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**Title/Titre :** Dissolved Oxygen and Oxygen Ingress

**Total Package Oxygen Ingress: Interpretation  
of changes in the level of DO and TPO**

**Speaker/  
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# Background

- The methods discussed have evolved from 26 years of development work on gaskets, coatings, barriers and scavengers for beer, juice, food and wine packaging.
- As they are presented, they have been in use for 16 years
- Many other methods and instruments have been evaluated, each with their pros and cons but this has proven to be the most versatile, reliable and accurate for the industries we are involved with.



# Beverage Shelf Life Assumptions & Terms

- The amount of oxygen that accumulates in the package and beverage (Total Oxygen Pickup) is directly related to the oxidation of the beverage.
- It is not possible to measure the oxygen pickup in wine, beer, or juice as they consume the oxygen as it enters the package.
- Total oxygen pickup (TOP) is the sum of the oxygen that gets into the package during filling, from headspace, during closing and from ingress.
- Total Package Oxygen (TPO) is all the oxygen in the package available to react with the beverage, ((mg dissolved + mg headspace)/liters of beverage).



# BIB Total Oxygen Pick-up

- Mixed into wine during filling
- Additional oxygen in the headspace or cone
- Oxygen absorbed from the bag, gland, tap and air pockets within components
- Ingress through each component of the package
- Ingress through component failure
  - Gland to tap fit
  - Tap seal
  - Weld failure
  - Stress cracking



# Oxygen Ingress Method Comparison

## Dry Testing

- Mocon Ox-Tran, Illinois Instruments, etc.
- Moisture controlled by humidity
- Test time in days
- OTR gives value under set or “standard” conditions
- Measures sections of the package
- Difficult to extrapolate into shelf-life predictions
- Quality control test

## Filled Package Testing

- Orbisphere, Steinfurth, OXY QC, Pre-sens, Oxy-sense, etc.
- Moisture and ethanol controlled by liