity in the surrounding atmosphere or vice versa. The A_w values have been determined on a scale of 0 to 1 and they are in agreement with the full scale of decimals of 0 to 100% relative humidity.

In the present work all determination were made on the basis of relative humidity and also in order to conform with stored product technology the terms of EMC and ERH will be used. However, in referring to literature data on food technology or microbiology, the term A_w will be used.

Literature data on MC/ERH relationship of prunes:

Stencl et al. (1999) recently reported on EMC of prunes. They investigated moisture equilibrium data for adsorption and desorption of water from prunes at temperatures in the range of 15-45°C and water activity ranging from 0.4 to 0.99. The experimental procedure used was a gravimetric dynamic method with continuous registration of sample weight changes. They developed a special laboratory drying device for the purpose. In spite of the sophisticated laboratory apparatus they based the final moisture content on simulated commercially dried samples and then stored them at an average temperature of 40°C and an average RH for 2 days. Then it was reported that the final moisture content was 18-19% (w.b.) i.e. about 0.220 kg/kg moisture content (d.b.). It is not obvious that a constant weight was reached in determining the final moisture content. Also the maximum EMC (d.b.) reached was 0.240 kg/kg at a water activity of 0.99 which is equivalent to 19.4% moisture content (w.b.). Data on EMC from (Stencl et al., 1999) were not in agreement with values reported by other researchers for dried fruits rich in

sugar content and the values obtained in the present report (Fig. 1.11). Therefore, their results were not included in this discussion.

On the other hand, Stencl et al. (1999) reported that sorption capacity decreased as temperature increased. But the differences between equilibrium moisture contents at a constant water activity were small in the temperature range measured. Rehydration of the dried material resulted in hysteresis.

Stencl et al. (1999) evaluated four models available in the literature (Chung-Pfost, Halsey, Henderson, and Oswin) (Chen and Morey, 1989) to determine the best fit for their experimental data. They found that the modified Halsey equation was a good model for moisture adsorption and desorption of prunes (Stencl et al., 1999).

Bolin (1980) determined the moisture sorption isotherms for raisins and prunes, with raisins producing hysteresis at the lower and higher ends of the curves. According to his findings maturity of the fresh fruit influenced the sorption isotherms but not storage time. Optimum water activities for minimizing a product's degradation rate during storage were determined for prunes and raisins to be about 0.1. In his work Bolin (1980) used the AOAC (1970) procedure to determine the fruit moisture content, presumably for 6 h drying. The moisture content values reported by Bolin (1980) are lower than those reported by Tsami *et al.* (1990) at the high water activity region above 0.7. It may be speculated that the drying process for moisture content determination did not sufficiently remove the water from the prunes. However, Bolin (1980) predicted that in the future, A_w will be used to a greater extent in marketing and grading channels. He commented that A_w gives more information than moisture content alone because it is the basic controlling factor in the preservation of dried fruits.

Tsami *et al.* (1990) reported on moisture sorption isotherms of prunes at 15, 30°, 45° and 60°C. They used the AOAC (1980) procedure to determine the fruit moisture content, in a vacuum oven and 6 h drying time. Their experimental curves showed an inverse effect of temperature at high moisture content due to high sugar content of dried fruits. They used mathematical models to predict experimental data for a water activity range of 0-0.95. The results reported by Tsami *et al.* (1990) are the closest possible to the EMC values obtained in the present study. Tsami *et al.* (1990) reports a moisture content of 21.8% and the present report 22.4% for "**dryer samples**" and 22.8% for "**moisturized samples**". The higher the water activity was the closer were EMC values reported by Tsami *et al.*, (1990) and in this report (Fig. 1.7 and 1.9).

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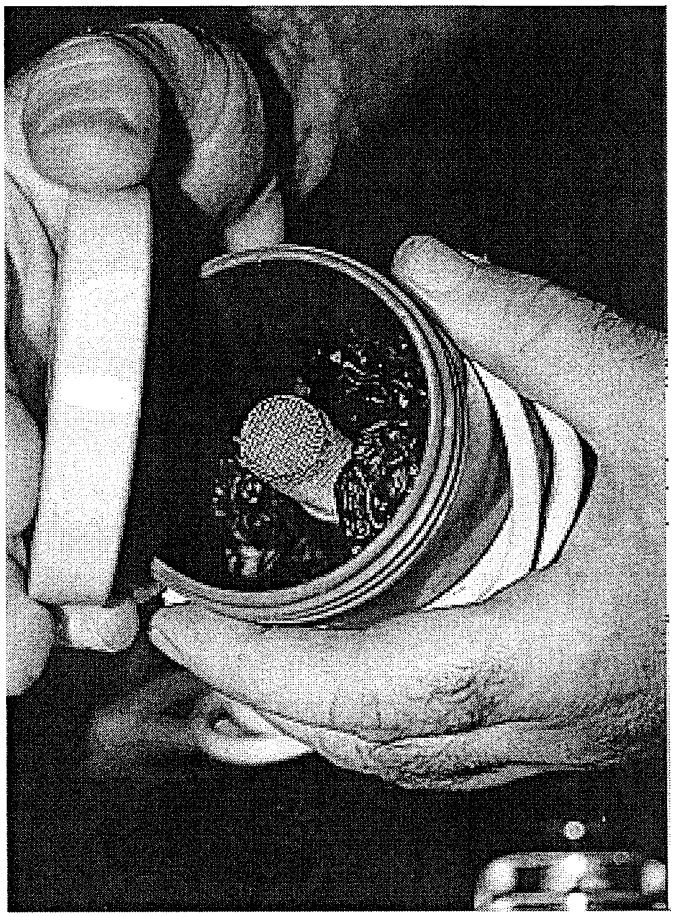

Fig. 1.1 – The RH equilibration chamber containing 150 g of prunes and the RH sensor at the center of the chamber.

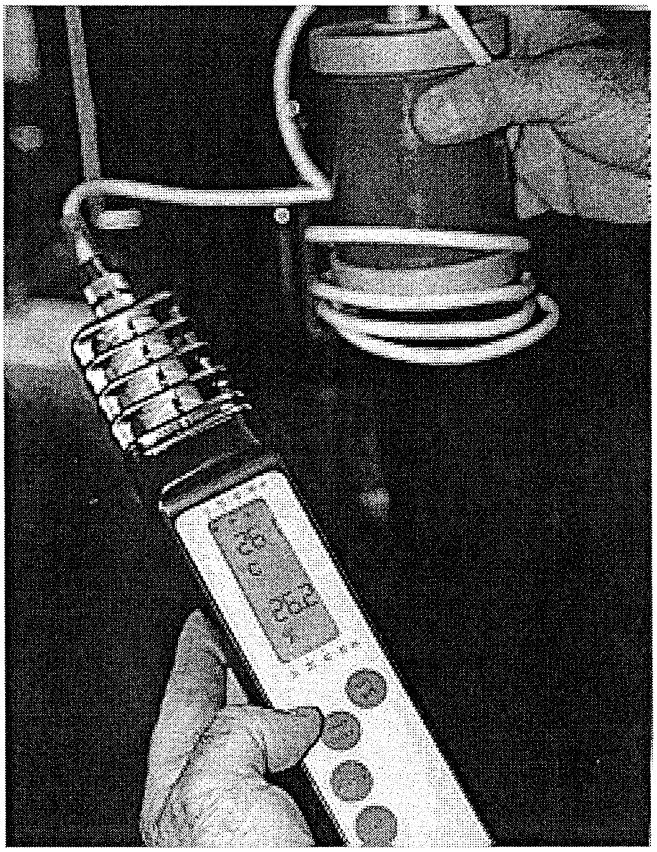

Fig. 1.2 – The Novasina ms1, with the monitor connected to the sensor in the RH equilibration chamber.

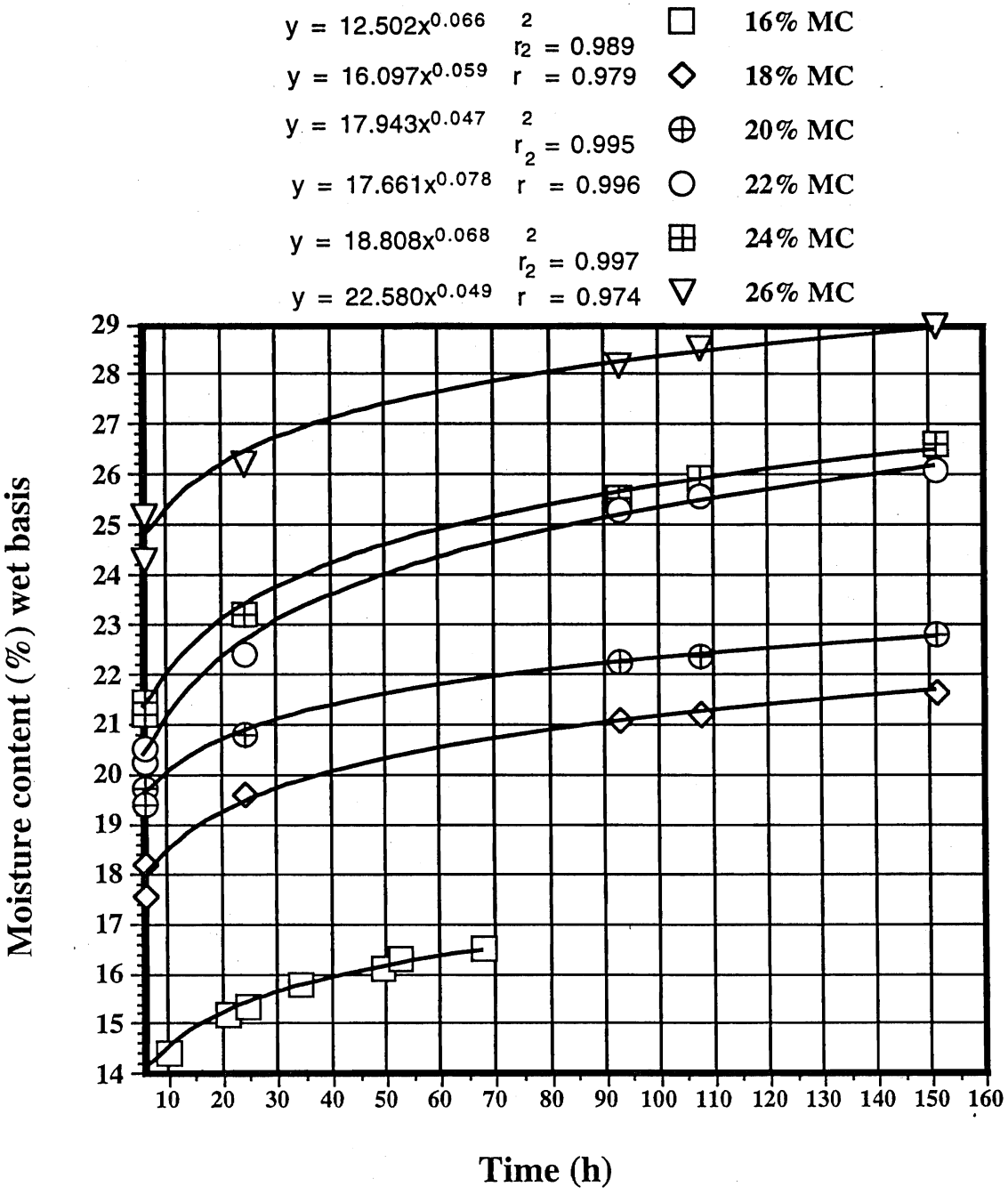

Fig. 1.3 – Weight loss attributed to moisture content of prunes exposed to 70°C in a vacuum drying oven in relation to time. Results obtained for **"moisturized samples"** of prunes in the intended range of 16% to 26% moisture content.

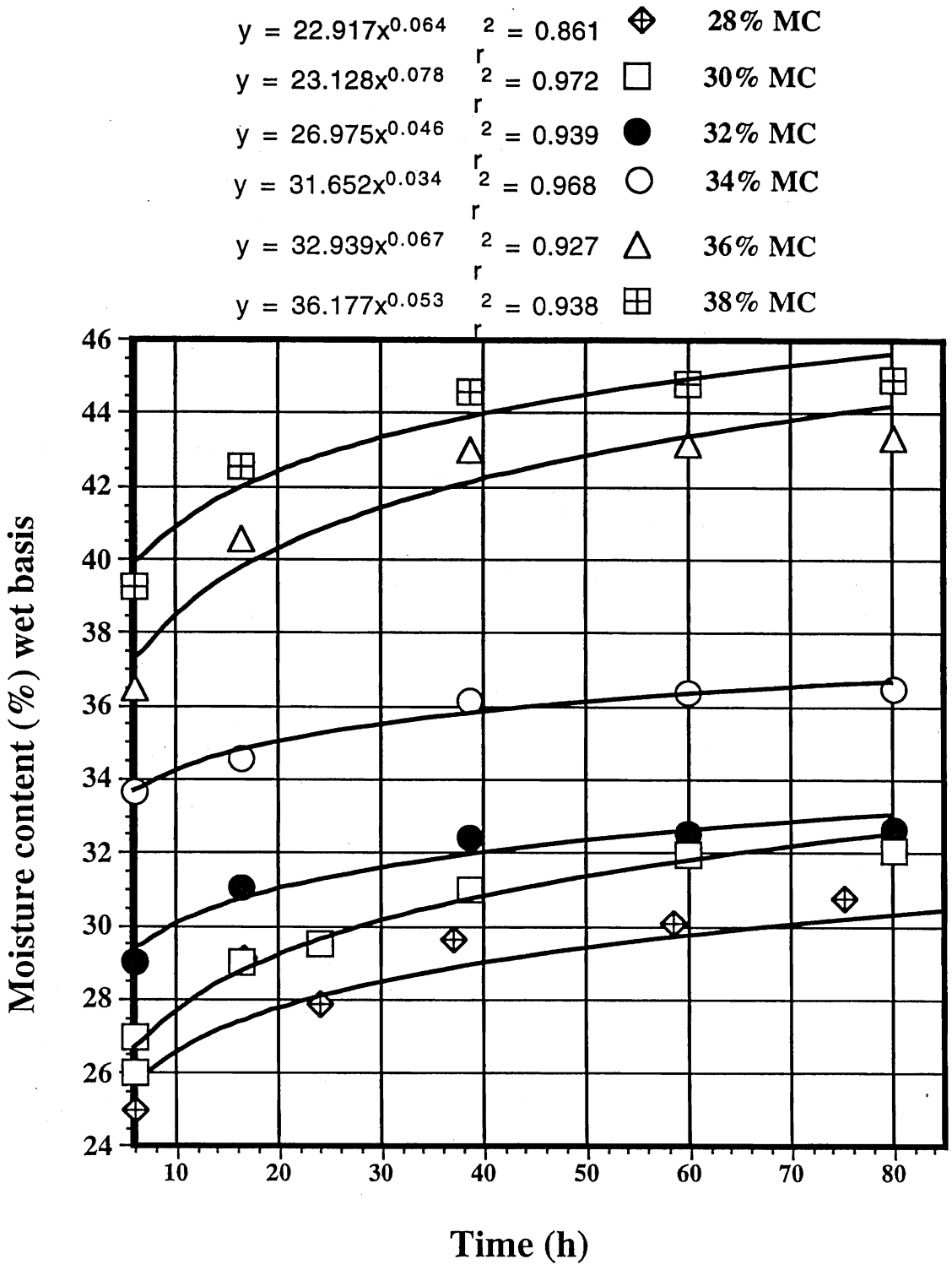

Fig. 1.4 – Weight loss attributed to moisture content of prunes exposed to 70°C in a vacuum drying oven in relation to time. Results obtained for **"moisturized samples"** of prunes in the intended range of 28% to 38% moisture content.

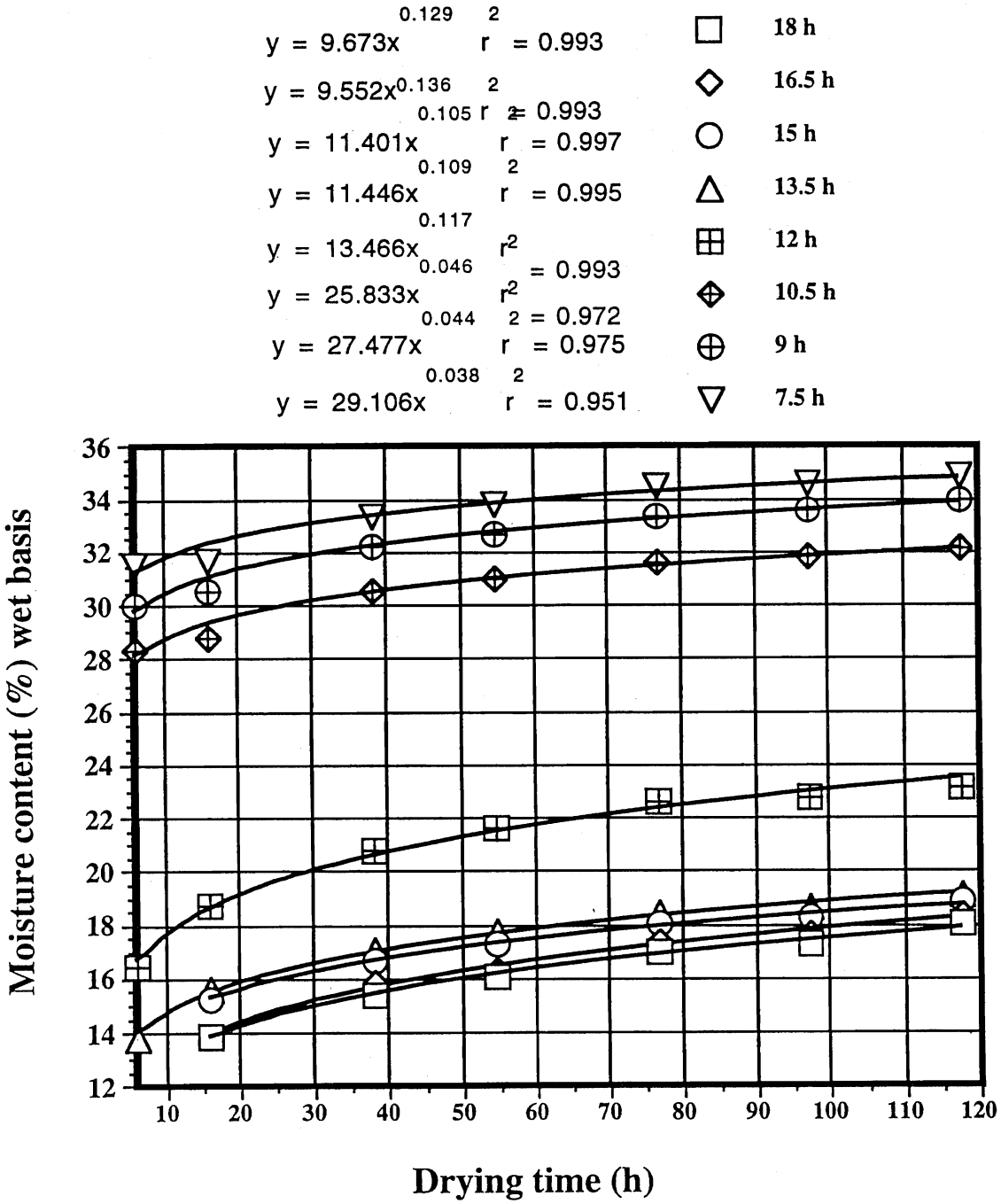

Fig. 1.5 - Weight loss attributed to moisture content of prunes exposed to 70°C in vacuum drying oven in relation to time. Results obtained for "**dryer samples**" of prunes taken from the dryer after drying times ranging from 7.5 to 18 h.

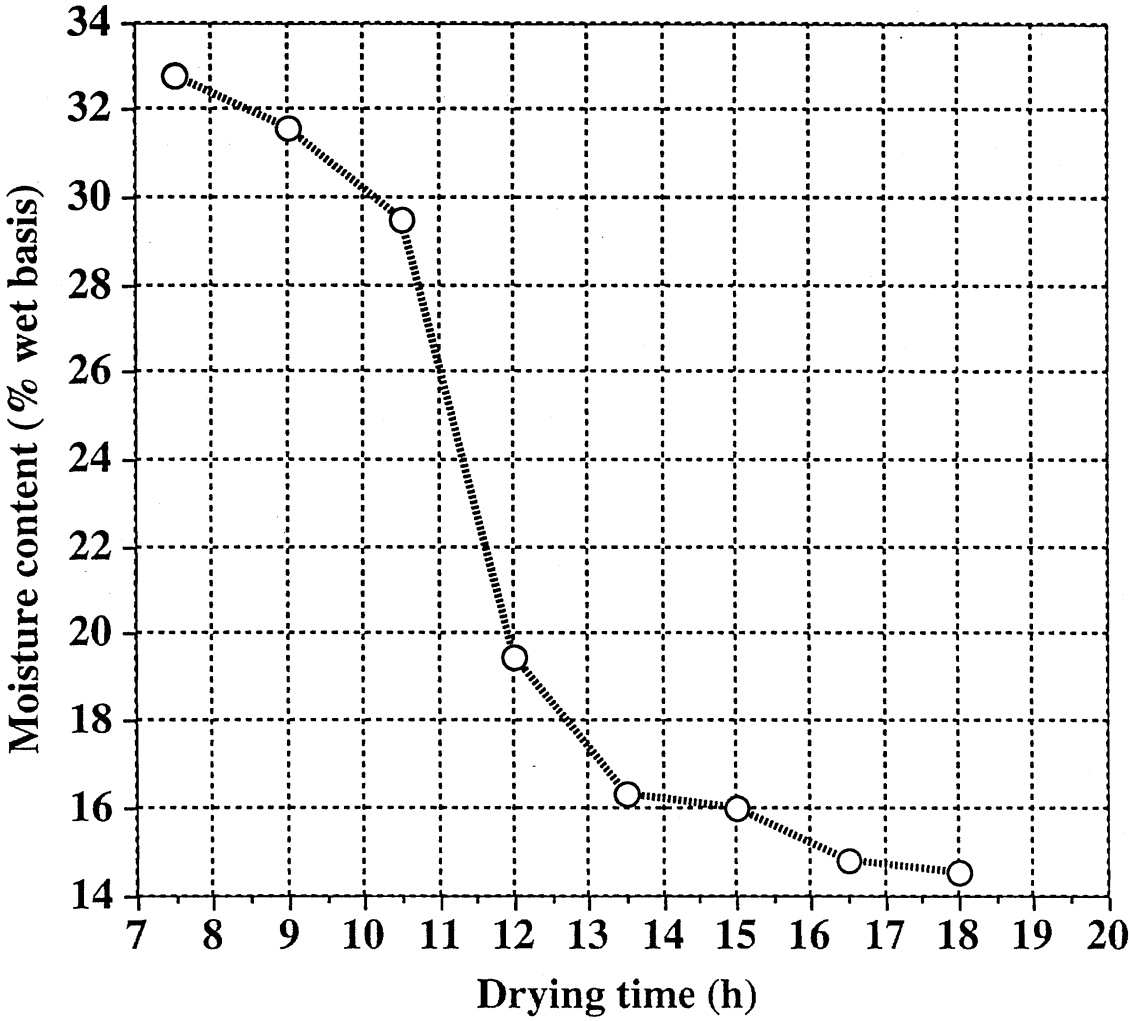

Fig. 1.6 - Moisture content of prune samples taken from a commercial dryer at different stages of drying from 7.5 to 18 h after the beginning of drying. Moisture content of "**dryer samples**" was determined in vacuum oven at 70°C and 24 h drying.

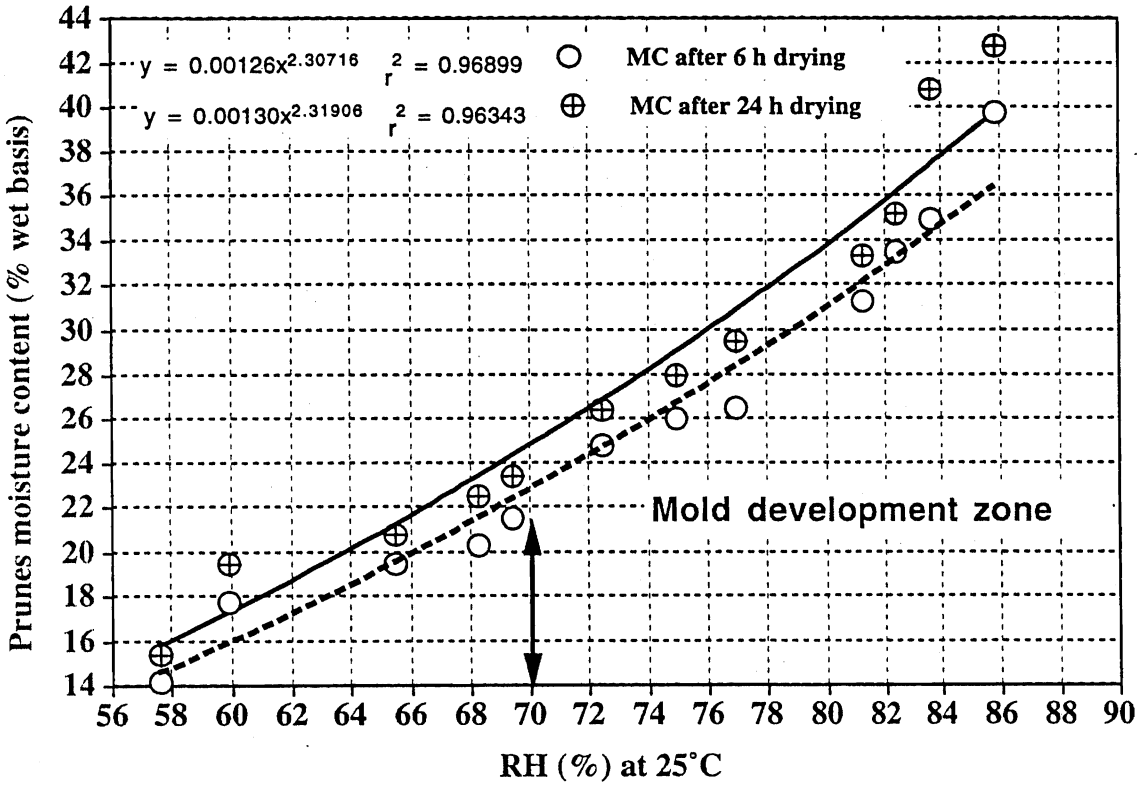

Fig. 1.7 - Moisture content/equilibrium relative humidity relationship of prunes at 25°C for moisture content values obtained in vacuum oven after drying for 6 h and 24 h. In these tests the relative humidity values were determined on **"moisturized samples".**

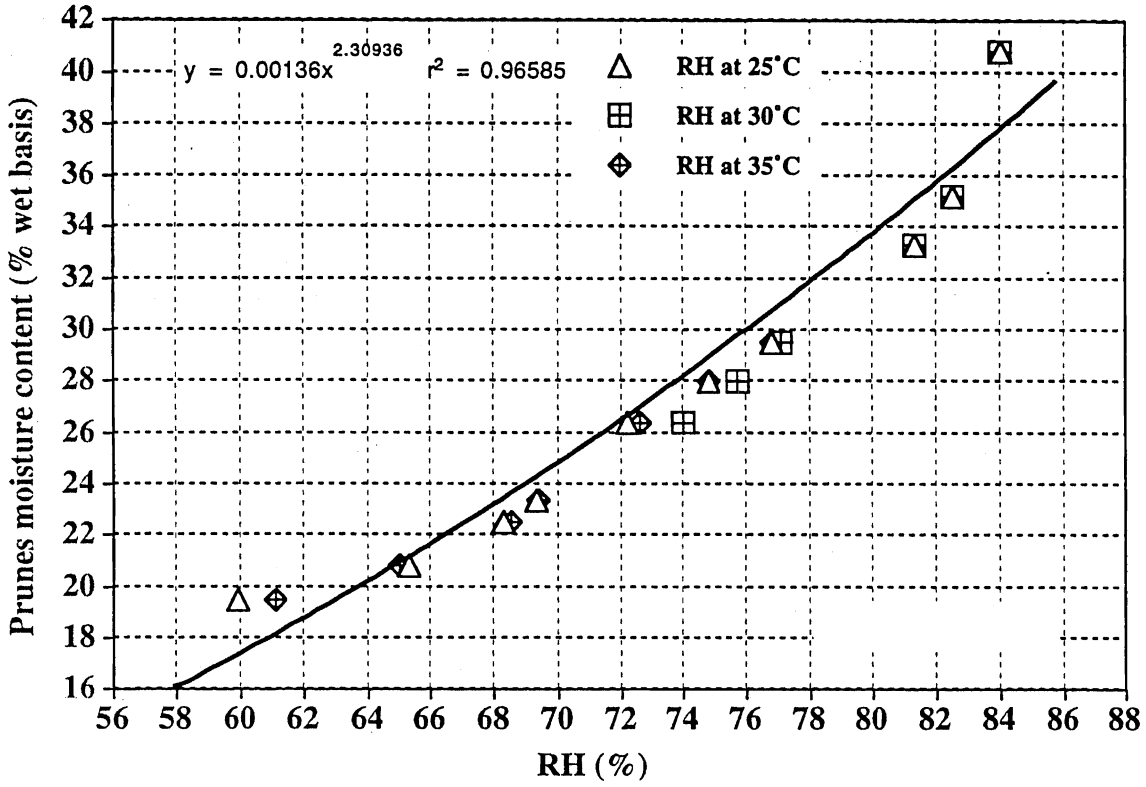

Fig. 1.8 - Moisture content/equilibrium relative humidity relationship of prunes at 25°, 30° and 35° C for moisture content values obtained in vacuum oven after drying for 24 h. In these tests the relative humidity values were determined on "**moisturized samples**".

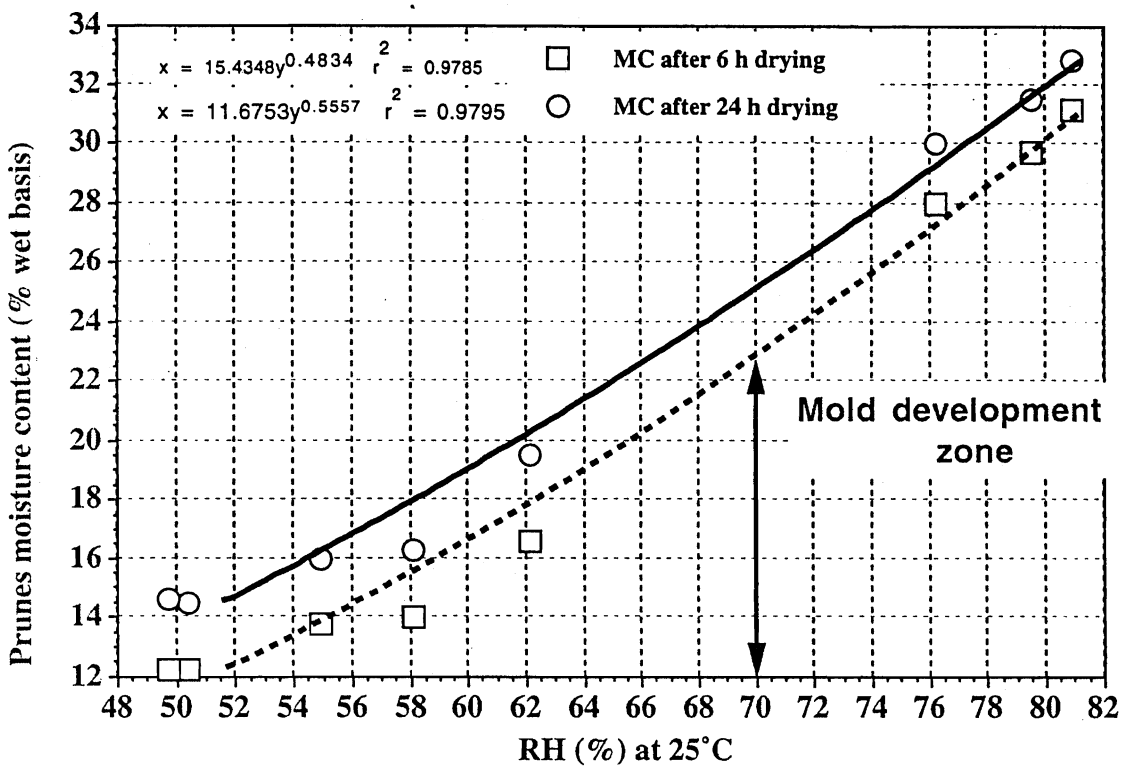

Fig. 1.9 - Moisture content/equilibrium relative humidity relationship of prunes at 25°C for moisture content values obtained in vacuum oven after drying for 6 h and 24 h. In these tests the relative humidity values were determined on **"dryer samples"**.

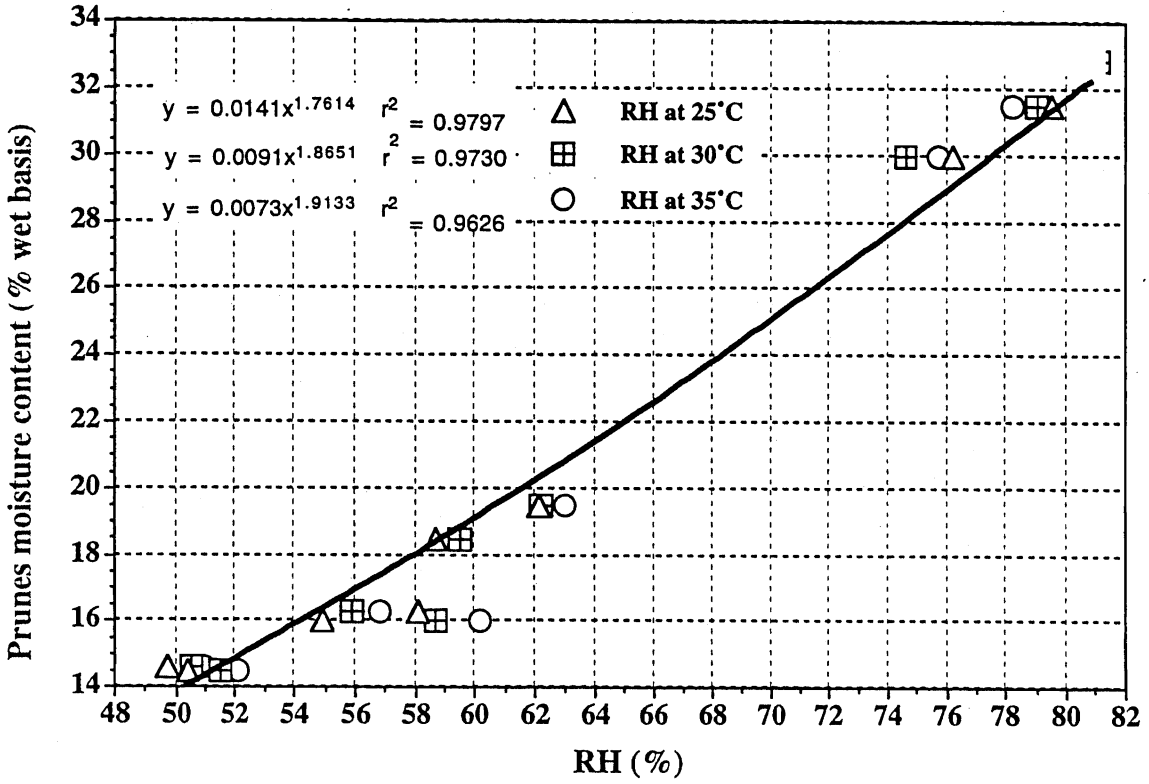

Fig. 1.10 - Moisture content/equilibrium relative humidity relationship of prunes at 25°, 30° and 35° C for moisture content values obtained in vacuum oven after drying for 24 h. In these tests the relative humidity values were determined on **"dryer samples"**.

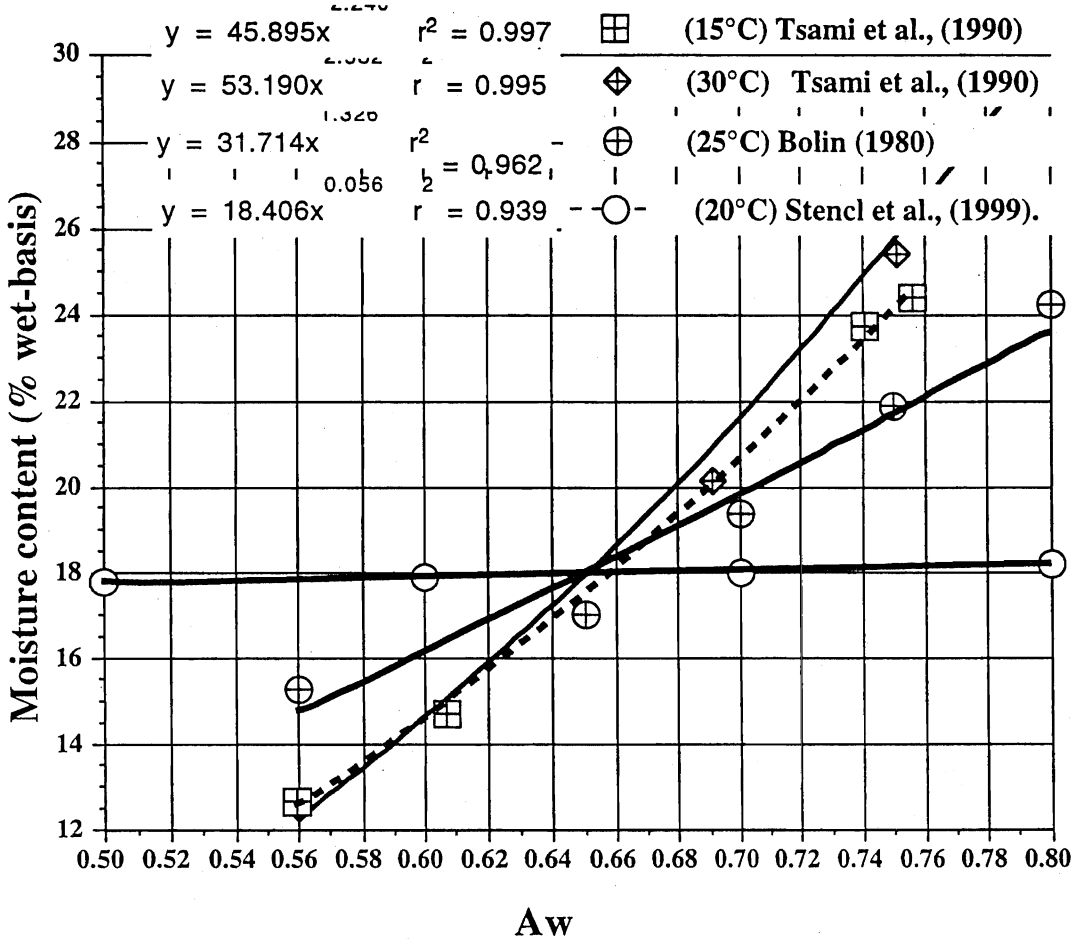

Fig. 1.11 - Equilibrium moisture content values at different water activity (A_w) values of prunes at different temperatures given by Bolin (1980), Stencl *et al.*, (1999) and Tsami *et al.*, (1990). The original moisture content data quoted in dry basis or in kg/kg was converted to percent moisture content wet basis.

STORAGE OF PRUNES UNDER CONTROLLED ATMOSPHERES FOR QUALITY PRESERVATION AND INSECT CONTROL

II - EFFECT OF WATER ACTIVITY ON RESPIRATION RATES OF CALIFORNIA PRUNES

INTRODUCTION

Plums in California after harvest are transported to commercial dryers, dried and then stored at ambient temperatures. The drying process takes 18 h or more in drying tunnels at 55° to 85°C and reduce moisture content to 21 to 22% as determined by the Dried Fruit Association moisture tester (Cunniff, 1995). Low water activity retards the growth of yeasts and molds on dried prunes (Pitt et al., 1968; Tanaka and Miller, 1961). Some xerophytic microflora may develop at extremely low moisture levels. The predominant spoilage fungi of dried and high-moisture prunes are *Aspergillus glaucus*, *Xeromyces bisporus,* and *Chrysosporium* spp. *Xeromyces bisporus* was shown to asexually sporulate at a water activity of 0.663 in 80 days at 25°C (Pitt et al., 1968). Before marketing for consumption dried prunes are sized, washed, and hydrated with steam. After hydration, prunes may also be pitted. At 30°C, prune equilibrium desorption moisture content is 25.8% and the water activity is 0.691 (Tsami et al., 1990). Hydrated prunes usually exceed 30% moisture. Potassium sorbate is an effective antimicrobial agent for higher moisture content prunes (Nury et al., 1960). To retard spoilage, potassium sorbate is added to hydrated prunes before packaging. The addition of preservatives has been under criticism (Sofos and Busta, 1981). The prune industry has expressed interest in developing alternatives to potassium sorbate for prunes destined for export.

Many Studies have been done to prevent mold growth by controlling some growth factors such as temperature, a_w, and atmospheric conditions. A few fungi are capable of growth in environments with low water activity (a_w). Many *Aspergillus* species are xerophilic and are usually capable of growing on media containing high concentrations of salt or sugar (Thom and Raper, 1945). *Eurotium amstelodami* was isolated at 0.77 a_w, (Kinderlerer, 1984) and 0.753 a_w (Wheeler and Hocking, 1988) and it could germinate at a_w as low as 0.738 (Pitt and Christian, 1968). However, growth and sporulation of the *Aspergillus glaucus* group (Carbone and Johnson, 1964) and *Eyrotium rubrum* (Kushner et al., 1979) occurred at higher a_w values.

The combined effect of both a_w and low storage temperature on the inhibition of *Aspergillus niger, Penicillium spp.*. and *Rhizopus spp.*, resulted in longer food shelf lives than those predicted from single variable experiments (Horner and Anagnostopoulos, 1973). Modified atmospheres (MA) involving reduced O_2 levels and elevated levels of CO_2, were used in combination with other environmental factors to control growth and mycotoxin production by several molds. Northolt and Bullerman (1982) reported that MA combined with a low a_w or low temperature can constitute an effective preservative measure of fungal growth. Combination of low a_w and low headspace O_2 (< 1%) was also reported to inhibit completely mold growth in packaged peanuts (Ellis et al., 1994). Smith et al. (1988) showed that a_w, pH, headspace O_2 and CO_2, and storage temperature

were the important factors influencing the growth of *A. niger* in gas packaged bakery products.

El Halouat and Debevere (1997) studied the combined effect of different CO_2 enriched atmospheres containing various levels or O_2, media a_w and incubation temperatures to control spore germination and growth of molds on synthetic media. Their objective was to choose storage conditions which would maintain molds at safe and acceptable levels in high moisture dried fruits. In their work, 0.83 a_w and higher was necessary for conidial germination during 45 days of incubation at 20° and 30°C in an atmosphere containing 16% CO_2 and 4% O_2 for *A. niger, E. amstelodami, P. chrysogemon* and *F. oxysporum.*

Most storage fungi are inhibited by atmospheres with less than 1%O_2, while CO_2 concentrations greater than 80% may be required to prevent fungal deterioration. Insect survival is even more sensitive than fungal growth to low O_2 and high CO_2. Concentrations of CO_2 between 20 and 60% have been shown to prevent or significantly reduce mycotoxin production by some *Fusarium, Aspergillus,* and *Penicillium* species. Likewise, production of T-2 toxin by *Fusarium sporotrichioides* was totally inhibited under 60% CO_2 and 20%O_2.

At moisture contents below the level permitting bacterial growth, namely at a_w <0.87, most storage fungi are fully inhibited in atmospheres containing less than 1% oxygen (O_2). In addition, risks of mycotoxin production are nullified at reduced O_2 concentrations. The objective of preventing losses using the aspects of microfloral and atmospheric gas composition interactions has not yet been addressed to the preservation of dried fruits, particularly raisins and prunes. In particular the subject of dried fruit stored at high initial moisture contents in airtight conditions to prevent spoilage requires fuller investigation.

Based on studies of mold survival at low O_2 and high CO_2 levels, it was hypothesized that prunes stored in modified atmospheres will tolerate higher a_w levels than those required at normal atmospheres. Also the possibility that prunes, based on their physiological state and infection level by microorganisms, may generate the modified atmospheres that inhibit mold activity in airtight conditions was of interest. Therefore, the objective of this study was to investigate the respiration rate of moist prunes at various temperatures and water activities to determine if airtight conditions will be sufficient to create self-generated atmospheres to prevent microbial populations from causing damage to the prunes.

MATERIALS AND METHODS

Origin of prune samples:

Detailed description of the origin of prune samples is given in the first section of this report under "I - Equilibrium moisture content of California prunes". The samples of prunes used in this study were from two different crops; "**moisturized samples**" from the 1998 and "**dryer samples**" from the 1999 crop.

Moisturized samples

These were originally dry prune samples, but artificially moisturized at the laboratory conditions. The nominal moisture contents were approximately 18%, 20%, 22%, 24%, 26%, 28%, 30%, 32%, 34%, 36% and 38%. After moisture adjustment these samples were termed in this report as "**moisturized samples**".

Dryer samples

The samples were obtained by stopping the commercial drying process and sampling from the dryer. They were termed in this report as "**dryer samples**".

Moisture content:

Moisture content was based on nominal moisture content and 24 h drying time in a vacuum oven at 70°C.

Water activity (a_w):

The a_w was determined using Novasina ms1, Defensor with a "enMBRK-3" sensor as detailed in the previous section on equilibrium moisture content.

Aerobic plate count (APC):

The level of microorganisms on the prunes was determined by aerobic plate count (APC) carried out on single 50 g samples taken at the start of the experiments and at the end. The APC was carried out by the DFA of California according to the method developed by the Association of Official Analytical Chemists (AOAC) Official Methods of Analysis, sec. 966.23 (Maturin and Peeler, 1998).

Yeasts and molds

The level of yeasts and molds on the prunes was determined on the same 50 g samples as the APC. The yeasts and molds on prunes was carried out by the DFA of California according to the method developed by the Association of Official Analytical Chemists (AOAC) Official Methods of Analysis (Tournas et al., 1998).

Sugar content:

The liquid chromatographic method of AOAC (1995) was used by the DFA of California for the determination of sugar content in prunes.

Respiration rate of prunes:

The respiration rate was determined based on the oxygen consumption of the prunes. The oxygen concentration of the interstitial air space of ~ 500 g prunes was periodically

measured in a respirometer that consisted of 0.95 Liter mason jars with two 1/16" i.d. copper tubes soldered in lid (Fig. 2.1). An electrolytic sensor type oxygen monitor ("Oxychek-2", Bishop, UK) equipped with an internal pump delivering ~ 500 mL/min gas sample flow was used for oxygen levels in the jars. The "Oxychek-2" was equipped with inlet and outlet gas ports that enabled gas circulation by a closed loop gas flow system using PVC flexible 1/16" i.d. tubes connected with the two copper tubes soldered to the jar lid (Fig. 2.1). The copper tubes had different lengths from inside the jars, one ended at ~ 20 mm and the other at ~ 180 mm from the center of the lid reaching at ~ 15 mm from the bottom serving as gas inlet into the jar. The top end of each copper tube was equipped with T-type two-way valves from outside the jars situated between each flexible and copper tube. One port of the valve was directly connected to the copper tube, the second port to the oxygen monitor and the third port to the atmosphere. Depending on the position of the valve, gas flow was conveyed either from the jars into the oxygen monitor or from the monitor to the atmosphere.

Since at start of a reading the air volume in the flexible tubing and the oxygen monitor would influence the respirometer concentration that may have a different oxygen composition, that volume was estimated as 4.9 mL. The approximate oxygen concentration change due to that volume amongst two successive readings was about 0.1% in jars without prunes. The equivalent oxygen entry into the respirometer was adjusted to all the readings.

To calculate the respiration rate, each jar volume was carefully measured volumetrically using water at 20°C. In addition, the prune volume was estimated after measuring their density by volume displacement and weight. A sample of 5 prunes was used from each moisture content for density determination. Prune density varied in the range of 1.264 and 1.303 g/mL for the "**moisturized samples**" and in the range of 1.203 and 1.289 g/mL for the "**dryer samples**". A consistent correlation was not obtained between the water activity and the density of prunes.

The jars containing prunes were stored at three temperatures; 25°, 30° and 35°C. Since a pressure build up was observed, particularly in those jars containing high moisture prunes, that pressure was measured using a manometer (Fig. 2.2). The Oxychek-2 sensor and its pump were influenced when excessive pressure developed. At the highest moisture levels and when the oxygen level fell rapidly, up to 27 kPa pressure was observed in the jars. But usually even at intermediate moisture levels the pressure build up was not apparent. Before an oxygen reading was taken, that excessive pressure was released.

To take a reading, after the oxygen monitor was connected appropriately to the respirometer, the two T-type valves were kept at a position such that the gas flow would be from the monitor to the exhaust port. In that position the monitor was activated to measure atmospheric oxygen concentration and adjust the calibration of the instrument to 20.9% oxygen. In this position the tubes remain connected to the respirometer, but measurement is that of the atmospheric oxygen. Then the T-type valves were switched simultaneously to the ports to provide a closed loop gas flow between the respirometer and the monitor. At the end of the reading and before disconnecting the monitor, the

valves were returned to the initial position in which the monitor remained connected but it measured atmospheric oxygen. This procedure was necessary to obtain repetitive and reliable results.

The oxygen monitor was calibrated and zeroed using known gas concentrations in atmospheres containing up to 100% nitrogen. Also, to ensure that the carbon dioxide would not interfere the readings, similar calibration was carried out using atmospheres containing up to 100% carbon dioxide. This calibration and zeroing procedure was repeated three times during the experiments and the instrument was found stable without change.

RESULTS and DISCUSSION

Microflora load:

The aerobic plate count (APC) is intended to indicate the level of microorganisms in a product. Fig. 2.3 shows the ACP carried out on samples of prunes at different water activity levels. The test on samples defined as initial was carried out after the prunes were moisturized and kept for two months at 0°±2°C before they were placed in the sealed respirometer at temperatures of 25°, 30° and 35°C. It was important to ensure that microorganisms' development did not take place while the prunes were kept at the low temperature. On samples taken before sealing the prunes in the respirometer the microorganisms remained at acceptable levels, except at 0.83 a_w. The increase in APC of the 0.83 a_w sample could be a contamination that may have occurred after the sample was removed from the cold chamber. However, since these determinations were carried out without replicates, the increase of the APC may be explained after a more detailed study is carried out. The samples kept in the respirometer at 35°C for 35 days showed low APC without significant changes among the tested samples deriving from different moisture contents (Final Aerob. in Fig. 2.3). The APC of final samples was carried out only on those samples where prune respiration was at detectable levels.

Microscopic foodborne yeasts and molds have the ability to attack prunes due to their relatively versatile environmental requirements. The majority of yeasts and molds are obligate aerobes, i.e. they require free oxygen for growth. Their temperature range is also broad between 10° and 35°C. Moisture requirements for molds are low, most species can grow at a a_w of 0.85 or less, although yeasts generally require a higher a_w (Tournas et al., 1998). Results on yeast counts carried out on prunes are shown in Fig. 2.4. Yeast counts on initial samples remained low indicating that storage during the moisturizing period at 0°C did not cause development of yeasts. But on three samples kept in the respirometer yeast counts were markedly higher than the initial samples. In one sample yeast counts were at the level of initial samples, indicating the existence of aerobic and anaerobic yeasts in the samples. In that low yeast count level at 0.84 a_w, it may be that the aerobic yeasts were inhibited due to the low oxygen content that prevailed in the respirometer. Alternatively, it may also be possible that some contamination occurred in those prune samples with high yeast counts.

Mold count gave the most meaningful results as expressed in Fig. 2.5. Accordingly their development on the initial samples stored in the cold chamber at 0°C was not intensive but a live mold population survived. However, after sealed storage in the respirometer, mold counts were extremely low indicating that those aerobic molds could not survive the modified atmosphere conditions in the respirometer. El Halouat and Debevere (1997) studied the effect of water activity, modified atmosphere packaging and storage temperature on spore germination of molds isolated from prunes. Their results showed that under anaerobic atmospheres, germination and growth of all tested species were completely inhibited at low a_w, while at high a_w because of residual oxygen, conidia germinated but failed to grow. At any a_w value between 0.88 and 0.92, conidia failed to germinate when 100% carbon dioxide was applied. Similar results were obtained for *E. amstellodami* and *F. oxysporum* in 80% carbon dioxide – 20% nitrogen and in 60% carbon dioxide – 40% nitrogen. Under aerobic conditions, at 5% oxygen germination and growth occurred only at high a_w, while 10 or 20% oxygen combined with either 80 or 60% carbon dioxide conidial germination and mold growth were only delayed comparing to the control in air. Results on mold development shown in Fig. 2.5 are in agreement with the detailed study of El Halouat and Debevere (1997). In fact, even after exposure in the respirometer for over 5 months, no mold development could be observed at any tested moisture level.

Respiration of "moisturized samples" prunes:

Respiration of "**moisturized samples**" is shown in Fig. 2.6, 2.7 and 2.8 at temperatures of 25°, 30° and 35°C, respectively. In these figures the higher the water activity the more intense the oxygen consumption by prunes. In most cases a nearly linear relationship was observed between oxygen depletion and time. This linear relationship was needed to determine the respiration rate by using the equation that defines the slope of the line.

For the highest a_w a very low level of oxygen, an almost anaerobic condition was achieved within less than two days at 25°C (Fig. 2.6). However, at higher temperatures, anaerobic conditions were achieved only at above 0.824 (Fig. 2.7 and 2.8). The exposure time for developing a low oxygen atmosphere is a function of the availability of oxygen in the enclosure containing the prunes. In this study an approximate weight of prunes of 500 g was used in each respirometer. A minimal head space that was about 10% of the bulk volume of prunes was necessary to close the respirometer jars without damaging the prunes by the gas sampling copper tube. In these tests it was possible to calculate the interstitial free space and the total free space not occupied by prunes. The interstitial free space in the respirometer was estimated as about 50% of the bulk volume. This is a value higher than other commodities stored in bulk, like grain products. For example for wheat grain in bulk the interstitial air space is considered as 40%. But at commercial scale the interstitial free space of prunes may be lower than the estimated 50% free space for prunes as in the 0.95 L respirometer jars. For comparison, the results presented in Fig. 2.6, 2.7 and 2.8 need to be adjusted to the correct free space of each respirometer. The free space in prunes is influenced by compactness but to a lesser extent also by the prune size and its moisture content.

Respiration of "dryer samples" prunes:

Respiration of **"dryer samples"** is shown in Fig. 2.9, 2.10 and 2.11 at temperatures of 25°, 30° and 35°C, respectively. Similarly as in the **"moisturized samples"**, the higher the water activity the more intense the oxygen consumption by prunes. Again, in most cases a nearly linear relationship was observed between oxygen depletion and time.

For the **"dryer samples",** even at the highest water activity of 0.810, anaerobic conditions could not be achieved within 145 h at 35°C (Fig. 2.11). These **"dryer samples"** represented the moisture levels achieved during the drying process. The 0.624 a_w is represented by a sample taken after 12 h drying in the commercial dehydrator. Samples with a_w higher than 0.624 caused marked changes in the depletion of oxygen content. Therefore, this suggests that prunes dried for only 12 h could be stored safely without the possibility of microorganism development. This aspect of drying for shorter periods of time deserves further investigation.

Dried prunes, especially those dried in commercial dehydrators at elevated temperatures such as 80°- 86°C, are physiologically considered as non-living organisms. Therefore the observed respiration processes could be attributed only to the prunes microorganism load and its composition.

Respiration rates of "moisturized samples" prunes:

Based on values obtained from Fig. 2.6, 2.7 and 2.8, the respiration rate at each temperature and water activity values was graphed in Fig. 2.12. These results are in essence very descriptive as they determine when an intensive deterioration of prunes may occur under aerobic conditions. These lines also enable prediction of the heating process and its intensity, if moist prunes are stored at normal atmospheres. Literature data on respiration of prunes are lacking.

Respiration rates of "dryer samples" prunes:

Values obtained from Fig. 2.9, 2.10 and 2.11, allowed calculating the respiration rates shown in Fig. 2.13. Respiration rates shown in Fig. 2.13 are comparable to results given in Fig.2.12, except that the lines in Fig. 2.12 show a sudden increase in respiration rate only above a_w 0.84

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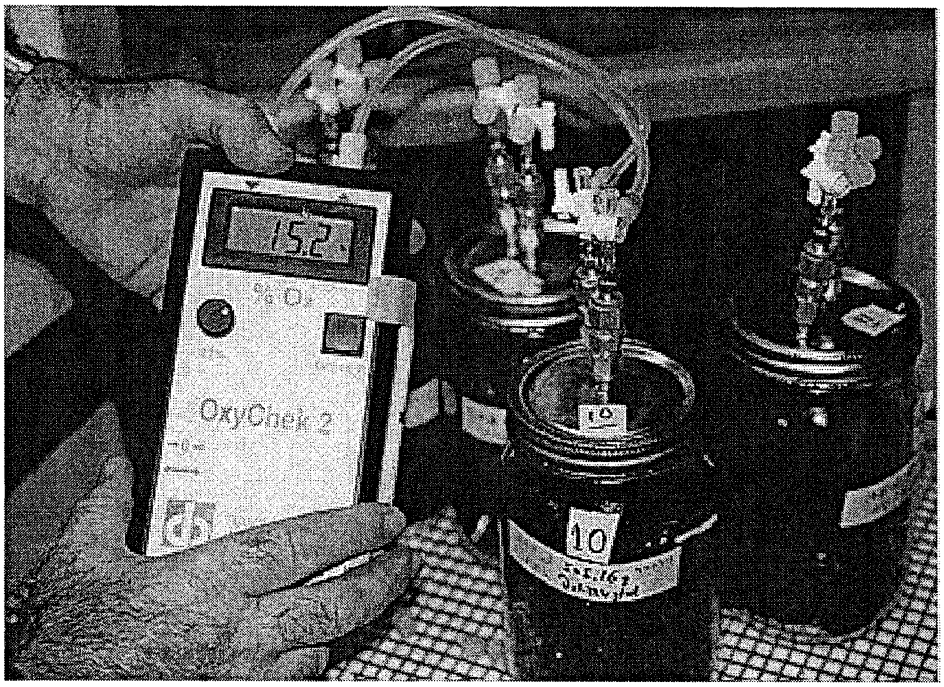

Fig. 2.1 – Respirometer jars containing prunes equipped with T-type valves and connected to the electrolytic oxygen monitor in closed loop gas flow system.

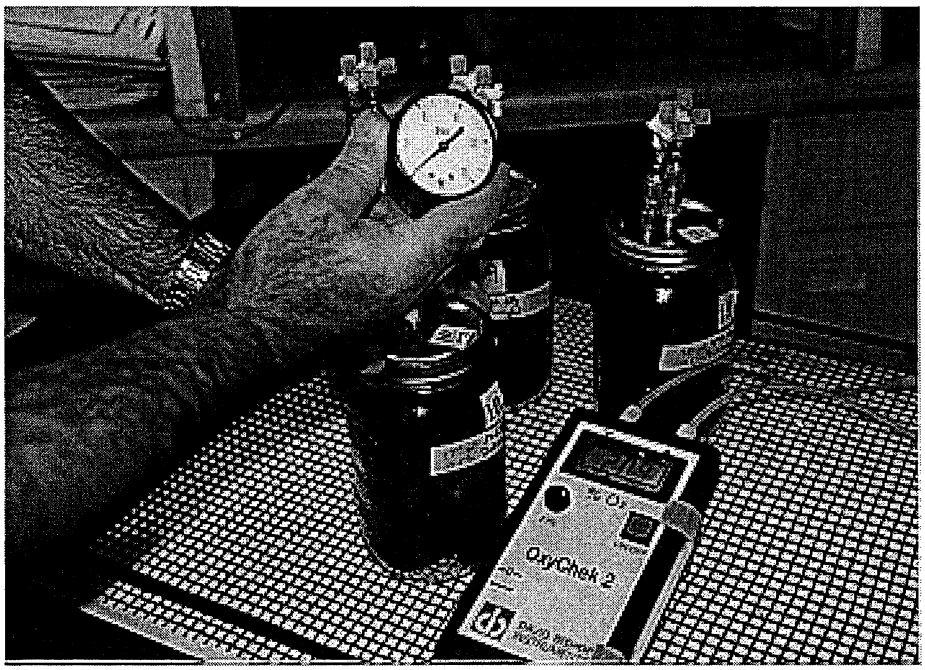

Fig. 2.2 – Manometer for measuring pressure build up in the respirometer jars containing prunes before determining the oxygen level.

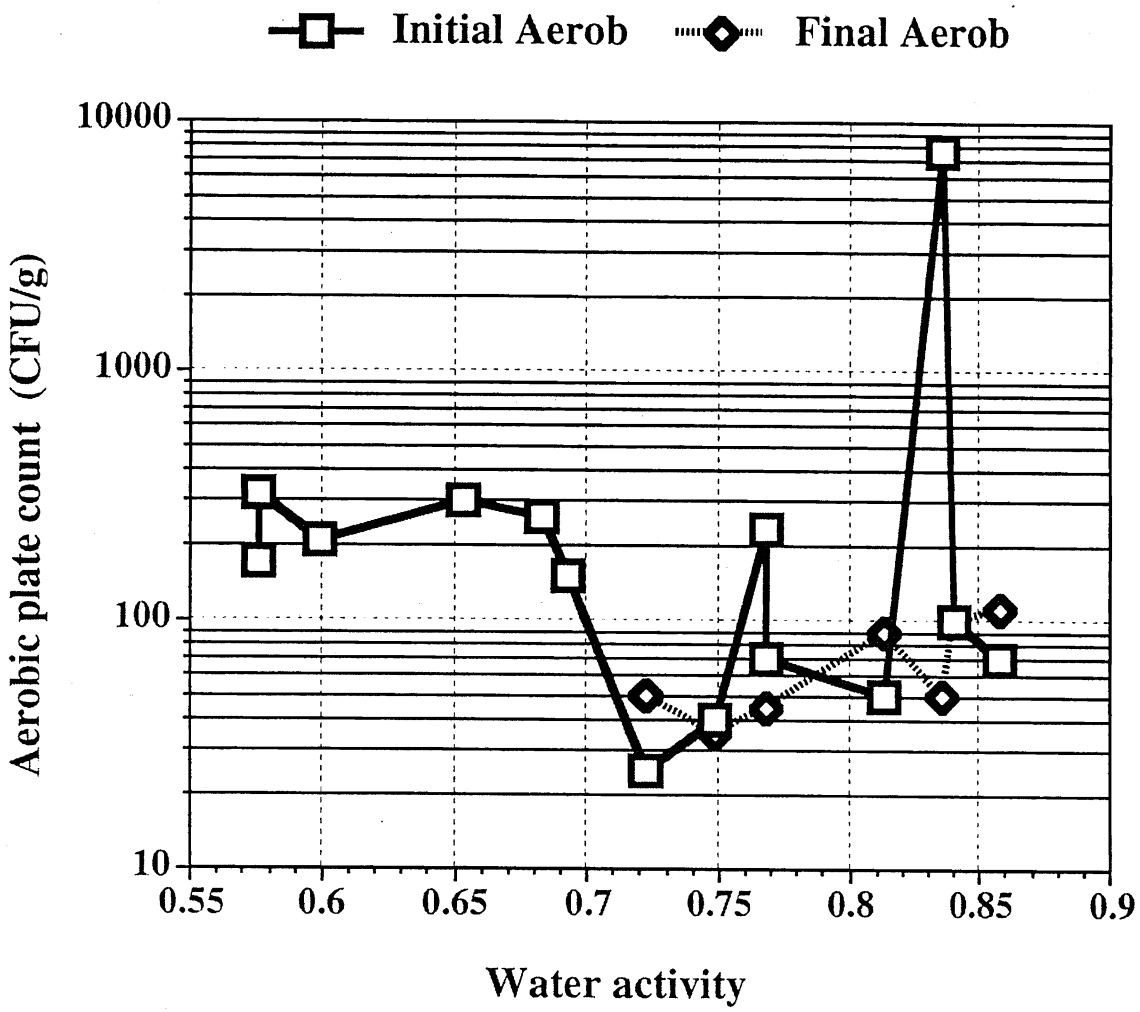

Fig. 2.3 – Aerobic plate count (APC) in CFU/g in relation to water activity of prune samples before sealing in the respirometer (Initial Aerob) and after 35 days in sealed conditions in the respirometer at 35°C (Final Aerob).

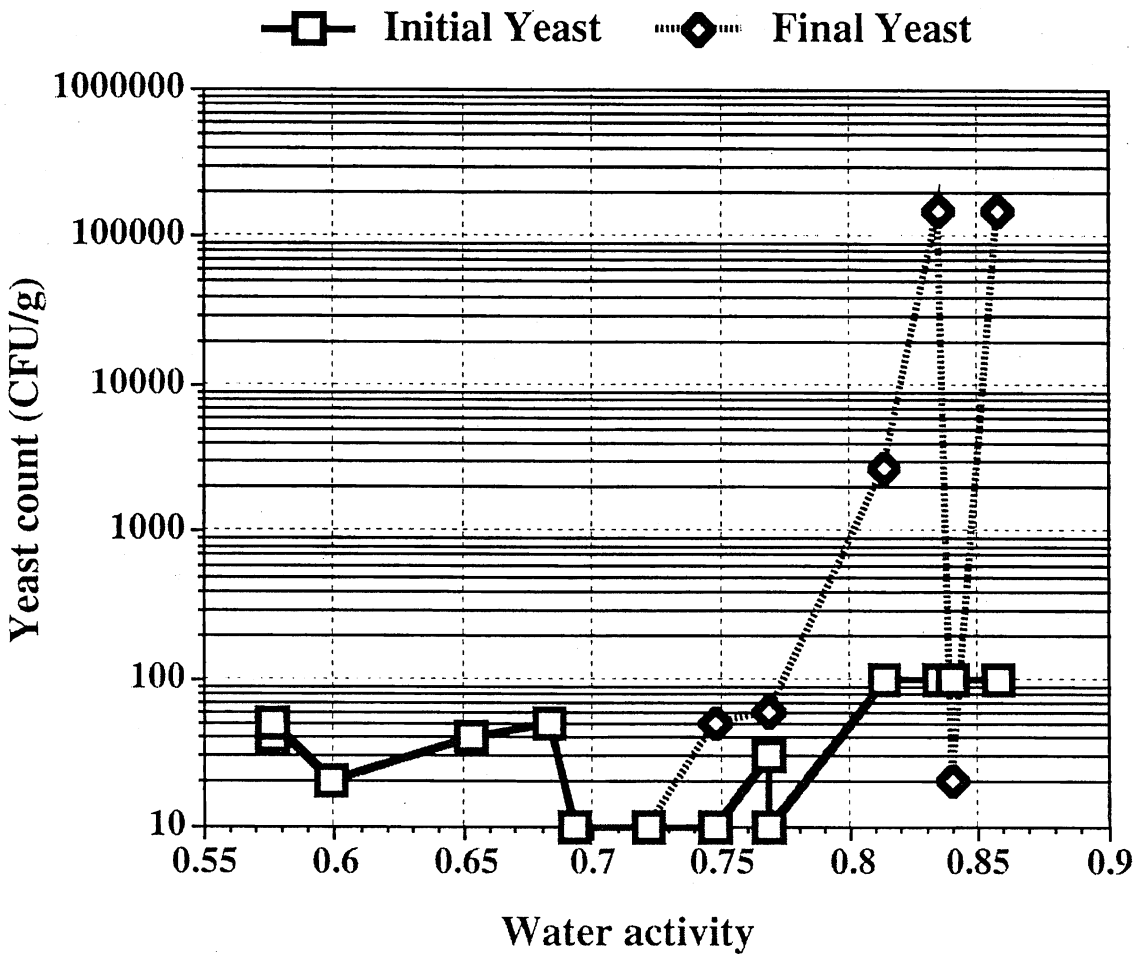

Fig. 2.4 – Yeast count in CFU/g in relation to water activity of prune samples before sealing in the respirometer (Initial Yeast) and after 35 days in sealed conditions in the respirometer at 35°C (Final Yeast).

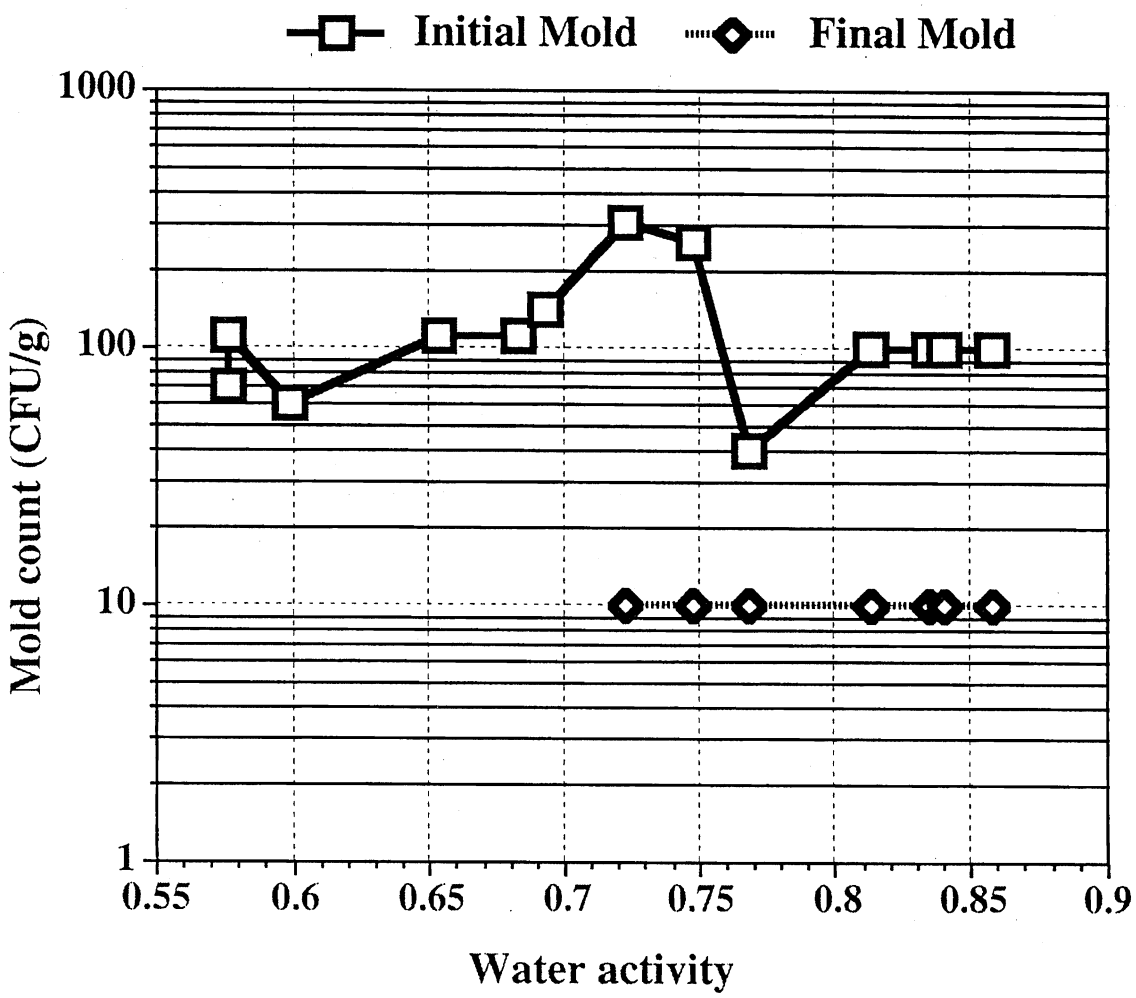

Fig. 2.5 – Mold count in CFU/g in relation to water activity of prune samples before sealing in the respirometer (Initial Mold) and after 35 days in sealed conditions in the respirometer at 35°C (Final Mold).

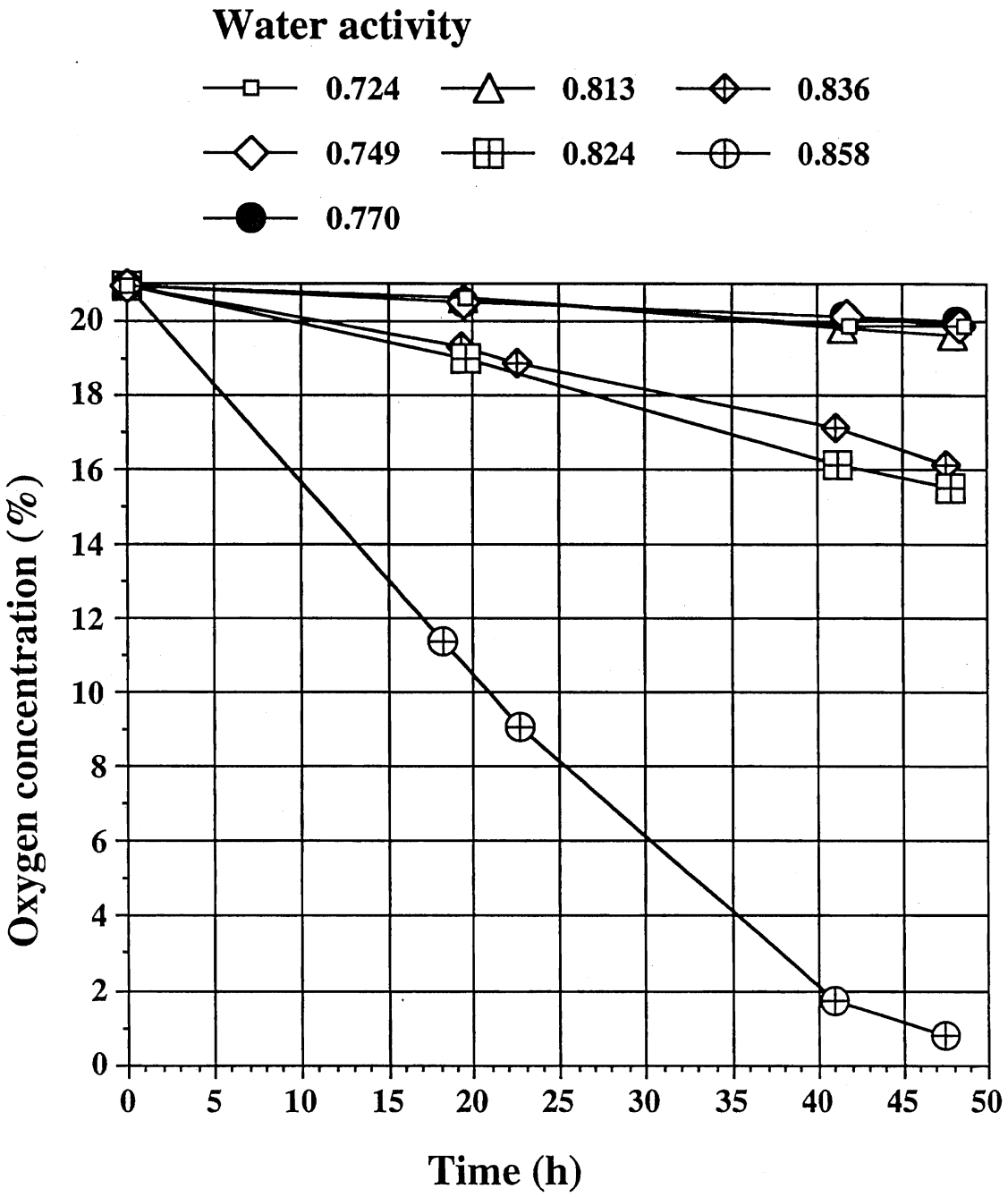

Fig. 2.6 – Oxygen depletion in the respirometer as a result of respiration of prune samples defined as "**moisturized samples**" at 25°C and various water activities.

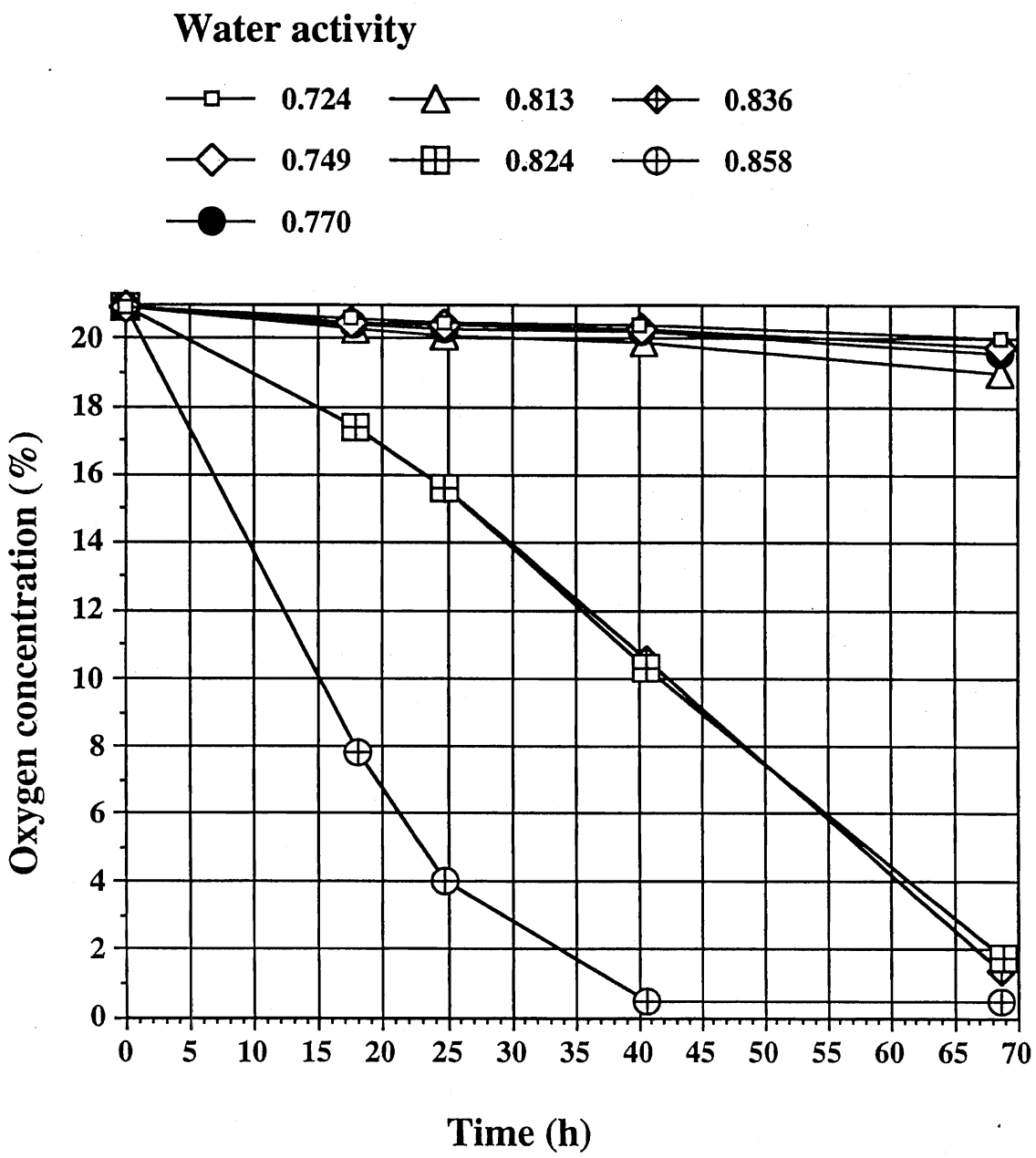

Fig. 2.7 – Oxygen depletion in the respirometer as a result of respiration of prune samples defined as "**moisturized samples**" at 30°C and various water activities.

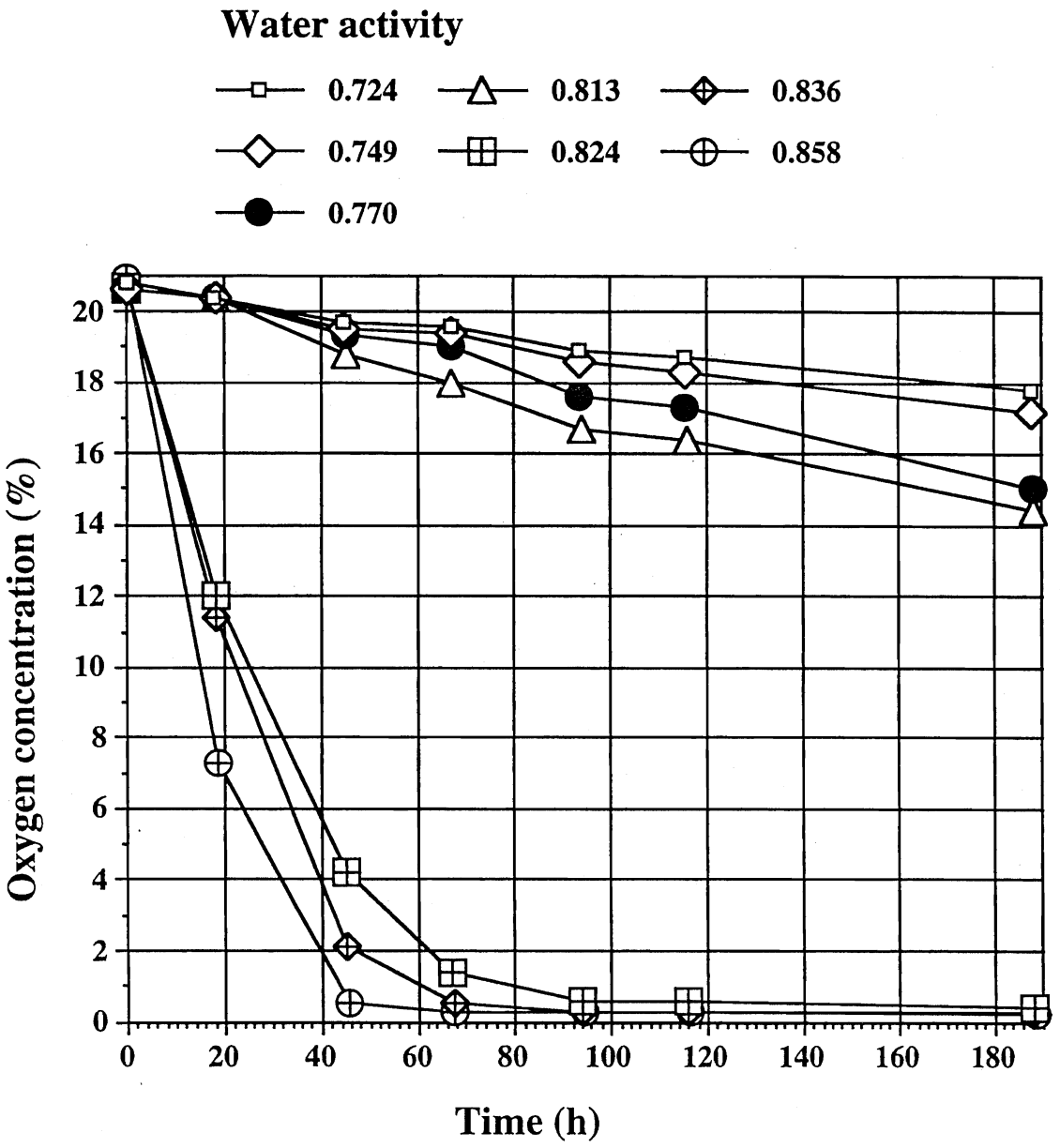

Fig. 2.8 – Oxygen depletion in the respirometer as a result of respiration of prune samples defined as "**moisturized samples**" at 35°C and various water activities.

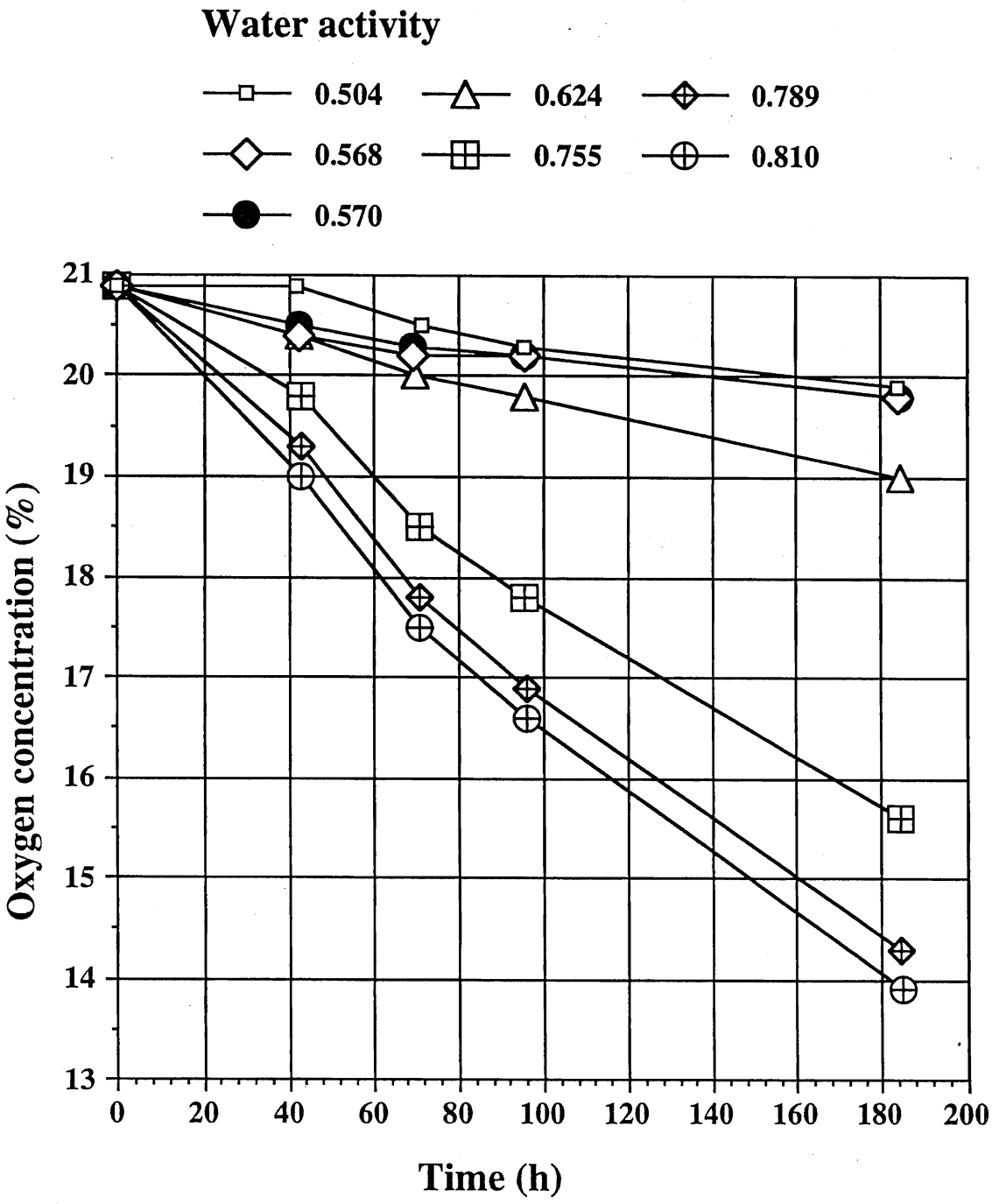

Fig. 2.9 – Oxygen depletion in the respirometer as a result of respiration of prune samples defined as **"dryer samples"** at 25°C and various water activities.

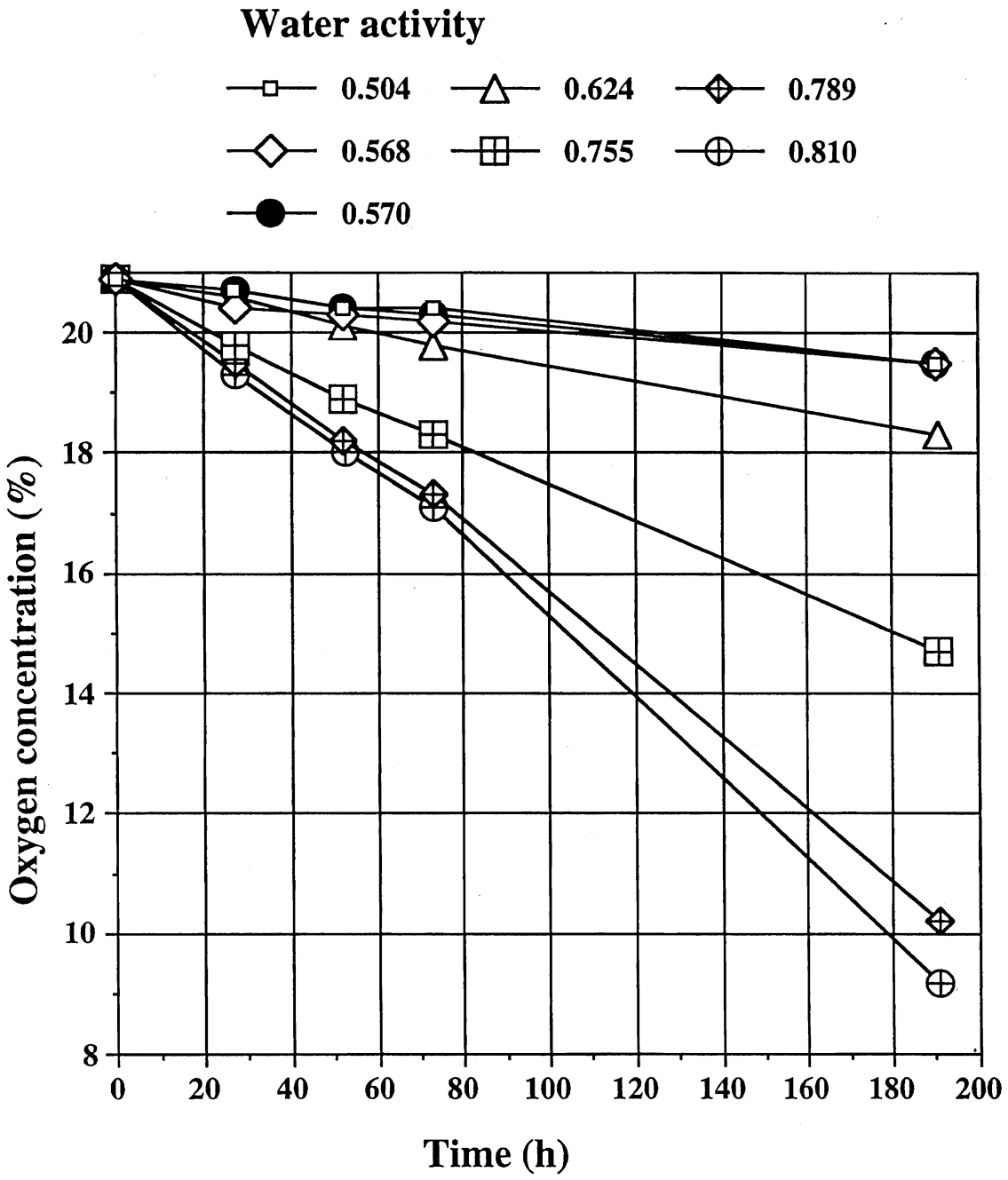

Fig. 2.10 – Oxygen depletion in the respirometer as a result of respiration of prune samples defined as **"dryer samples"** at 30°C and various water activities.

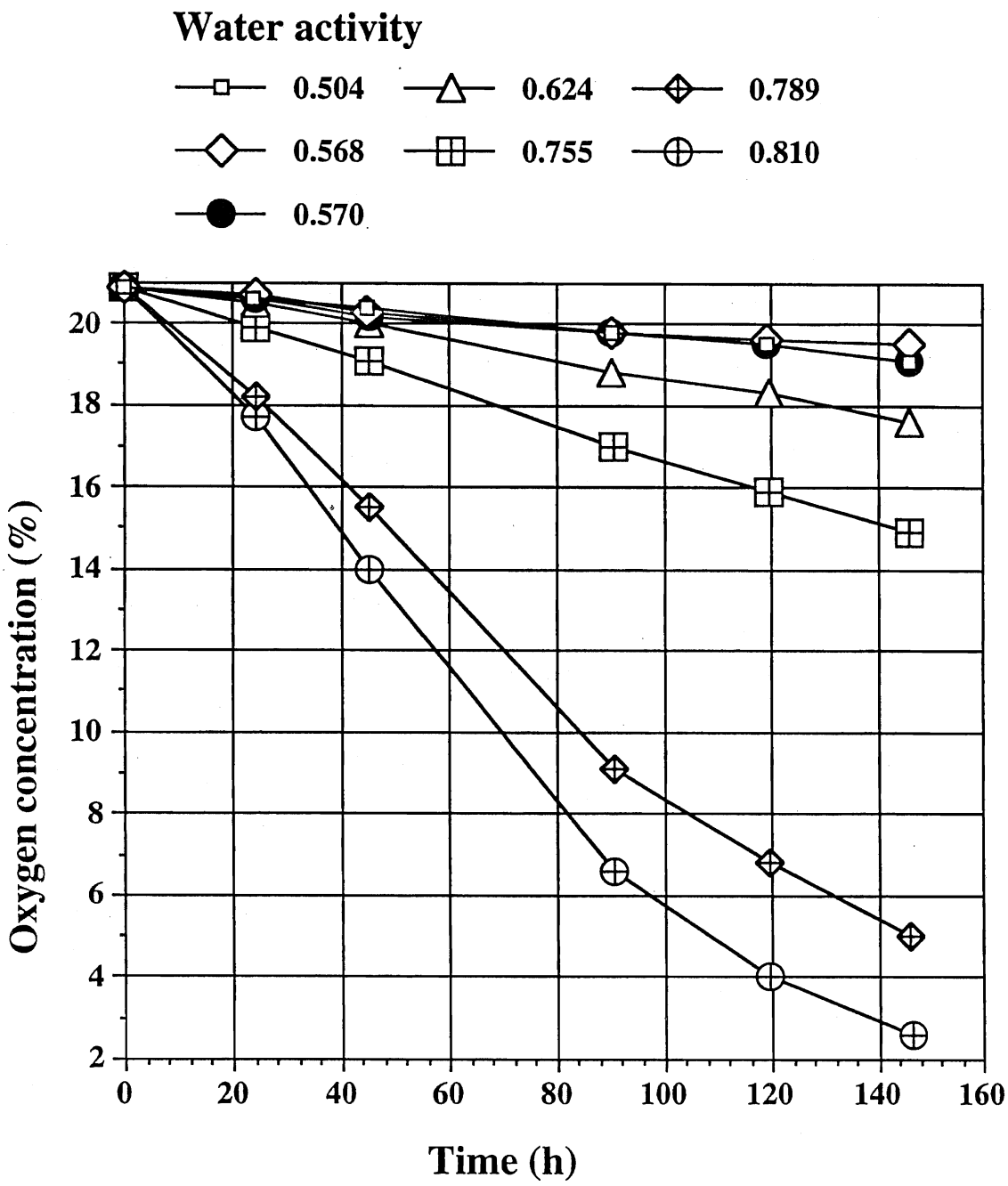

Fig. 2.11 – Oxygen depletion in the respirometer as a result of respiration of prune samples defined as **"dryer samples"** at 35°C and various water activities.

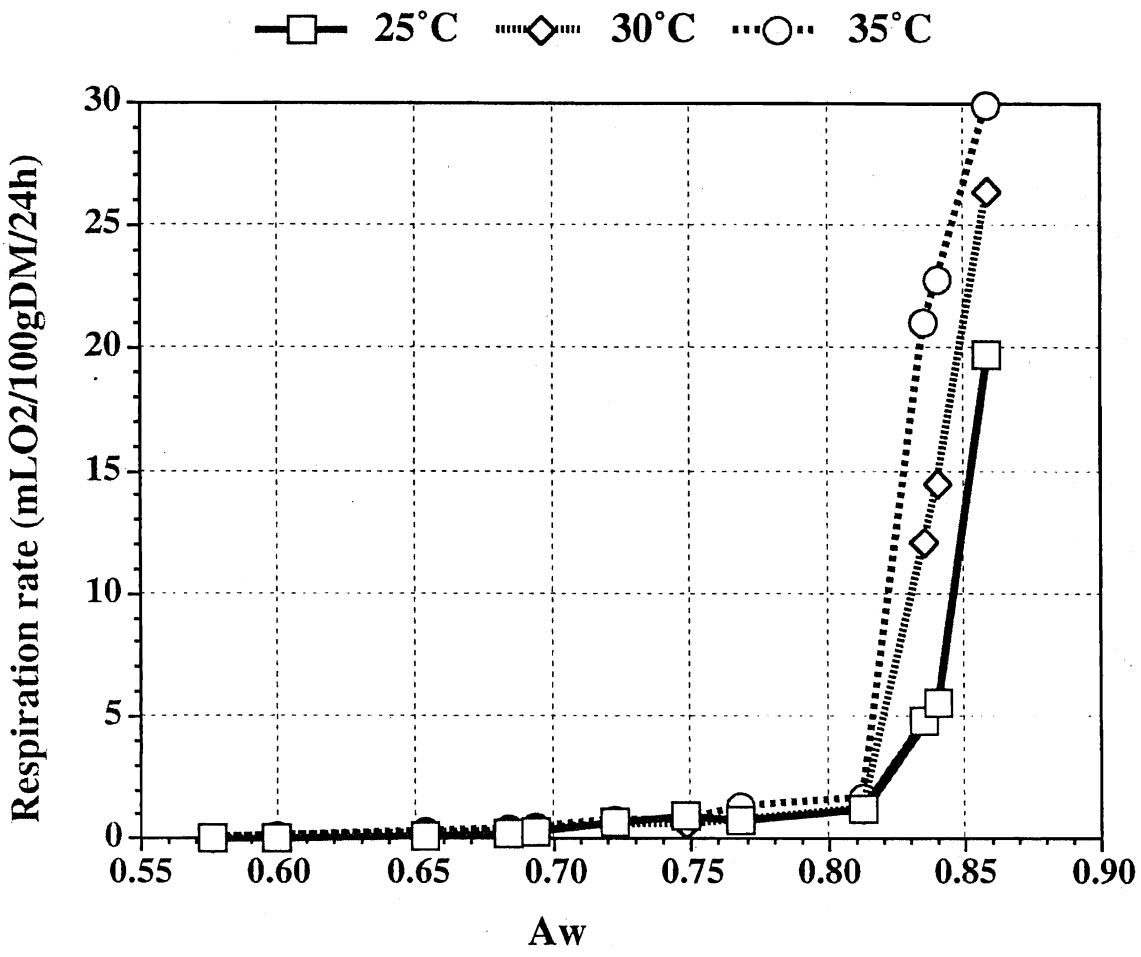

Fig. 2.12 – Respiration rate of prunes at 25°, 30° and 35°C at different water activity (A_w) values. Respiration rates were determined on "**moisturized samples**" after they had reached equilibrium moisture content.

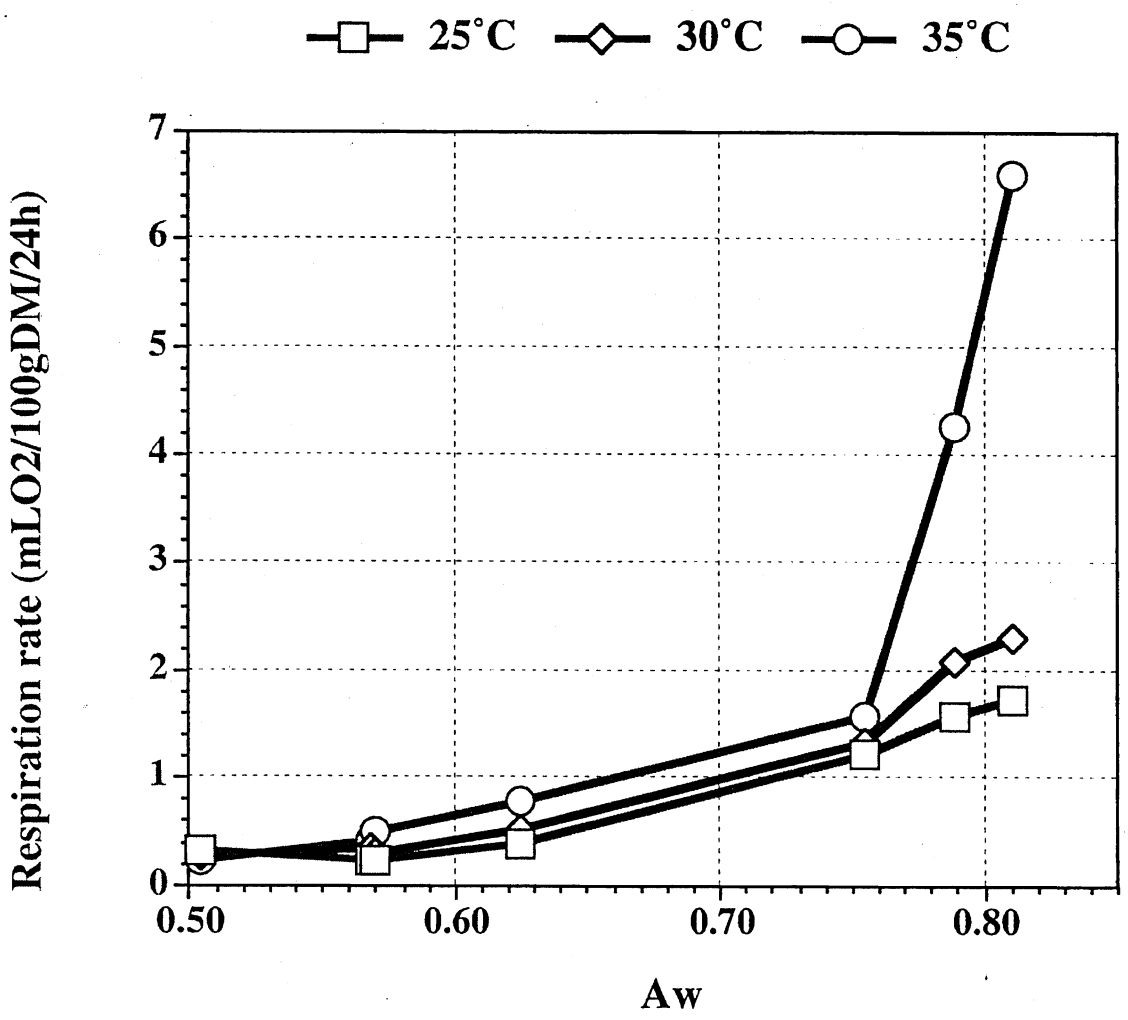

Fig. 2.13 – Respiration rate of prunes at 25°, 30° and 35°C at different water activity (A_w) values. Respiration rates were determined on **"dryer samples"** taken from a commercial dryer.

STORAGE OF PRUNES UNDER CONTROLLED ATMOSPHERES FOR QUALITY PRESERVATION AND INSECT CONTROL

III – CRITICAL LIMITS OF DEGREE OF SEALING FOR SUCCESSFUL APPLICATION OF CONTROLLED ATMOSPHERE OR FUMIGATION

INTRODUCTION

A fundamental requirement for the successful application of gaseous treatments to control stored-product insects is a well-sealed structure. These gaseous treatments include the application of modified atmosphere (MA), controlled atmosphere (CA) and fumigation. In the sealed structure, the desired gas concentration should be maintained at a sufficient level to control insects, otherwise the gas concentration would decrease rapidly without effect. The requirement for gastight storages for application of CA's and MA's appears to be more critical than the requirement for application of fumigants (Bond, 1984). In spite of the trend towards improved sealing of existing silos in some countries (Newman, 1990; Delmenico, 1993), the objective has been either to obtain increased fumigation efficiency, or to convert structures for storage under CA's. To control stored-product insects, Jay (1971) recommended a concentration of 60% carbon dioxide (CO_2) in air for 4 days at a temperature of 27°C or above. In the context of MA's, sealed storage of grain termed "air-tight storage" or "hermetic storage" is also considered (Hyde, *et al.,* 1973; De Lima, 1990). In the hermetic storage method, the structure should be sufficiently airtight to enable insects and other aerobic organisms in the grain mass to reduce oxygen (O_2) concentrations below those permitting insect development.

Fumigants have been used for many years with limited requirements for structural tightness, and covering the stack or the storage under plastic sheets was usually considered satisfactory. Gastightness has for years been a problem for the application of fumigants in storage. The consequences of poorly sealed storages under fumigation should be considered in view of the development of insect resistance to fumigants in poorly sealed structures (Banks and Desmarchelier, 1979; Banks, 1981; Zettler, 1993).

Methods to determine gastightness have been investigated for different purposes. For the analysis of the energy requirements of buildings, air infiltration is a primary source of energy loss and this infiltration can be measured experimentally. CO_2 has also been used experimentally as a tracer gas (Navarro, 1997). Hunt (1980) reviewed some tracer gas techniques to measure air infiltration into buildings and compared fan-pressurization-evacuation procedures to estimate comparative tightness of those structures. The dynamic characteristics of air infiltration into buildings have been studied in order to predict the heating and cooling load of seasonal energy requirements (Hill and Kusuda, 1975). The ASHRAE Handbook of Fundamentals describes the air change method and the crack

method in predicting air infiltration rates (Anon., 1972). The crack method or the constant pressure test is usually regarded as more accurate as long as the leak characteristics can be evaluated properly (Hill and Kusuda, 1975). With this method airflow is expressed as:

$Q = b.P^{n}$

where Q = the volumetric flow rate of air; b= the proportionate constant; n = the exponent and P= the pressure difference exerted on an enclosure.

Meiering (1982) investigated a constant pressure test and a variable pressure test for measuring specific silo permeability in silage systems, where the sealed shell is designed to limit entry of O_2 to minimize losses in quality. The effect of variations in environmental temperature and atmospheric pressure on O_2 intake of silos was simulated, and permeability limits required for proper O_2 control in silos containing silage were defined. Gas interchange within freight containers and factors leading to gas interchange between containers and external atmosphere were detailed by Banks *et al.*, (1975). They found that the relationship between applied pressure and gas leak rate gave a useful measure of gastightness. Banks and Annis (1977) developed a practical guide for storage of dry grain under MA and specified requirements for silo gastightness. Their specifications correspond to pressure decay times needed to maintain the atmospheric composition in the silos. Sharp (1982), using the constant pressure test, measured the gastight level of sealed structures. These tests are designed to estimate the permissible limits for effectively maintaining the gas composition in the stores during the treatment.

A decision of the degree of gastightness that is satisfactory or what gas concentrations can be maintained under given environmental and structural conditions should be made prior to the gaseous treatment. This decision should be weighed against the investment involved in sealing a leaky structure to prevent excessive loss of the treatment gas.

The objective of this study was to demonstrate the critical limits of degree of sealing using the variable pressure test for successful controlled atmosphere and fumigation treatments to control dried prunes insects.

MATERIALS AND METHODS

Structure for Gaseous Treatments

A fumigatable flexible structure using heavy-duty liner for outdoor storage of stacked commodities of 7.5 m^3 volume was used. Similar structures termed storage cubes (like the Volcani Cube®) are designed for use as fumigation chambers or for modified atmosphere storage of commodities (Donahaye *et al.*, 1991). The cube was 137.5 cm high, 295 cm long and 185 cm wide and equipped with two ports, one for gas supply and the other for exhaust. To maintain the dimensions, the cube was supported from inside using empty cardboard, polystyrene and two standard wood boxes. For gas containment tests the cube was erected at the HCRL.

To evaluate the influence of temperature on the rate of gas exchange the cube was tested when it was under cover by providing shading to minimize direct solar heating effect, and when it was exposed to direct solar heating. The heating effect of the sun could be taken advantage of only after 10 AM because the cube was located adjacent to a structure on the eastern side of the cube (Fig. 3.1). This location was found most suitable because the cube could be covered to provide shading without having to relocate it (Fig. 3.2).

Variable pressure test:

A vacuum cleaner delivering 3 m^3/min of air at 2,000 Pa and an inclined manometer, catalogue no. 246, Dwyer Instruments Inc. Michigan City, IN., to read up to 1,500 Pa, was used for pressure measurements (Fig. 3.3). The cube was equipped with a 3.8 cm diameter ball valve.

As a flexible structure, pressure tests in the structure were performed by creating a negative pressure by evacuation until the sheeting adhered to the packed material. The variable pressure tests were performed while the rate of heating or cooling, resulting in expansion and contraction of the structure due to ambient climatic conditions, was kept at a minimum. To avoid these fluctuating variables, the tests were carried out under as stable temperature and barometric conditions as possible.

Presentation of Results

Results as time in minutes for the pressure to fall between the two time limits were recorded. The same limits were used each time a particular leak size was tested. Half-life pressure decay times were correlated with daily ventilation rates of O_2, CO_2, phosphine and methyl bromide.

Ambient Conditions:

Ambient temperatures were recorded with Datapod DP-220 data logger (Omnidata, Logan, UT). Barometric pressure was recorded using a mechanical barograph (Precision Microbarograph, Cat. No. 5-800A, Belfort Instrument Co. Baltimore, Maryland), with weekly recording charts. Both the data logger and the barograph were housed on top of the cube. The barograph was periodically checked against official barometric recordings given by the local meteorological weather channel on the TV and was found to be in full agreement.

Predetermined orifices:

The relationship between ventilation rate and gas exchange was studied in a series of tests with different sizes of cross section leak areas having openings of 1.6 mm, 3.2 mm and 6.4 mm i.d. orifices with wall thickness of 4 mm were employed. The orifices were made by drilling holes in PVC caps mounted on the structure (Fig. 3.2).

Generation of the gaseous atmospheres in the cube

Ventilation rate from the cube was compared on four different gases; oxygen, carbon dioxide, phosphine and methyl bromide.

For the generation of a low oxygen atmosphere, nitrogen was used from a pressurized cylinder of 2500 psi (178 kg/cm^2). Using a regulator the nitrogen supply line was maintained at 15 psi. In this way a cylinder of 7.22 m^3 could be discharged into the cube in 5 h or at a rate of 24 L/min. This gas flow rate was just sufficient to avoid pressure build up during the purge phase of nitrogen while the exhaust port of 3.8 cm i.d. was kept open. At least two cylinders of the same nitrogen volume were required to create an atmosphere of 5.1% oxygen.

For a carbon dioxide rich atmosphere, carbon dioxide was used from a pressurized cylinder of 1150 psi (82 kg/cm^2) containing 60 lb (~ 27.24 kg or 13.88 m^3 at NTP). Using a regulator the carbon dioxide supply line was maintained at 15 psi. In this way a cylinder of 13.88 m^3 could be discharged into the cube in 6 h or at a rate of 38.6 L/min. This gas flow rate was just sufficient to avoid ice formation on the regulator and pressure build up during the purge phase of carbon dioxide while the exhaust port was kept open (Fig. 3.5). One cylinder of carbon dioxide was required to create an atmosphere of 76.6% carbon dioxide and 4% oxygen.

For generating phosphine, 225 pellets of 0.6 g each were used to obtain a calculated 1500-ppm of phosphine. The pellets were placed in a sachet made of filter paper that was attached inside the cube after inserting it through the exit port. Phosphine generation is dependent on the atmospheric humidity. Generation was low, because in addition to the fact that the cube was empty and no humidity source was available within the cube, the high temperatures prevailing during the day caused a further drop in relative humidity. To enhance phosphine release the sachet was wetted from time to time, up to twice a day. It took about 97 h to reach a concentration of 1470 ppm.

Methyl bromide was generated from a 4 lb cylinder and discharged in liquid form (Fig. 3.6). At the start of dosing methyl bromide flow was possible in gas state, but very quickly the temperature in the cylinder fell because of evaporation and the flow ceased. Then the cylinder was turned upside down to enable discharge in liquid state. An initial dosage of 40 g/m^3 was attempted but a strong sorption, apparently by the cardboard and polystyrene boxes in the cube, was observed. It took about 5 min to discharge 300 g methyl bromide.

Determination of gas concentrations

An electrolytic sensor type oxygen monitor ("Oxychek-2", Bishop, UK) equipped with an internal pump delivering ~ 500 mL/min gas sample flow was used for oxygen levels in the cube.

An infrared Analyser Series 1400, Servomax Company, Inc., Norwood, MA. This instrument was equipped with an infrared detector and capable of measuring CO_2 up to

100%. Since the instrument was not equipped with an internal pump, suction of the gas sample from the cube was carried out using the internal pump of Oxychek$_2$.

Phosphine samples were taken using a gas sampling tube inserted into the plastic structure. Periodic daily gas samples were taken and the gas concentrations were measured using a phosphine detector equipped with an electrochemical sensor (PortaSens Series B16 Model 321010001) (Fig.3.3).

Methyl bromide samples were taken using a 100 mL syringe and injected in a gas chromatograph, Varian model 3800, equipped with flame ionizing detector and a 1 cc gas sampling loop. Conditions for measuring the methyl bromide concentrations were as follows: 2 mm i.d. x 2 m Teflon column packed with 10% OV-101 on Gas-Chrom Q (100/120 mesh), He carrier gas at 20 mL/min, H_2 (FID) at 30 mL/min, air (FID) at 250 mL/min, oven temperature at 100°C, FID detector at 200°C, and gas sampling loop injection temperature at 110°C.

RESULTS and DISCUSSION

Comparative results with variable pressure test

In a variable pressure test, the structure is pressurized to a value above or below atmospheric, using a fan. The air supply is then shut off and the pressure is allowed to fall by natural leakage to a new value. The time taken to fall from the high (positive or negative) pressure serves as a measure of the degree of sealing. Time elapsed to half the initial pressure is usually considered for comparisons of gastightness level.

The presentation of results was based on the half-life pressure decay time. Half-life of pressure decay in relation of orifice sizes is given in Fig. 3.8. The cube was tested under negative pressure except for one control in positive pressure. As shown in Fig. 3.8, it was possible to correlate the leak size with the pressure decay time. Complete airtight conditions could not be achieved for the cube. Several attempts were made to improve the degree of sealing, but they resulted in only minor improvements without obtaining a straight parallel line to the horizontal axis (Fig. 3.8), when tests were carried out in negative pressure. Test for gastightness using positive pressure resulted in an almost straight line. But this should be attributed to the small volume displacement through the leaks, relative to the volume created under positive pressure. Also it is most probable that some leaks enhance air infiltration under positive pressure and others under negative pressure. Depending on their position and configuration along the walls of the cube, the higher the pressure exerted on the cube the greater will be the gas leakage they will promote. By comparing the positive and negative pressure tests, it was concluded that the leaks in the cube were at sizes and locations that would not permit their detection by the conventional method of using soapy water, to create bubbles on the leaks. Therefore, it was decided to use the control line obtained in negative pressure tests as a base line for ventilation rate achieved without mounting the predetermined orifices on the cube. In the presence of predetermined orifices, the lines obtained with 1.6 mm, 3.2 mm and 6.4

mm i.d. orifices were proportional, suggesting that the total leak area of the sealed cube, could be equivalent to less than 0.8 mm^2 or of several leaks of equivalent total area.

Fig. 3.8 shows that the initial pressures for the tests were maintained in the range of 1,100 –1,120 Pa (4.5" water column) and the half-life was estimated at 555 Pa. Analyzing the data would reveal that at 555 Pa the approximate half-life pressure decay times for the predetermined orifices of 6.4, 3.2, 1.6 mm i.d. and the control were 1, 2.5, 3.5 and 4.5 min, respectively. These values were used for correlating the gas loss rate from the cube as measured during the tests.

A constant static pressure test is more accurate than a variable pressure decay test and has the advantage of being independent of bin volume. However, the variable pressure decay test is quicker and therefore the most practical means of measuring gastightness in grain storage (Anon., 1989; Navarro, 1997; Zahradnik, 1968). To minimize the thermal influence, tests should be carried out preferably before sunrise and in still weather. A pressure of 250 Pa may be taken as an upper limit, but for some structures even this pressure may cause poor seals to fail. Welded steel cells and concrete silos may be able to withstand 500 Pa, but higher pressures are usually unnecessary. In the present studies a maximum negative pressure of 1,120 Pa was chosen as a basis for comparison of the degree of gastightness using different orifice sizes. These tests were considered as pilot plant tests and therefore a maximum pressure was considered more meaningful to exemplify the extreme high-pressure test conditions, from which information on the influence of orifices could be obtained. By using the high initial pressure, lower ranges of pressures such as the recommended 500 Pa or 250 Pa can also be compared using the data in Fig. 3.8. The other reason for selecting the initial pressure as 4.5" water column was because the inclined manometer could read only up to 6" water column (~ 1,500 Pa). Also, the vacuum pump used in the tests performed best in this range and the rigid structure formed using the empty boxes could not withstand higher negative pressures without deformation.

Changes in ambient temperature

Daily changes in the ambient temperature as recorded during the experiments on gas loss rate are shown in Fig. 3.9. This figure is composed of bi-weekly measurements of daily temperature fluctuations. Extreme high temperatures typical for the Fresno area located in the central San Joaquin valley as high as 43°C were recorded in July and August. The daily lows for the same period were within the range of 18° and 23°C. The extreme daily difference of over 20°C in dry-bulb temperature was considered an important factor to enhance ventilation rate of the cube. Then later in September and until the end of the experiments, the temperatures dropped progressively to the daily range of 10° to 20°C in early November.

Fluctuations in temperature of the atmosphere within the cube result from solar radiation, ambient air temperature, wind, precipitation, and depend on the thermal properties of the construction material of the cube. The total number of temperature changes is directly proportional to the frequency and amplitude of temperature fluctuation in the cube void space. Therefore, changes in the gas temperature were approximated by linear functions

and the temperature rate of change was expressed as °C/h (Meiering, 1982). Since air infiltrates into the cube void space when a decrease in temperature occurs, the proportion of temperature rate of change with time to the initial gas temperature in the cube can be considered as the influence of temperature on the volume of air which infiltrates into the cube.

Changes in ambient relative humidity

Daily changes in the ambient relative humidity as recorded during the experiments on gas loss rate are shown in Fig. 3.10. This figure is also composed of bi-weekly measurements of daily relative humidity fluctuations. Extreme low day humidities typical for the Fresno area were recorded in July and August. The daily high relative humidities for the same period were within the range of 40 to 60%. The extreme low humidities were considered an important factor only in the release of phosphine gas from tablets requiring air moisture. Then later in September and until the end of the experiments the humidities increased progressively to the daily range of 40 to 100% in November.

Changes in ambient barometric pressure

Typical daily changes in the ambient barometric pressure, recorded in inches during the experiments on gas loss rate are shown in a section of the barograph in Fig. 3.11. It was difficult to interpret the fluctuations in barometric pressure. Also comparison of barometric pressure data from one area with another is further difficult.

Similar to changes in temperature, the increase in barometric pressure causes air infiltration into the cube. Changes in barometric pressure may be approximated by a linear function where the rate of atmospheric pressure change is expressed in Pa/h (Meiering, 1982). Since the atmospheric pressure would affect the effective total void volume of the cube, the volume of air entering the cube is proportional to atmospheric pressure change (Navarro, 1997).

In calculating ventilation rate, the basic assumption is that the volume infiltrating the cube is not restricted by leaks. Obviously in a gastight structure not equipped with a pressure relief valve, air infiltration into the cube during sudden changes in temperature or barometric pressure will be independent of the leak characteristic. Therefore, to express the barometric pressure changes in a meaningful way that would enable comparison with other conditions, such as maritime climate that is subject to intensive changes, Fig. 3.12 was prepared. Barometric pressure data were processed to express average weekly barometer rises in Pa/h and the number of weekly changes on top of each histogram. From Fig. 3.12 it is clear that the weekly changes in barometric pressure were very stable with about 7 changes/week in comparison to similar data collected from a maritime climate with 14-18 changes/week. Also the hourly barometric pressure variations were within the range of 1.2 to 3.1 Pa/h. Based on these data it is possible to estimate the influence barometric pressure will have on air infiltration rate or gas loss from a treated structure.

Infiltration rate of oxygen into the cube

Prior to the test on infiltration rate of oxygen, the cube was purged with nitrogen to reduce the oxygen concentration to about 5.1%. Then the gas decay rate in relation to the cube situation, whether it was exposed or shaded, was recorded. The infiltration rate results in both situations (exposed and shaded) were correlated to half-life pressure decay times as they were obtained in Fig. 3.8. Highly significant correlation was obtained for each situation to show that the half-life pressure decay time is a reliable criterion to predict gas loss from nitrogen treated structures. These tests were carried out from June 28 to July 14, 1999. For this period of time the ambient temperatures, humidity and barometric pressure can be compared with Figs. 3.9a, 3.10a and 3.12.

Gas loss through the structural membrane during gaseous treatments is an important phenomenon. Membranes of concrete, plaster and plastic liners permit gas permeation and gas exchange. A variable pressure test, as used in the present work, is not capable of measuring the degree of such losses. The liner of which the cube is composed has a permeability rate of 87 ml O_2/m^2/day (Navarro *et al.*, 1994). The total surface area of the cube was calculated as 24.12 m^2 which would result in infiltration of 2.1 L of oxygen/day or increase of about 0.028% O_2/day. From these calculations it would appear that the main reason of the infiltration rates recorded during the experiments were not because of the permeation rate of oxygen through the plastic liner.

The suggested maximum infiltration rate for modified atmospheres is 0.5% O_2/day increase (Navarro *et al.*, 1993). This level of gastightness could be achieved only for pressure test values equivalent to 5 min half-life pressure decay. For the same level of gastightness gas loss was at a higher rate when exposed to solar irradiation. The lines shown in Fig.3.13 are almost parallel indicating the same effect of leakage caused by the predetermined orifices but at different intensity. The temperature and barometric pressure variation that influenced gas exchange dictated the intensity of the infiltration rate into the cube. The infiltration rate into the exposed cube was about 60% more than into the shaded cube.

Comparative studies with variable pressure tests are scarce. Navarro (1999) prepared provisional guidelines based on best estimates available in the literature. The suggested half-life pressure decay time was 5 min for successful modified atmosphere treatment of structures full with commodity of up to 500 m^3. Although data given by Navarro (1999) were calculated for larger volume structures than the cube used in the present tests, relative to the size of the cube the half-life pressure decay time should be longer than 5 min to achieve a successful modified atmosphere treatment. Therefore, the 5 min half-life pressure decay time shown in Fig. 3.13 is in agreement with the suggested provisional guidelines for modified atmosphere treatments given by Navarro (1999).

Loss rate of carbon dioxide from the cube

Loss rate of carbon dioxide is shown in Fig.3.14. Prior to the test, carbon dioxide concentration was increased to about 77%. The gas loss rate results, in both situations (exposed and shaded) were correlated to half-life pressure decay times as they were obtained in Fig. 3.8. Highly significant correlation was obtained for each situation and shows that the half-life pressure decay time is a reliable criterion to predict gas loss from carbon dioxide treated structures. These tests were carried out from July 15 to August 14, 1999. For this period of time the ambient temperatures, humidity and barometric pressure can be compared with Figs. 3.9a, 3.10a and 3.12.

The cube liner has a permeability rate of 414 ml CO_2/m^2/day (Navarro et al., 1994). Since the total surface area of the cube was calculated as 24.12 m^2, the estimated loss of carbon dioxide was about 10 L of CO_2/day or a decrease of about 0.133% CO_2/day. The gas losses experienced in the present tests ranged from 2 to about 7% CO_2/day. Similar to the tests on infiltration rate of oxygen described above, it would appear that the main reason for carbon dioxide losses were not because of the permeation rate of carbon dioxide through the plastic liner.

The lines shown in Fig.3.14, were almost parallel in some sections indicating the same effect of leakage caused by the predetermined orifices but at different intensity. For measurements carried out for the 2.5-min half-life pressure decay time, results in carbon dioxide loss rate were very similar for both situations (exposed and shaded). Examination of data on barometric pressure on the 6th week (Fig. 3.12) would reveal a low pressure rate of 1.5 Pa/h when the exposed cube was tested suggesting that the low gas exchange could be due to the low barometric pressure rate. The temperature and barometric pressure variation that influenced gas exchange dictated the intensity of gas loss rate from the cube. The carbon dioxide loss rate from the exposed cube was significantly higher than from the shaded cube.

For controlled atmosphere storage in Australia, with structures of 300 to 10,000 tonnes capacity, a decay time of 5 min. for an excess pressure drop of 2,500-1,500 Pa or 1,500-750 Pa or 500-250 Pa was regarded satisfactory (Banks *et al.,* 1980). According to Banks and Annis (1980) this range of pressures was chosen so that it is the highest usable without unduly stressing the fabric of the store. They commented also that above 10,000 tonnes capacity, pressure testing is difficult to carry out satisfactorily since it requires very stable atmospheric conditions. From analysis of the data presented by Banks *et al.,* (1980), it would appear that for storages with capacities in the range of 1,600-1,900 tonnes with an initial CO_2 concentration of about 60-85% for an average decay time of 11 min., the daily decay rate was about 4% CO_2. With a similar range of initial CO_2 concentration in a structure of 150 m3 capacity, daily gas loss was correlated to different levels of pressure decay times (Navarro *et al.,* 1998). Their comparison resulted in a pressure decay time of 3 min. for a daily decay rate of about 4% CO_2.

The influence of hermetic storage on controlling insects was examined using small scale (15, 30 and 52 m^3) capacity sealed plastic structures for outdoor storage of wheat, paddy and corn (Navarro *et al.,* 1995). Pressure decay rates were compared with daily CO_2

decay rates. With these structures successful insect controls were obtained with >1% CO_2 daily decay rate which was found to be equivalent to 5 min. half-life pressure decay time. Similarly comparative data were obtained using hermetic bunker storages of about 19,000 m^3 capacity, where successful results were obtained when the half life pressure decay was about 9 min. (Navarro *et al.*, 1984).

For modified atmosphere treatment using carbon dioxide a loss rate of up to 2%/day was found still within the acceptable limits (Navarro *et al.*, 1998). From the provisional guidelines based on best estimates available in the literature, Navarro (1999) suggested half-life pressure decay time of 5 min for successful modified atmosphere treatment of structures full with commodity of up to 500 m^3. The 5-min half-life pressure decay time shown in Fig. 3.14 is in agreement with the suggested provisional guidelines for modified atmosphere treatments given by Navarro (1999).

Phosphine loss rate from the cube

Loss rate of phosphine from the cube is shown in Fig.3.15. Prior to the test, phosphine concentration was increased to about 2000 ppm. The gas loss rate results, in both situations (exposed and shaded), were correlated to half-life pressure decay times as they were obtained in Fig. 3.8. Highly significant correlation was obtained for each situation to show that the half-life pressure decay time is a reliable criterion to predict gas loss from phosphine treated structures. These tests were carried out from August 26 to October 13, 1999. For this period of time the ambient temperatures, humidity and barometric pressure can be compared with Figs. 3.9b, 3.9c, 3.10b, 3.10c and 3.12.

Based on the dosage requirement for a successful fumigation for a 10 day exposure, a loss rate of up to 100 ppm phosphine was estimated to be within the acceptable limits for insect control. The lines shown in Fig. 3.15 are nearly parallel indicating the same effect of leakage caused by the predetermined orifices but at different intensity. The temperature and barometric pressure variation that influenced gas exchange dictated the intensity of gas loss rate from the cube. The gas loss rate from the exposed cube was significantly higher than from the shaded cube.

According to Banks and Annis (1984) daily ventilation rates tolerable in various insect control processes are estimated as 2.6% for hermetic storage, 5% for N_2 based CA, 7% for CO_2 based CA, and 10% for phosphine fumigation. Based on the proportions of ventilation rates, this would account for ventilation rates for phosphine fumigation being two fold that of N_2 based CA, and the latter being as much as twice that of hermetic storage.

Banks and Ripp (1984) tested sealed flat storages from 4,500 to 27,000 tonnes capacity and compared the fumigant effectiveness using phosphine with pressure decay time from 150 to 75 Pa. Their tests resulted in successful control of insects when half life pressure decay was 3 min. for the storage capacity of 15,600 and 16,500 tonnes, whereas full insect control could not be achieved when half life pressure decay was less than 1 min. for capacities of 4,800 tonnes. From the provisional guidelines based on best estimates

available in the literature, Navarro (1999) suggested half-life pressure decay time of 1.5 min for successful fumigation treatment of structures full with commodity of up to 500 m^3.

For shaded conditions a 3-min half-life pressure decay time shown in Fig. 3.15 is equivalent to a loss of 100 ppm phosphine/day and is significantly longer than the suggested provisional guidelines for fumigant treatments given by Navarro (1999). The 1.5 min half-life pressure decay time would result in a phosphine loss rate of about 135 ppm/day for a shaded structure. However, a better sealing equivalent to 4.5 min half-life pressure decay time would be required for the same structure when exposed to solar irradiation. Results shown in Fig. 3.15 were obtained in correlation to the different gastightness levels tested and reflect the most recent updated information available on phosphine loss. Therefore it is suggested that the recommendations made for successful phosphine treatments be based on a minimum loss rate of 100 ppm/day and the half-life pressure decay time for small structures adjusted to 3 min.

Methyl bromide loss rate from the cube

Loss rate of methyl bromide from the cube is shown in Fig.3.16. Prior to the test, methyl bromide concentration was increased to about 40 g/m^3. Results in both situations (exposed and shaded) were correlated to half-life pressure decay times (Fig. 3.8). Highly significant correlation was obtained for each situation to show that the half-life pressure decay time is a reliable criterion to predict gas loss from methyl bromide treated structures. Tests on the shaded structure were carried out during October 14-31 and test on exposed structures during November 1-17, 1999. For this period of time the ambient temperatures, humidity and barometric pressure can be compared with Figs. 3.9c, 3.9d, 3.10c, 3.10d and 3.12.

Although the lines shown in Fig. 3.16 are nearly parallel indicating the same effect of leakage caused by the predetermined orifices but their intensity were in reverse order of the results obtained in previous tests with nitrogen, carbon dioxide and phosphine. In Fig. 3.16, the gas loss rate from the shaded cube was significantly higher than from the exposed cube.

Examination of data on temperature during October 14-31 (Fig. 3.9d) would reveal a higher ambient temperature when the shaded cube was tested than during November 1-17 when the exposed cube was tested. This clearly shows that the expected high temperature variation could not be achieved for the exposed cube suggesting that the low gas exchange is due to the lower temperatures recorded during the same period. Again the temperature and barometric pressure variation that influenced gas exchange dictated the intensity of gas loss rate from the cube. But in this case methyl bromide loss rate from the shaded cube was significantly higher than from the exposed cube.

With sorptive fumigants like methyl bromide, a pressure decay test for the assessment of gas retention is not a precise concept since there are several forces that contribute to the gas loss through the leaks in the structure. Sorption by the treated material is a major cause for drop in gas concentration during the exposure time. Wheat flour treated using

methyl bromide in experimental jars resulted in sorption of 70% of the initial gas concentration after 24 h exposure at 25°C (Navarro, 1977). Since the rate of gas loss is independent of leakage from the enclosure, in well-sealed structures the overall gas loss rate will approach that expected from sorption only.

As a special case for hay fumigation applying methyl bromide, in containers of 12.2 m (40 ft) long, pressures from 200 to 100 Pa for a decay time of >10 sec was reported by Ball and van Graver (1997). Although the minimum 200 g h m^{-3} Ct product was attained using this standard decay time of >10 sec, gas loss was significant. For exposure times of 12-15 h, methyl bromide concentration dropped from 58 g m^{-3} to the range of 12-18 g m^{-3} and after 22-27 h exposure to the range of 10-18.5 g m^{-3}, pressure halving times ranged from 11 to 85 sec. In their tests the calculated methyl bromide loss from the treated container was 43 g/m^3/day (Ball and van Graver, 1997). Based on the dosage requirement for a successful fumigation for a 24 h exposure, a loss rate of up to 1.0 g/m^3/day was proposed in the present study (Fig. 3.16). However, analysis of data given by Ball and van Graver (1997) reveal the high tolerance methyl bromide has to leakage under commercial applications. The proposed 1.0 g/m^3/day limit would be from an environmental safety aspect a more acceptable limit than higher loss rates that would be tolerated from the insect control aspect.

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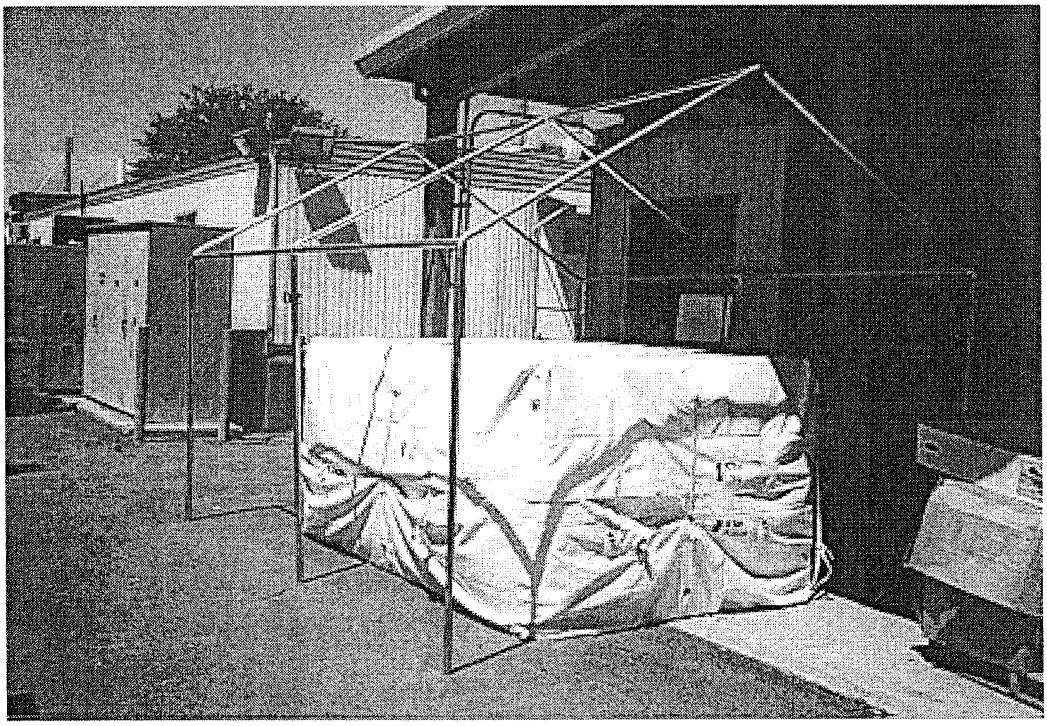

Fig. 3.1 – Exposed cube for testing the relationship between degree of gastightness and rate of gas loss.

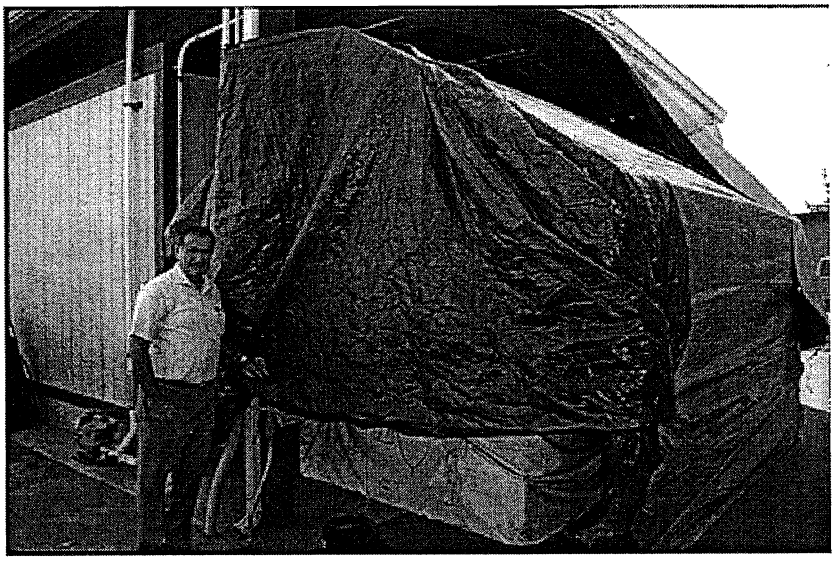

Fig. 3.2 – Shaded cube to demonstrate the influence of reducing temperature variation on gas retention.

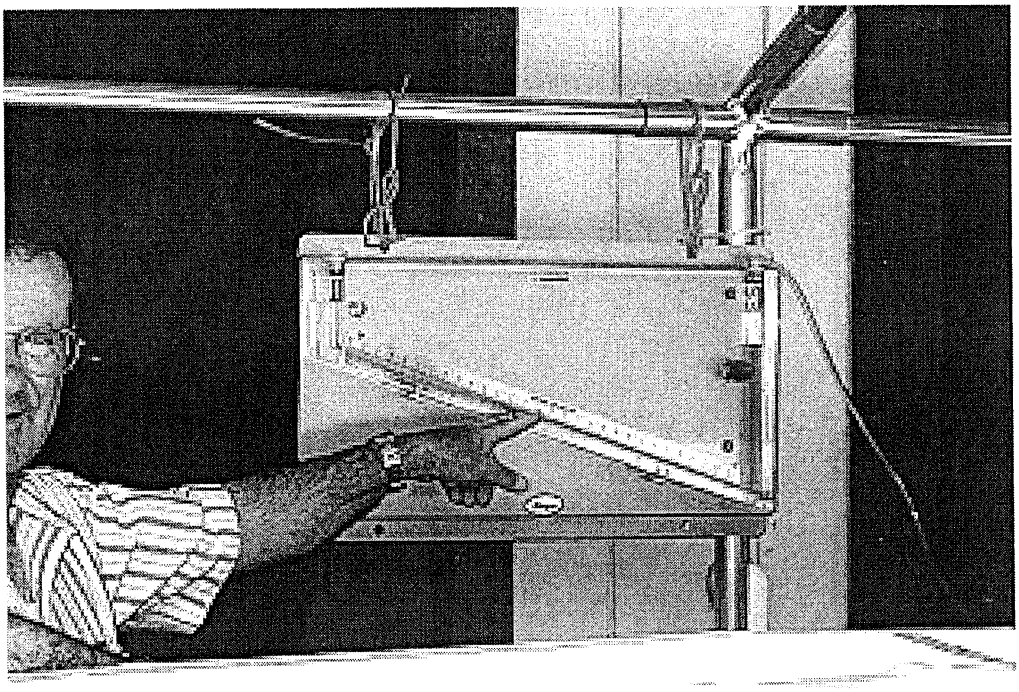

Fig. 3.3 – Inclined manometer used for testing the degree of gastightness of the cube using variable pressure test.

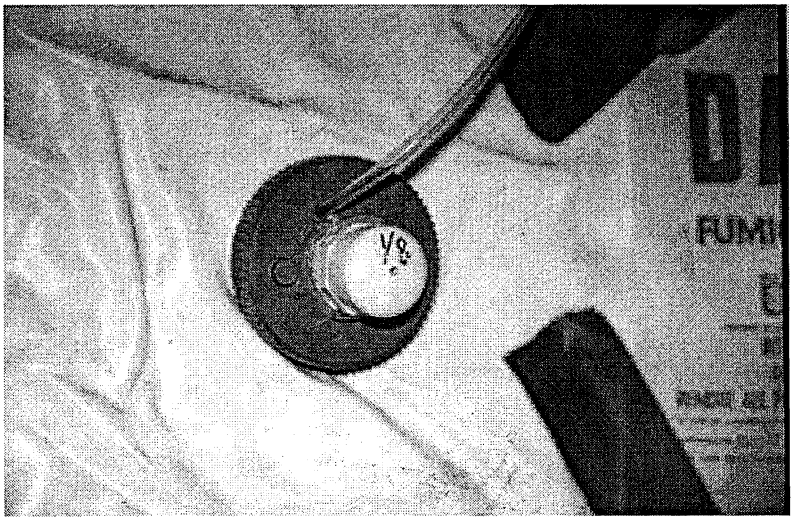

Fig. 3.4 – Orifices mounted on the cube to serve predetermined leaks.

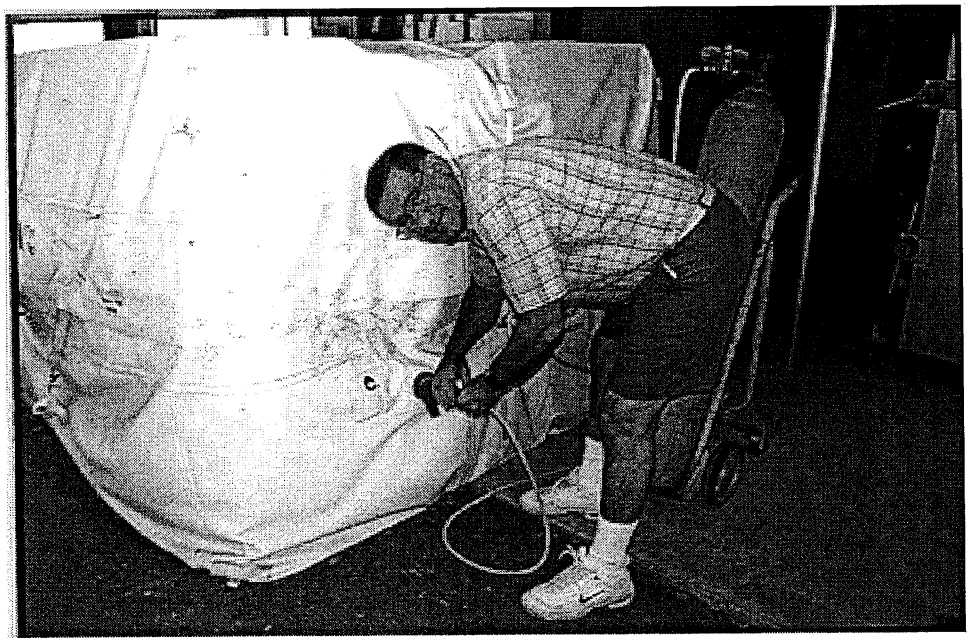

Fig. 3.5 – Purging the cube with carbon dioxide supplied from a pressurized cylinder.

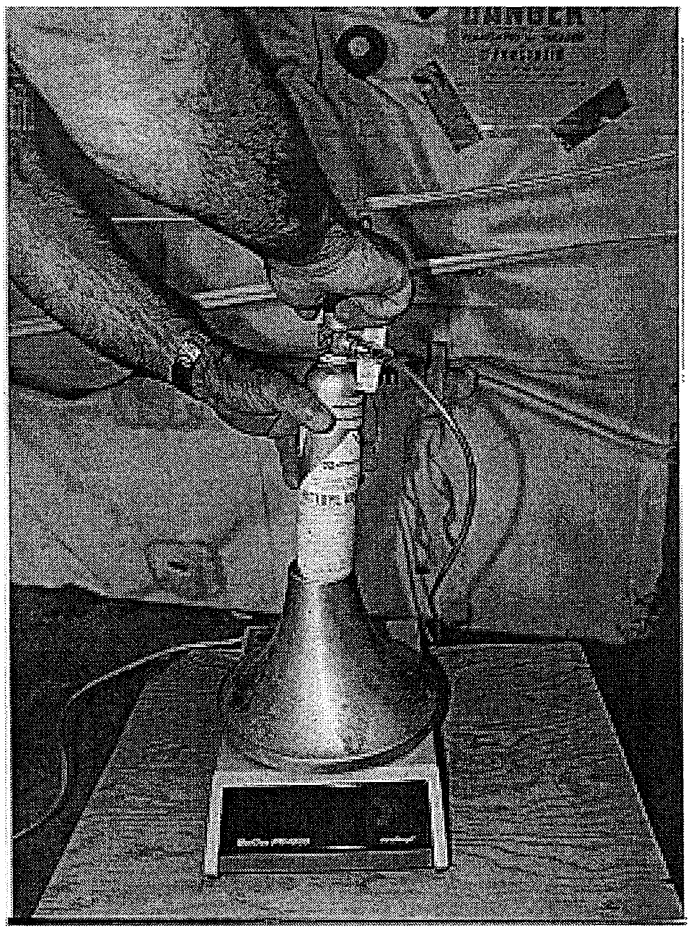

Fig. 3.6 – Weighing methyl bromide cylinder for generating gas concentration in the cube.

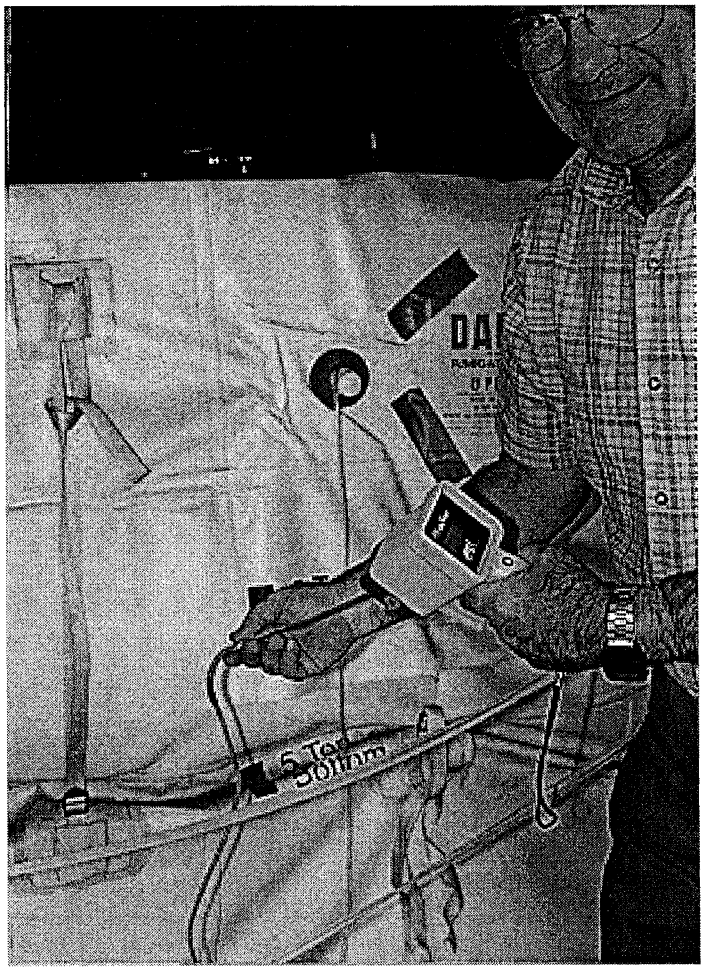

Fig. 3.7 – Monitoring phosphine concentrations using the PortaSens detector equipped with electrochemical sensor.

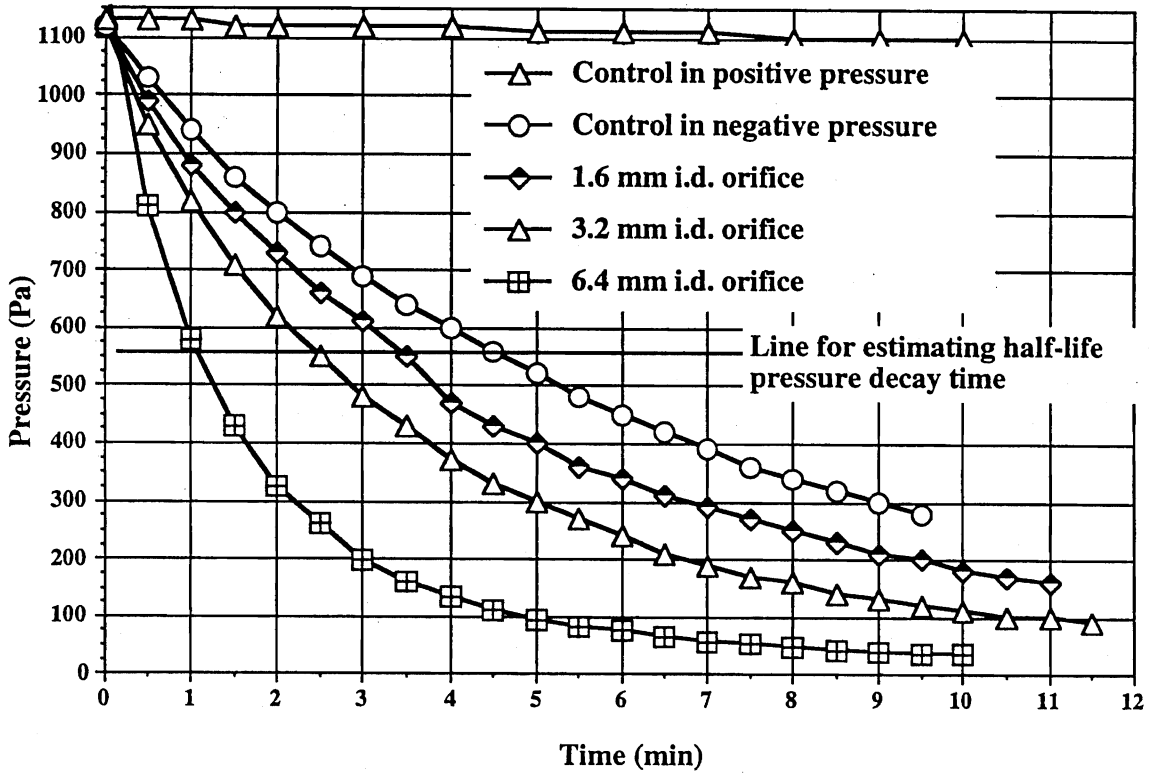

Fig. 3.8 – Pressure decay determined for orifices of different sizes mounted on the cube. The cube was tested under negative pressure except for one control in positive pressure.

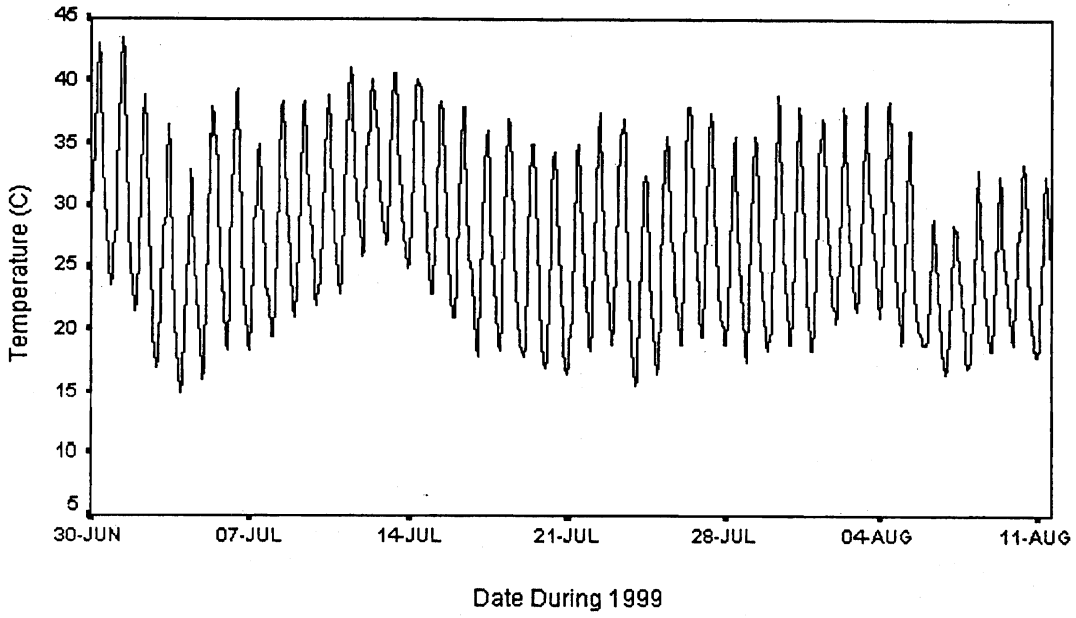

Fig. 3.9a – Daily changes in the ambient temperature as recorded during the experiments on gas loss rate between June 30 and August 11, 1999.

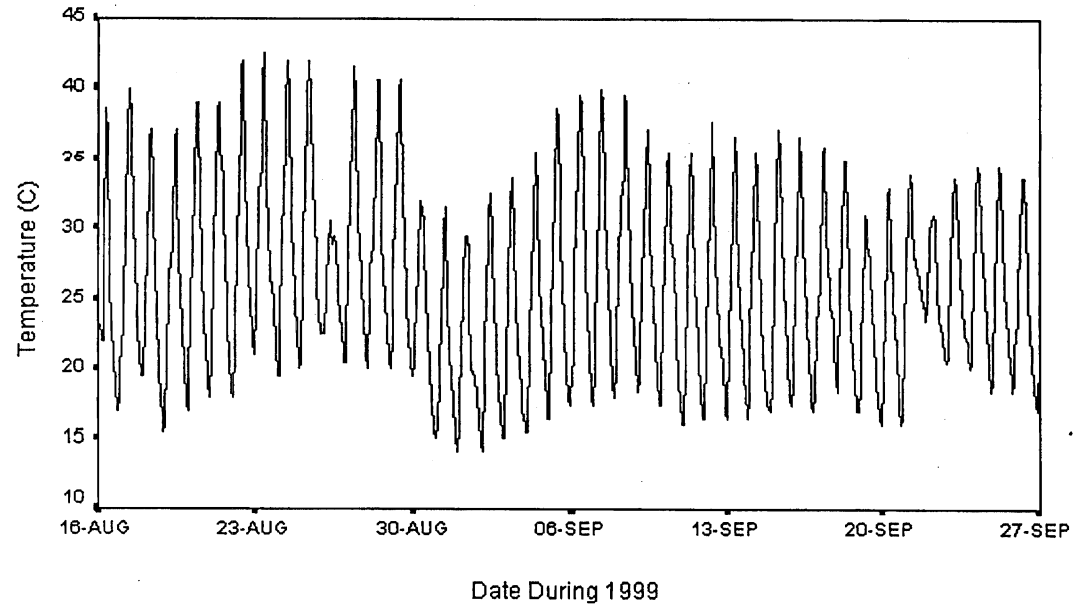

Fig. 3.9b – Daily changes in the ambient temperature as recorded during the experiments on gas loss rate between August 16 and September 27, 1999.

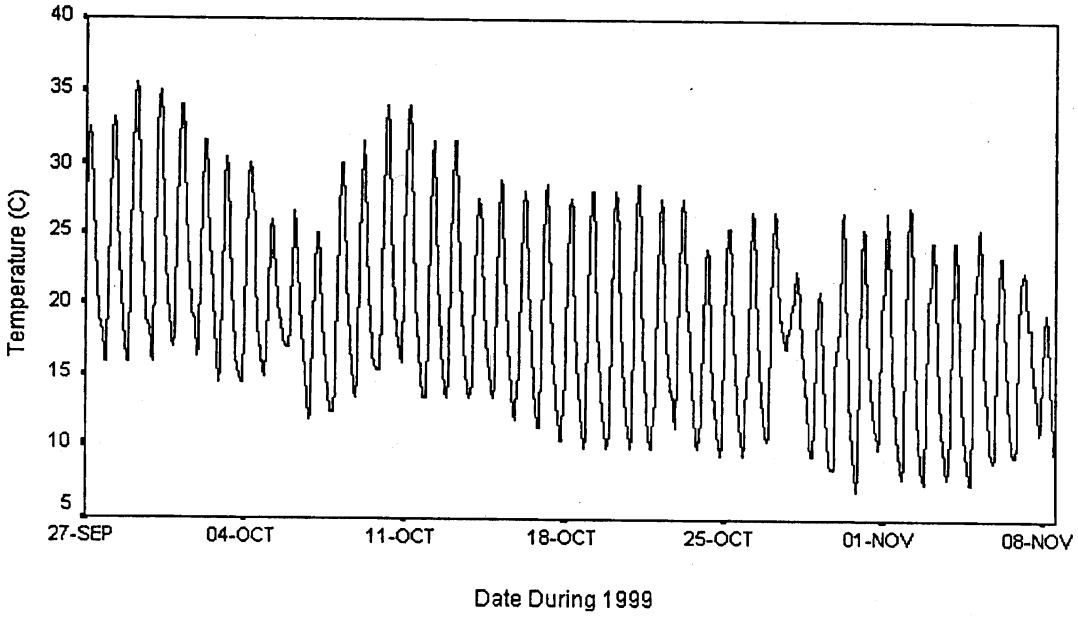

Fig. 3.9c – Daily changes in the ambient temperature as recorded during the experiments on gas loss rate between September 27 and November 8, 1999.

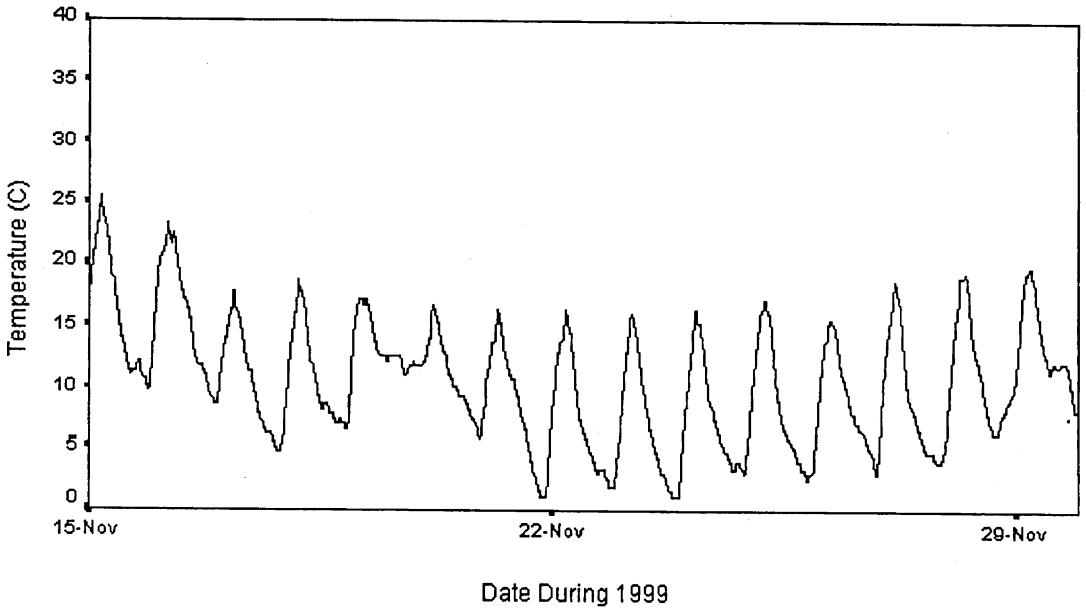

Fig. 3.9d – Daily changes in the ambient temperature as recorded during the experiments on gas loss rate between November 15 and November 29, 1999.

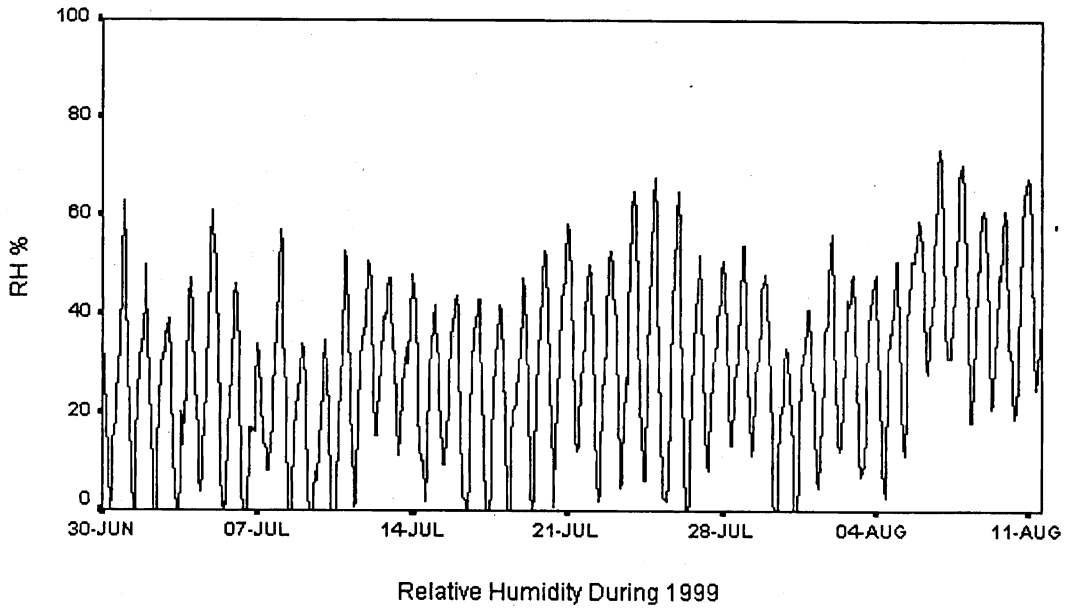

Fig. 3.10a – Daily changes in the ambient relative humidity as recorded during the experiments on gas loss rate between June 30 and August 11, 1999.

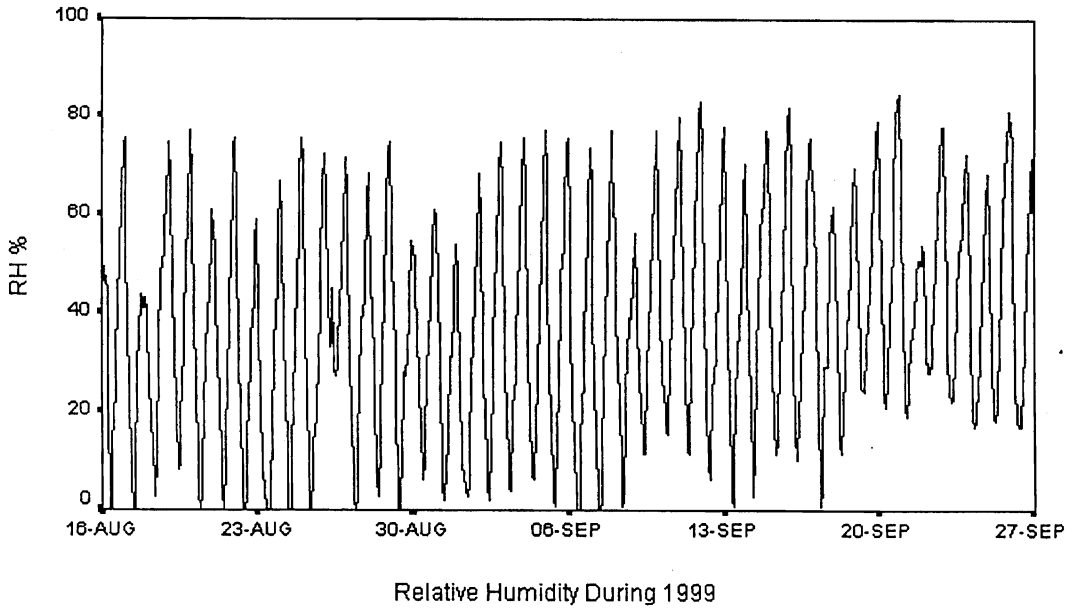

Fig. 3.10b – Daily changes in the ambient relative humidity as recorded during the experiments on gas loss rate between August 16 and September 27, 1999.

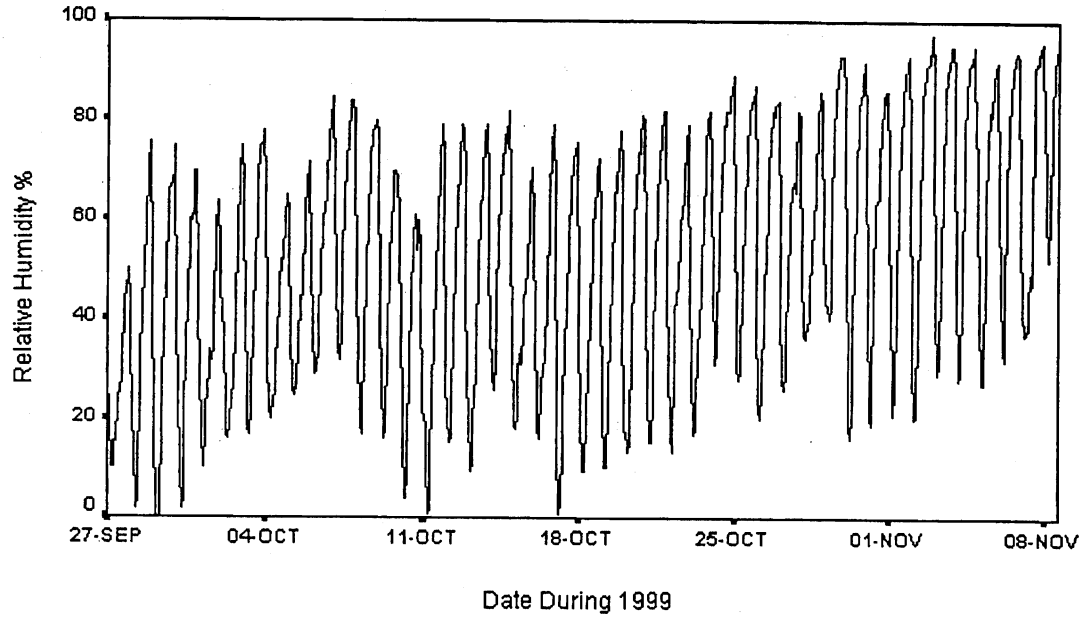

Fig. 3.10c – Daily changes in the ambient relative humidity as recorded during the experiments on gas loss rate between September 27 and November 8, 1999.

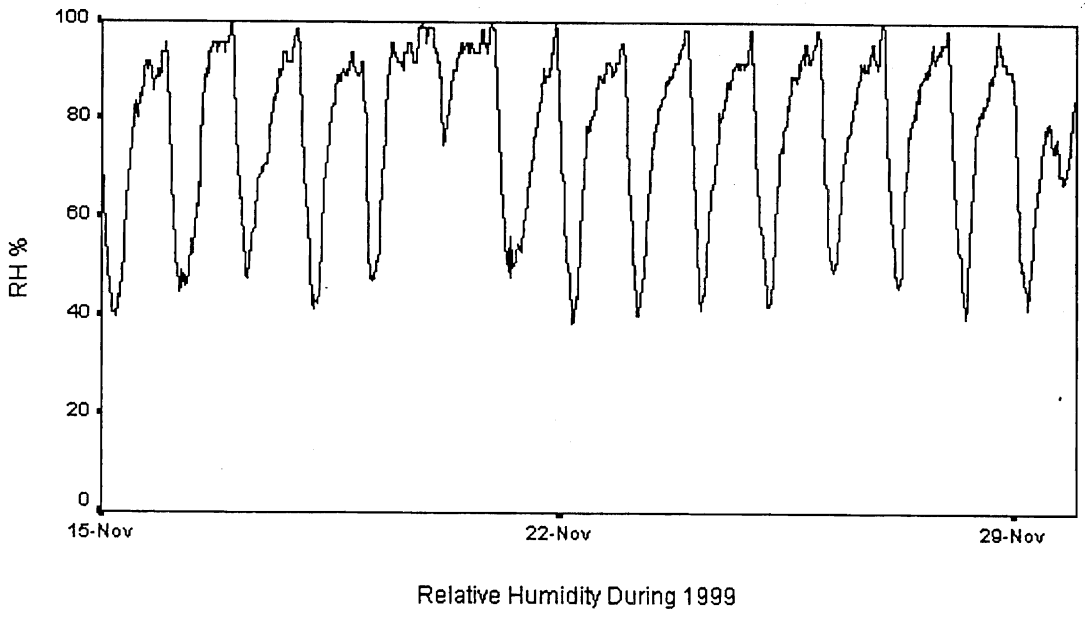

Fig. 3.10d – Daily changes in the ambient relative humidity as recorded during the experiments on gas loss rate between November 15 and November 29, 1999.

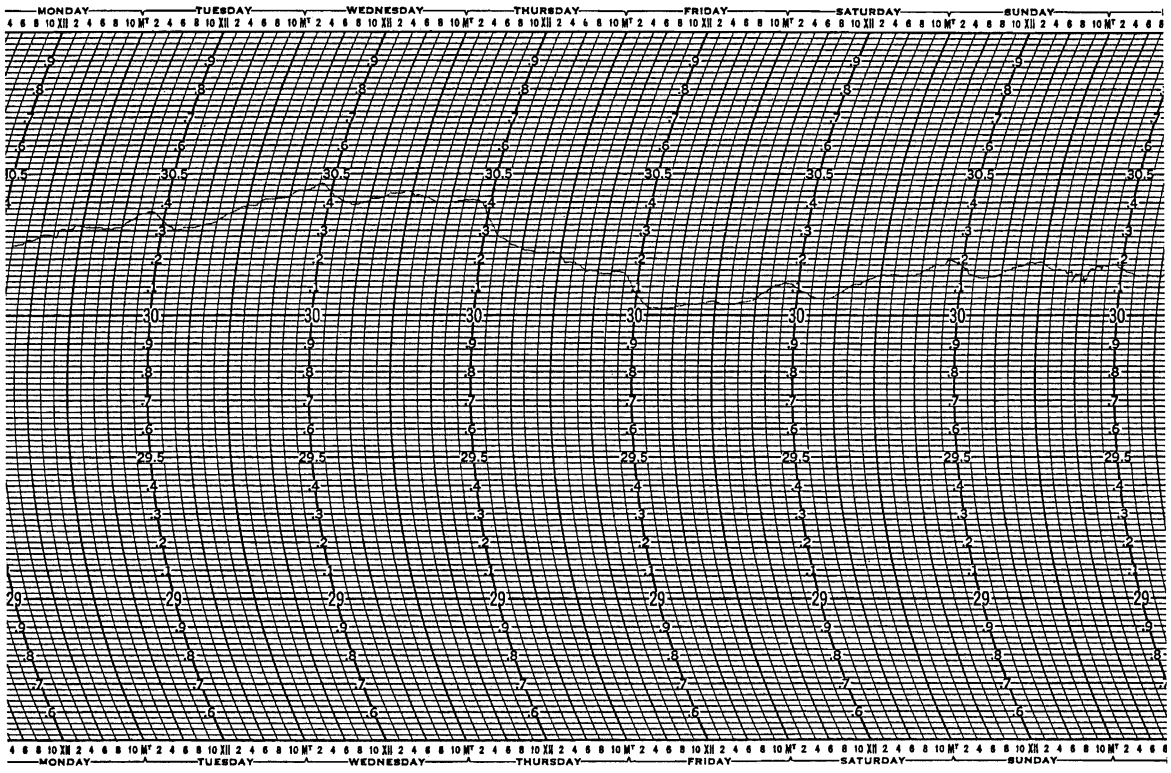

Fig. 3.11 – Section of barograph showing the daily variations in barometric pressure as recorded during the experiments on gas loss rate.

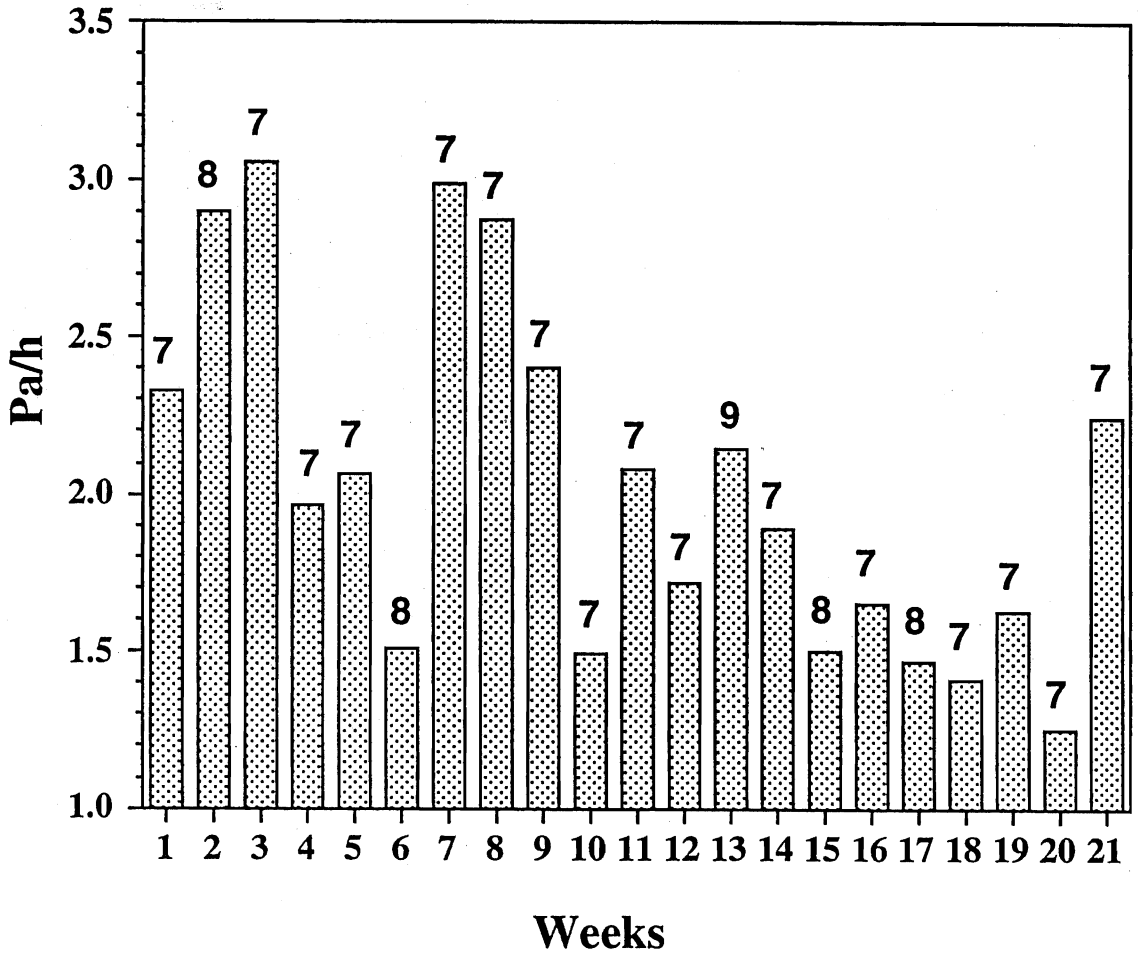

Fig. 3.12 – Histogram showing the average weekly barometer rises expressed in Pa/h and the number of weekly changes on top of each histogram. Start of recording was on June 30, 1999 and the last reading was on November 29, 1999 (data missing on the week starting October 4).

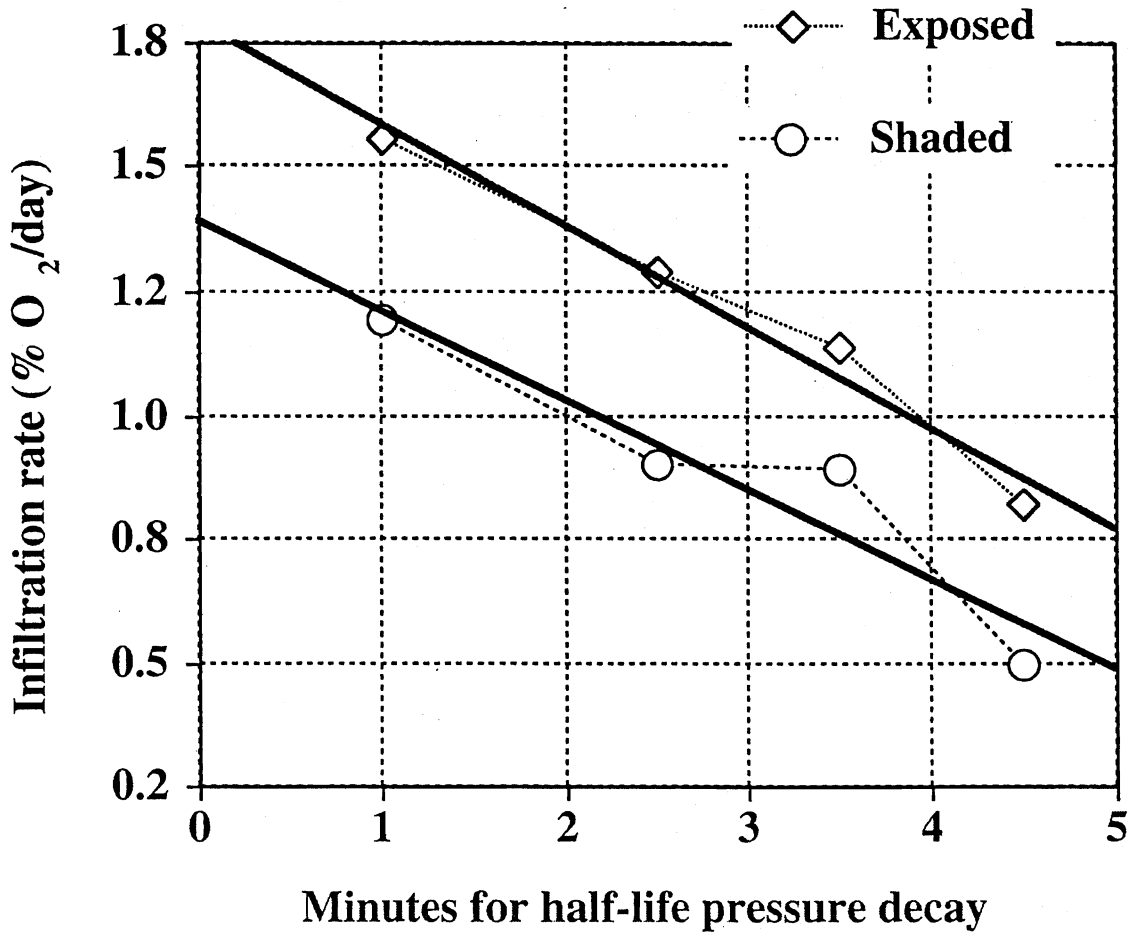

Fig. 3.13 – Infiltration rate of oxygen into a nitrogen treated empty structure of 7.5 m^3 capacity in relation to half-life pressure decay time. The suggested maximum infiltration rate for modified atmospheres is 0.5% O_2/day increase.

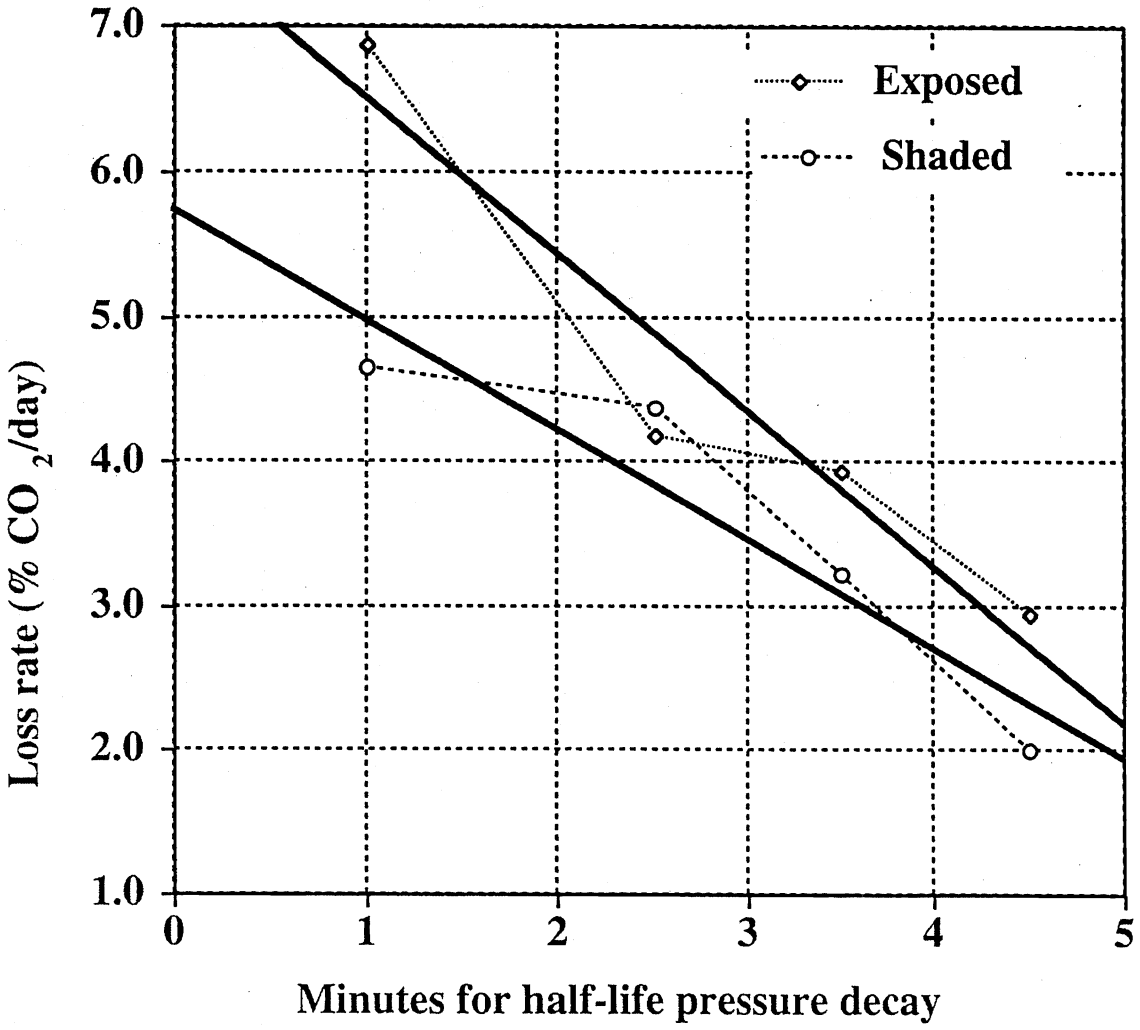

Fig. 3.14 – Loss rate of carbon dioxide from a treated empty structure of 7.5 m^3 capacity in relation to half-life pressure decay time. The suggested maximum loss rate for carbon dioxide is 2%/day.

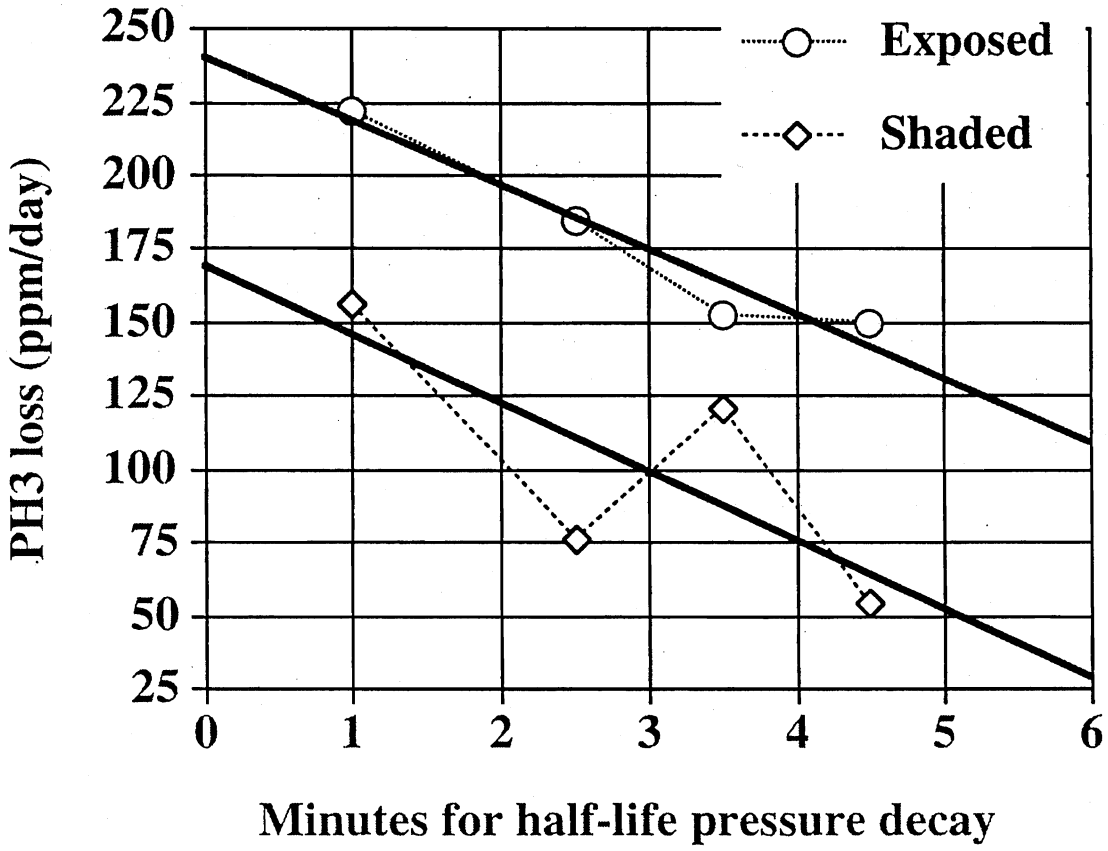

Fig. 3.15 – Phosphine loss from an empty structure of 7.5 m^3 capacity in relation to half-life pressure decay time. Phosphine loss should not exceed 100ppm/day.

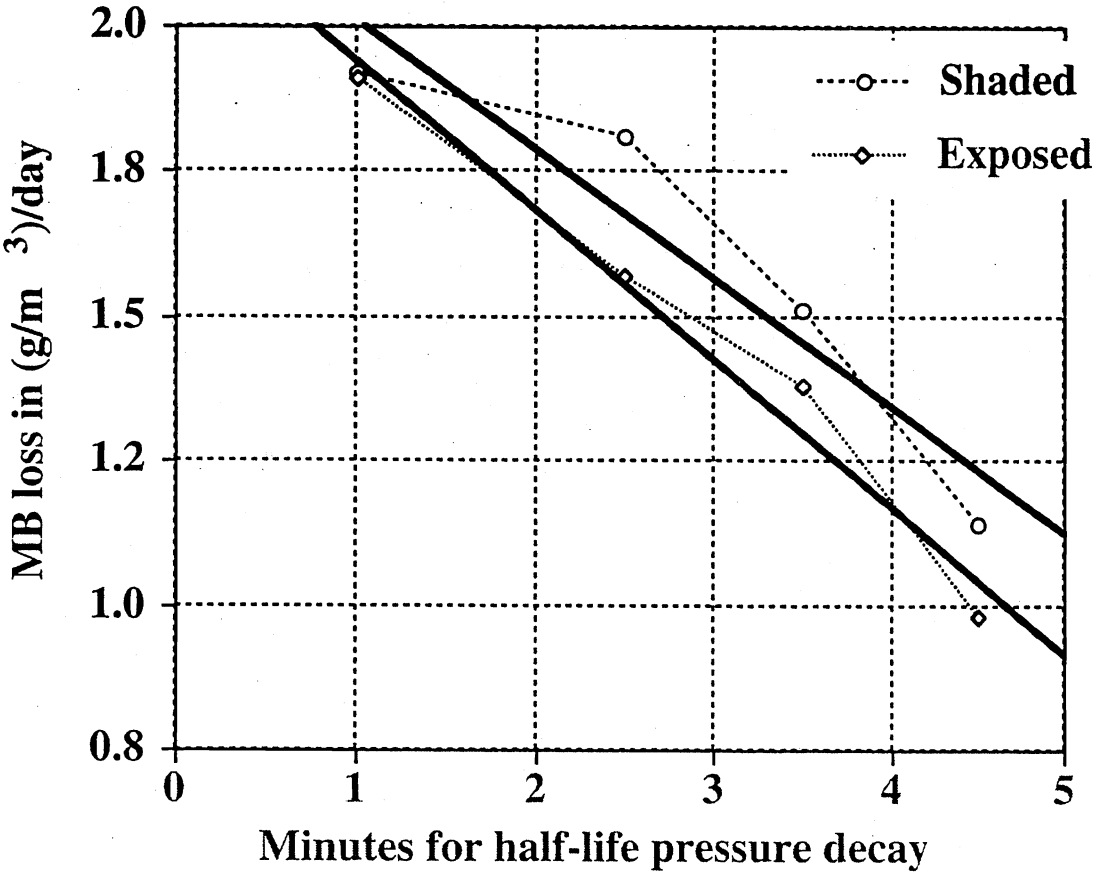

Fig. 3.16 – Methyl bromide (MB) loss from an empty structure of 7.5 m^3 capacity in relation to half-life pressure decay time. From an environmental safety aspect a limit of MB loss of 1.0 g/m^3/day was considered acceptable. Shaded structure was tested in October. Exposed structure was tested in November, when ambient temperatures were lower then in October.

APPENDIX I - USE OF VACUUM FOR QUALITY PRESERVATION AND INSECT CONTROL – DEMONSTRATION TRIALS

I – VACUUM AND CARBON DIOXIDE TREATMENTS OF COCOA

INTRODUCTION

The major producers of cocoa are, in descending order, Cote d'Ivoire (1 millions tons); Indonesia (450,000 tons); Ghana (335,000); Nigeria (155,000); Cameroon (120,000); Malaysia (120,000) and Costa Rica (44,000 tons). The U.S. imports cocoa from all these countries.

There are two strategies for controlling insect infestations in imported cocoa. If organically grown cocoa is infested, it is transported in refrigerated containers from the port of entry to New Jersey where it is fumigated with carbon dioxide for 24 hours at 115°F. Non-organic cocoa is treated with methyl bromide. After either process, cocoa is then stored for up to three months, at which time inspections are made. If insect infestation is found, the carbon dioxide fumigation is repeated. A desirable goal would be to replace these strategies with a simple treatment, taking less than two weeks, such as the application of vacuum.

Although carbon dioxide is more toxic than a hypoxic environment obtained through vacuum, it is sufficiently toxic to control stored product insects. In addition, the vacuum technology seems more practical to use in the field because it requires no carbon dioxide cylinders or monitoring equipment. A trial was designed to test the effectiveness of vacuum technology in controlling insect pests of stored cocoa. This test was done on September 27, 1999, in Foxboro, MA, in cooperation of GrainPro, the Organic Commodity Project, and the Mesoamerican Development Institute under a cooperative research agreement funded by the US-Israel Science and Technology Fund (USISTF) in which Shlomo Navarro is a cooperating investigator. Mortality data in this report were supplied by Dr. Tom Phillips, cooperating researcher in the USISTF, Oklahoma State University, OK.

When a commodity is pressurized to 25mmHg absolute pressure (vacuum), most remaining gas in the atmosphere is associated with the partial pressure of water due to the moisture content of the commodity and very little of that atmosphere contains residual oxygen. Larvae and pupae of storage pests are more resistant to hypoxia than are adult insects and their eggs.

The objective of this demonstration trial was to compare conventional carbon dioxide fumigation to vacuum in separate cubes filled with cocoa, similar to that described in the gas retention trials, to demonstrate the feasibility of using vacuum.

Materials and Methods

Cocoa bags stacked on pallets were loaded into two cubes of 15-m^3 volume and sealed. One cube was treated using carbon dioxide at ambient pressure and the other was evacuated using an industrial pump (Fig. I.1). Caged insects of all life stages of *Ephestia cautella, Plodia interpunctella* and *Tribolium castaneum* were placed at three different levels, at four corners and in the center of the stacks. These insects particularly *Ephestia cautella*, are known to be pests of stored cocoa. Mortality counts were based on the percentage of survivors in the treated vials relative to the untreated controls. End points for scoring treatment effects were survival of individuals to the next life stage. Egg survival was determined by the surviving larvae two weeks later, and for pupae adult emergence were calculated for mortality. Mortality counts were made after 3, 10 and 17 days. The cocoa treatments in vacuum, in carbon dioxide, and in a control stack all were stored in a warehouse at 23°C.

Results and Disussion

None of the *E. cautella* eggs survived the experiment (treatment or control), so we could not evaluate effects of the treatments, though we got some results from treated pupae.

In the case of *T. castaneum*, flour infested with 10 adult beetles one week prior to the experiment was used. These adults oviposited up to the point of the treatment, and presumably some of those eggs hatched in to larvae prior to the test. Thus eggs and larvae were treated together, and the endpoint scored was total adults after 6 weeks less the original 10 at start. An entry of "NA" means the data are not available, either due to the vials being lost or destroyed, or if there was no survival in controls. All mean mortality values are based on 2 or 3 bioassay vials (replicates). Mortality data in Tables 1 to 3 show that the effectiveness of vacuum is comparable to carbon dioxide treatment. For both treatments at the 17 days exposure, complete mortality for *E. cautella* and *P. interpunctella* was observed. The results for *T. castaneum* for the same exposure period were inconclusive.

Table 1. Effects of vacuum and CO_2 on Almond moth pupae, *Cadra cautella*, treated in bag stacks of cocoa.

	Mortality Percent relative to Controls	
Days	Vacuum	CO2
3	100	100
10	NA	NA
17	100	100

Table 2. Effects of vacuum and CO2 on eggs and pupae of Indianmeal moth, *Plodia interpunctella*, treated in bag stacks of cocoa.

		Mortality Percent relative to Controls	
Life stage	Days	Vacuum	CO2
Eggs			
	3	100	99.3
	10	100	98.0
	17	100	100
Pupae			
	3	100	88.7
	10	NA	NA
	17	100	100

Table 3. Effects of vacuum and CO2 on mixed eggs and larvae of the red flour beetle, *Tribolium castaneum*, treated in bag stacks of cocoa.

	Mortality Percent relative to Controls	
Days	Vacuum	CO2
3	75.5	88
10	99.0	99.7
17	NA	NA

APPENDIX II - USE OF VACUUM FOR QUALITY PRESERVATION AND INSECT CONTROL – DEMONSTRATION TRIALS

II – VACUUM TREATMENTS OF LEMONS AND NECTARINES

INTRODUCTION

The vacuum treatment in the demonstration trial in Foxboro reported in Appendix I indicated the feasibility of applying vacuum in a plastic structure where the enclosure takes the shape of contained commodity such as the cube shown in Fig. 3.1 and Fig. I.1.

The influence of low oxygen atmospheres on *Plodia interpunctella* and *Amyelois transitella* was demonstrated by Sodestrom et al., (1986) and on the codling moth, *Cydia pomonella* by Sodestrom et al., (1990; 1996). *P. interpunctella* is a cosmopolitan storage pest of many commodities and *A. transitella* is a common field and storage pest of almonds, pistachios and walnuts. *C. pomonella* is a quarantine pest of walnuts. It is common in North America but does not occur in Japan.

Responses of codling moth to oxygen deficient atmospheres have shown that diapausing larvae required an exposure time about 4 times that of nondiapausing larvae at 25°C (Sodestrom et al., 1990). However, for some agricultural commodities like walnuts, pre-shipment treatments may be scheduled to applications that are based on extended exposure times.

The possibility of applying vacuum treatment in the cube for controlling quarantine pests for fresh commodities like lemons and nectarines was also considered. Although long term storage of citrus is not recommended, extensive research has been undertaken in an attempt to establish the optimum temperature and atmospheric concentrations required to extend their storage life.

Ke and Kader (1990) showed that Valencia oranges can be treated with 0.5%, 0.25% or 0.02% oxygen at 5° or 10°C for up to 20 days without detrimental effects on their appearance or nutritional value. For lemons and nectarines also it would be necessary to determine which of the treatments might be officially approved. With the objective preliminary quality tests using lemons and nectarines responses to vacuum were tested.

Materials and Methods

Lemons and nectarines were from the 1999 harvest supplied by the Postharvest Quality and Plant Genetics and Commodity Protection Laboratories, respectively at the HCRL. A desiccator of 2.6 L capacity connected to a vacuum pump was used to create low pressure atmospheres of ~27-30". All tests were carried out at room temperature (~25°C) (Fig. II.1).

After 48 h treatment lemons were kept at 5°C for 14 days and then at room temperature for one day. Quality tests were carried out by examining the lemons externally and then internally, by cutting the fruits through the center.

Nectarine quality tests were carried out after vacuum treatment for 48 h at 25°C and storage for 6 days at normal atmosphere at 5°C. Nectarine quality was evaluated by cutting the fruits into two equal parts and examining the color change to the inner sections. Also a sheer press test was used to determine the firmness of the fruit to compare it after treatment with the control.

Results and Discussion

Lemons exposed to vacuum conditions for 48 h at ~ 25°C did not reveal any apparent difference from the control. However, on a personal communication with Luis Aung (Post-harvest Quality and Plant Genetics, ARS, HCRL, Fresno), the complex situation of lemon response to modified atmospheres was clarified. Therefore, it is suggested that these promising preliminary results be considered very carefully and further detailed tests be carried out for durability of lemons to modified atmosphere treatments.

Two tests of nectarines exposed to vacuum were carried out. The firmness test resulted in 3.5 kg/cm^2 for nectarines exposed to vacuum and 1.4 kg/cm^2 for the control. In the second test the pressure in the exposure chamber increased to 25-27" Hg and the vacuum treatment did not differ from the control. In addition the firmness level for both was 1.8 kg/cm^2. Visual inspection inside the nectarines revealed a slight darkening band around the stone covering an area of about 20% of the meat. From these preliminary observations it was deducted that nectarines are highly sensitive fruits to vacuum and that a more in depth work would be necessary to reveal the value of vacuum at different temperatures.

For fruits that are able to tolerate vacuum conditions, it is suggested that further tests are carried out under controlled conditions for each specific quarantine insect pest. However, more promising is the potential of vacuum treatment for dried fruits and nuts, because these commodities are better preserved under low oxygen conditions. Vacuum treatment in cubes, for commodities where exposure time does not pose a significant limitation, appears to be a promising alternative to methyl bromide.

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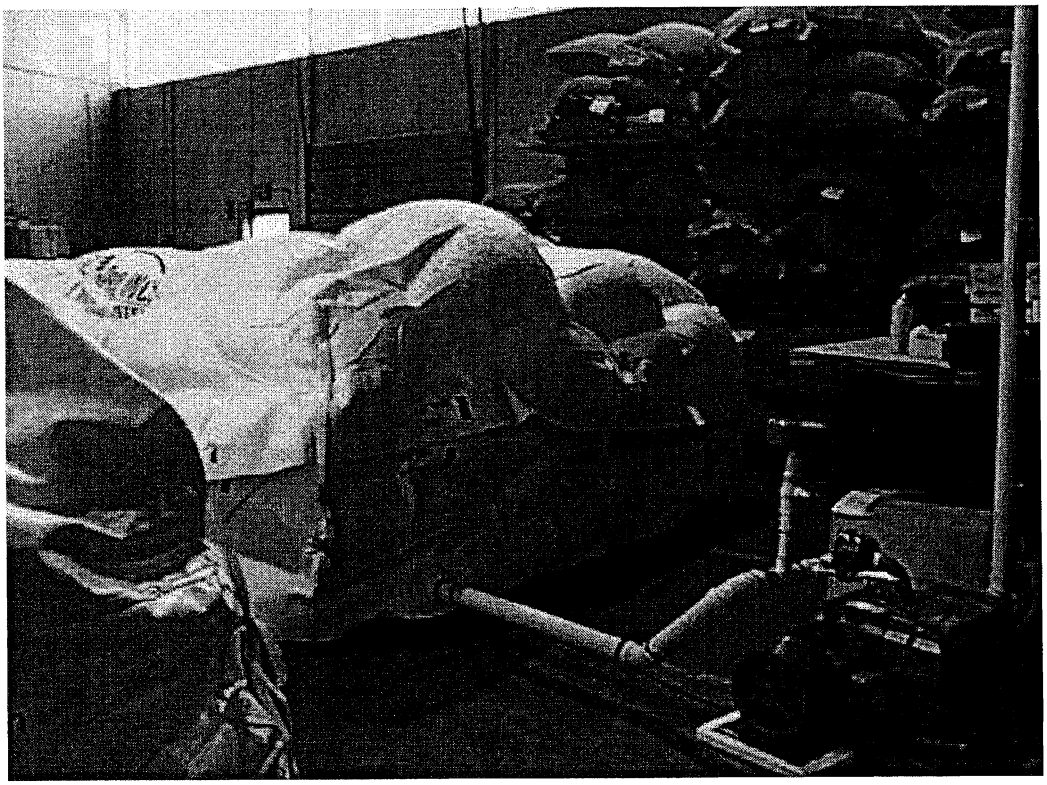

Fig. I.1 - Cocoa bags stacked on pallets loaded into two cubes of 15-m^3 volume. The cube on the left was treated using carbon dioxide and that at the center was evacuated using an industrial pump.

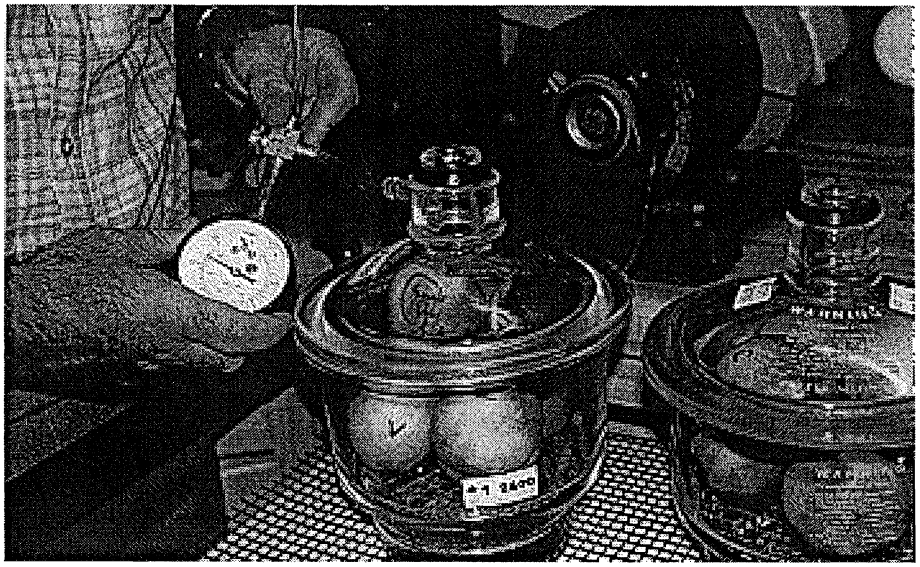

Fig. II.1 - Lemons and nectarines contained in desiccators of 2.6 L capacity connected to a vacuum pump to create low pressure atmospheres.

APPENDIX III - Testing three models of phosphine detectors

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INTRODUCTION

Work plan in the framework of Sabbatical included demonstration of phosphine gas containment in sealed structures. For this purpose a series of fumigation are planned to be carried out using controlled leak sizes to demonstrate the relationship between the ventilation rate and level of gas containment. This series of studies was termed **"Phosphine Retention (RR)"**. It was necessary to purchase a detector that will cover the range of phosphine concentrations used in commercial fumigation. Three models were received at the HCRL for evaluating their suitability of this particular and future work planned at the same laboratory. Therefore it was decided to test the repeatability, accuracy and working conditions of these instruments.

Materials:

A master cylinder containing factory calibrated 5180 ppm of PH3 in N2 atmosphere was used for preparing the different concentrations. This cylinder was equipped with a corrosion resistant stainless steel regulator to reduce gas pressure.

Two floating type rotameters both tested and calibrated for air at 70F and NTP conditions, one model Matheson # 610 with a maximum flow capacity of 100 ml/min, and the other Air Products Brooks # 09-1021 for a maximum flow 1000 ml/min were used for the preparation of the mixtures. The # 09-1021 model rotameter was equipped with two types of floating balls and used simultaneously, one made of glass was used for the lower range and capable of measuring up to 400 ml/min, and the other was of stainless steel to measure up to 1000 ml/min.

The make-up of the mixture to give the desired concentration was obtained from a N2 pressurized cylinder. A pressure resistant 1/4 " external diameter PVC tube was used to connect the pressure lines from the N2 and the PH3 cylinders to the rotameters. In addition a variety of tubes made of Tygon, Latex and PVC was used to make the connection between the rotameters and the supply line to the detectors to be tested.

1.2 The detectors

1.2.1.The ATI PortaSens Gas Detector - USA

The ATI PortaSens Gas Detector is equipped with an easy pistol grip, a reachargeable NiCad battery, an audible alarm, and a bendable (flexible) metal support probe that facilitates gas sampling. This is an electrolytic type detector. The instrument was designed to display read-out of up to 2000 ppm in intervals of 10 ppm. The internal pump has a suction capacity of 1 SCFH (472 ml/min). It has a removable flow meter to estimate the minimum flow required for taking gas samples. The same instrument may be eqipped with sensors capable of measuring three ranges; the ultra low range capable of measuring the range 0-1000 **ppb** in intervals of 0.1 ppb; the low range measuring 0-10.0 ppm in intervals of 0.1 ppm; and the high range capable of measuring 0-2000 ppm.

1.2.2 - **Drager Miniwarn** Germany:

The tested instrument was Model GD-29-54 Miniwarn – serial number ARMN-1573. This instrument is equipped with two sensors, one capable measuring at the low ranges of 0-10.0 ppm in interavls of 0.01 ppm, the 0-0.2 ppm and the high concentrations measuring in the range of 0-500 in intervals of 1 ppm. It has an audible alarm, a rechargeable battery and computer interface capabilities.

This is a versatile detector capable of measuring different gases including PH3 when equipped with the appropriate electrolytic sensor. It was designed to measure up to 500 ppm in the upper range and 0 to 0.2 ppm at the lower range. The gas samples need to be conveyed to the instrument using an external pump not supplied with the instrument.

1.2.3. - **Bedfont** – England:

This detector has a measuring range of up to 2,000 ppm of PH3. It has a syringe of 60-ml volume connected to one way valve and a T-tube to facilitate gas sampling. It is equipped with two calibration ranges for the zero and the span.

Methods:

Preparation of the gas mixtures was made using the two rotameters in parallel. The PH3 mixture in N2 was further diluted in N2 to obtain target test mixtures of 50, 250, 350, 450, 500, 750, 1000, 1250 and 1500 ppm in N2. The gas mixtures were conveyed through the gas lines shown in Fig. 1.

Fig. 1 – Experimental design of the PH3 and N2 gas lines for obtaining various PH3 concentrations for testing the detectors.

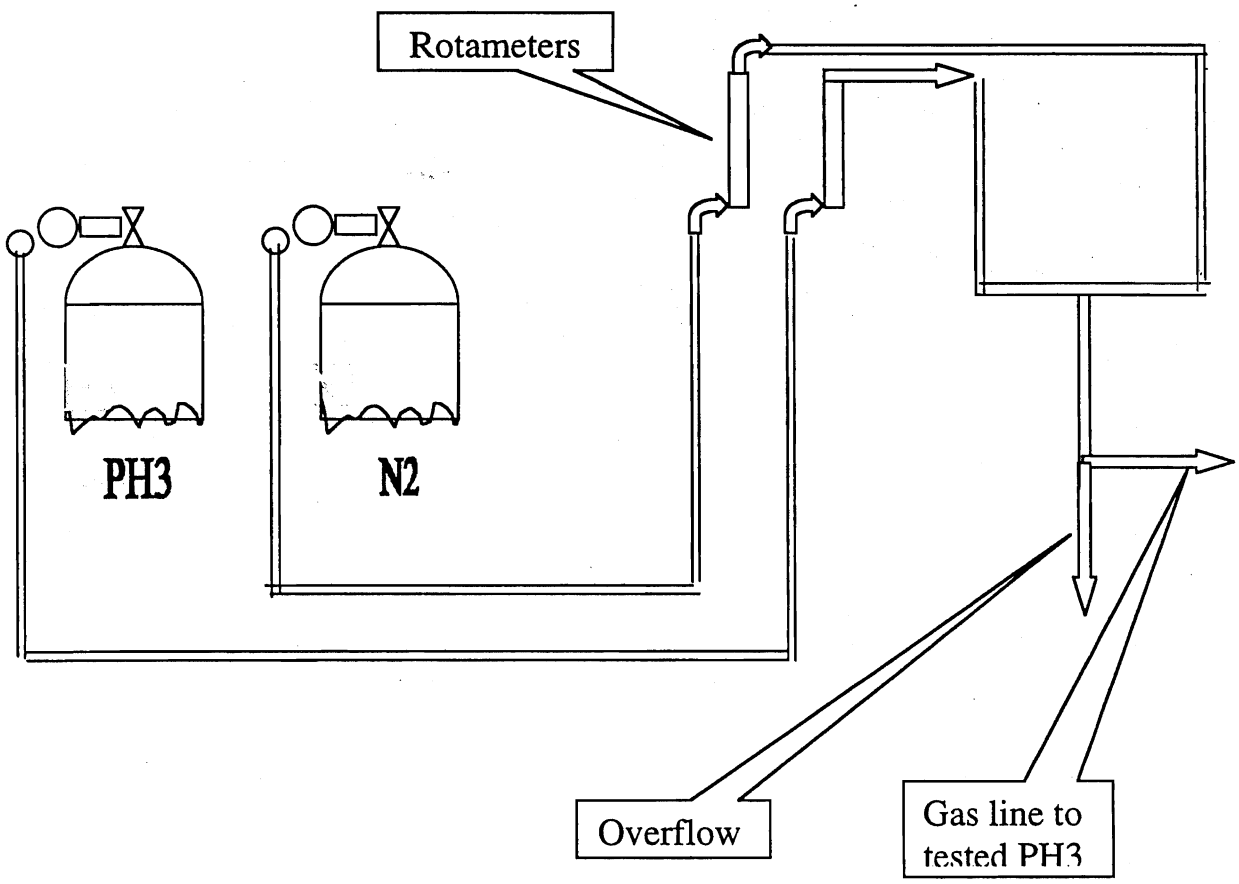
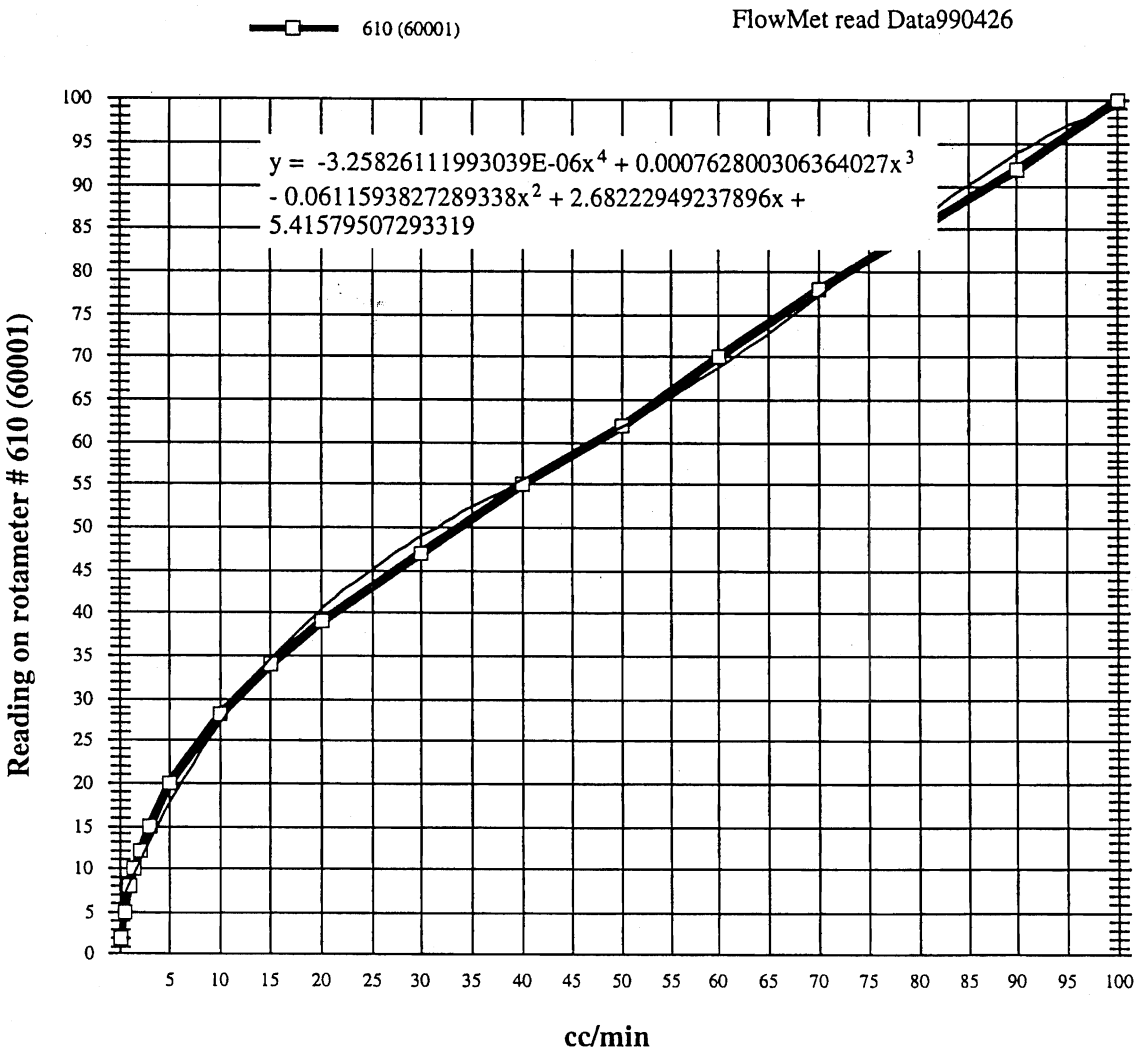


Fig. 2 – Calibration curve and calculated equation to fit the curve for rotameter Matheson # 601, capable of measuring gas flow up to 100 ml/min. This rotameter was used for measuring flow of PH3.



Calibration of rotameters was made by Dave Brandl using air at a temperature of 21°C and 760 mm Hg. Two separate charts were prepared for the rotameters and equations to represent the best fit of these curves are shown in Figures 2 and 3.

The equations obtained from these Figures were used in Table 1 to calculate the set point of the desired gas mixtures.

Fig. 3 – Calibration curves and calculated equations to fit the curve for rotameter Air Products # 09-1021 capable of measuring gas flow up to 1,000 ml/min. This rotameter was used for measuring flow of N2.

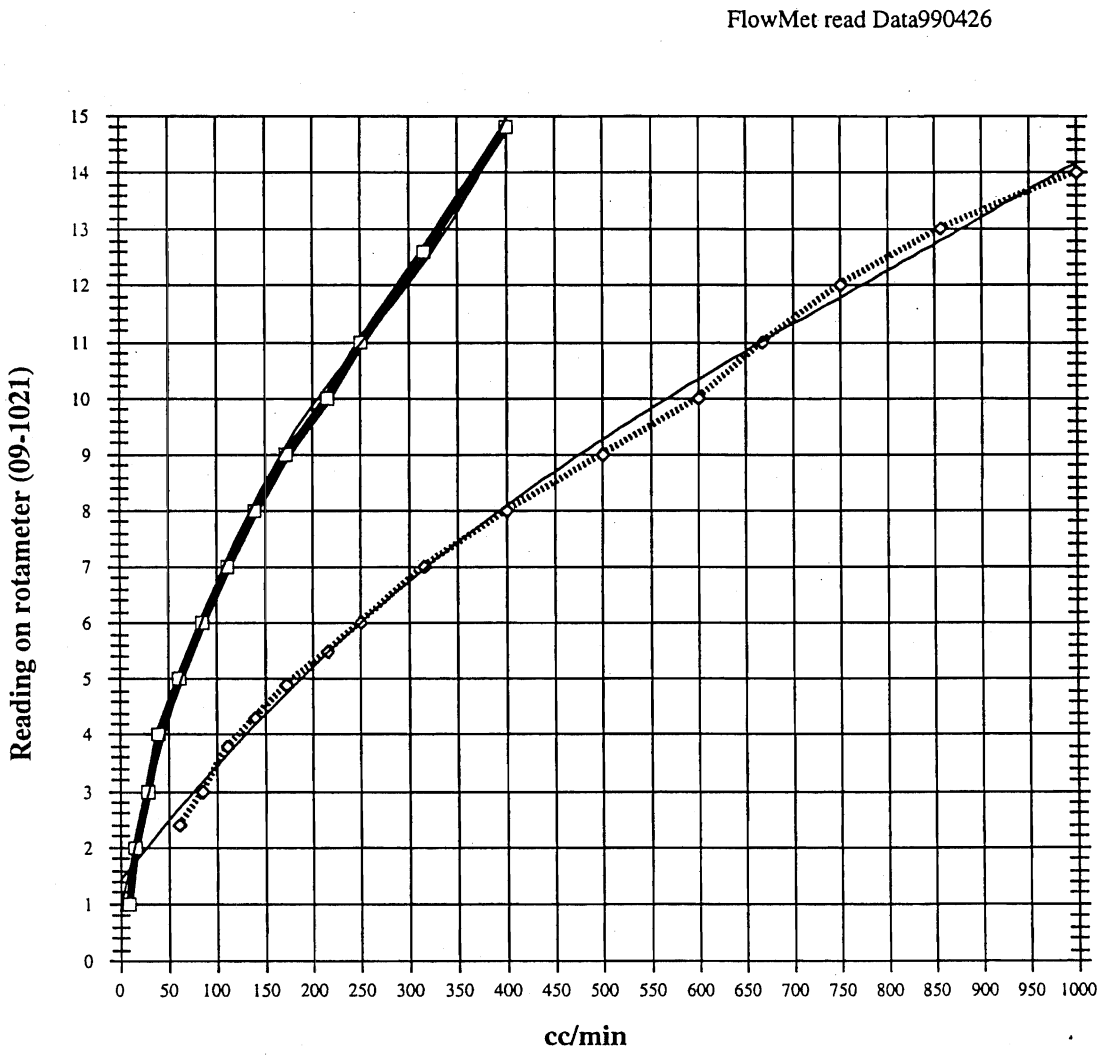


Table 1- Calculated rotameter readings to obtain the desired PH3 concentration in ppm. Table was prepared in an Excel spread sheet to calculate the rotameter readings using the equations representing the curve fits shown in Figures 2 and 3.

Desired PH3 ppm	Total flow ml/min	Initial PH3 ppm in N2	PH3 mix flow ml/min	N2 flow ml/min	PH3 Rot 610 reading	N2 Rot 09-steel	N2 Rot 09-glass
50	100	50	100	0	98.8	1.4	0.8
100	400	5180	8	392	22.8	8.0	14.6
250	400	5180	19	381	39.4	7.8	14.2
300	400	5180	23	377	43.3	7.8	14.1
450	400	5180	35	365	52.0	7.6	13.7
500	400	5180	39	361	54.5	7.6	13.6
750	400	5180	58	342	67.1	7.3	13.0
1000	400	5180	77	323	83.2	7.0	12.5
1250	400	5180	97	303	97.5	6.8	12.1
500	300	5180	87	213	91.3	5.4	10.1
750	250	5180	84	166	89.4	4.6	8.9

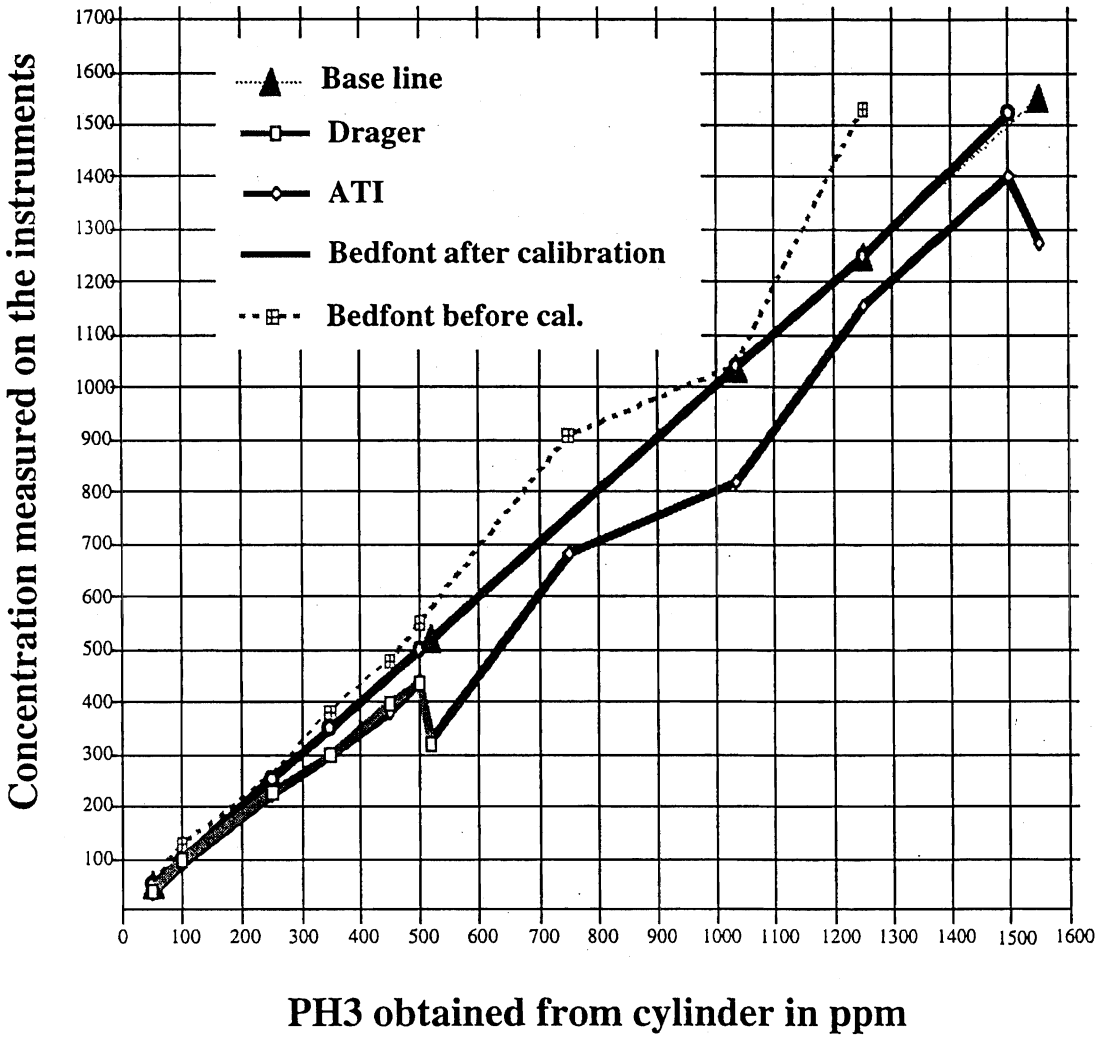
RESULTS:

Test results were plotted in Fig. 4 showing the measured and calculated PH3 concentrations in N2 atmosphere.

The Drager Miniwarn gave close values at the lower levels of PH3, but as the concentration reached to 500 ppm (maximum measuring capacity), greater deviation from the base line was obtained. It was also difficult to separate the audible alarm deriving from the presence of PH3 in the atmosphere from the battery low signal alarm. The recovery time lasted about 15 min between two readings. Since there was no internal pump, the stream line supplying the PH3 mixture at a rate of 300 to 500 ml/min was used during the tests. The instrument has a strong hysteresis. However, it responds quickly when measuring concentrations higher thn 50 ppm.

The ATI PortaSens Gas Detector measuring 0-2000 ppm in intervals of 10 ppm was tested. Fig. 4 shows that lower readings were obtained compared to the base line. Differences as much as 200 ppm were obtained when tested at concentrations above 500 ppm. The instrument responded very quickly and

Fig. 4 - Comparison of test results obtained with three different instruments. Bedfont was tested before and after calibration.



hysteresis was not apparent. A major disadvantage was that the instrument can be only factory calibrated. Very handy and field-friendly instrument.

Bedfont is equipped with calibration capabilities. Two tests were carried out; before and after calibration. Before calibration the instrument gave close results to the base line at the range of up to 50 ppm. At concentrations higher then 50 ppm there were fluctuations that

showed up to 250 ppm deviation from the base line. However, after calibration, it was possible to obtain the closest readings compared to the other two instruments. The sampling using the syringe was not an easy operation. Therefore, since the instrument is not equipped with an internal pump, the stream line supplying the PH3 mixture at a rate of 300 to 500 ml/min was used during the tests.

Conclusions:

- ATI was the only instrument that had an effective internal pump.
- Bedfont was the only instrument that had the calibration capability.
- Drager was capable of measuring up to 500 ppm maximum.
- ATI and Bedfont have the capability of measuring up to 2,000 ppm.
- Closest readings to the base line was obtained using Bedfont after its calibration.
- Drager has a recovery time that extended up to 15 min even when the instrument was esposed to fresh air.
- Bedfont and Drager (at the high range) have the capability to read in intervals of 1 ppm whereas ATI in intervals of 10 ppm.
- In view of the fact that in commercial fumigations the use of concentrations higher than 500 ppm is a common feature, and envisaging that in-situ measuring the PH3 concentrations is the objective for the HCRL, the two instruments ATI and Bedfont were found more appropriate to meet this requirement and therefeore they were recommended for purchase.

Acknowledgements:

Shlomo Navarro wishes to thank Jane Tabbets, David Brandl, Richard Gill, Jim Leesch and Larry Zettler in providing the necessary equipment, facilities and guidance in testing the instruments.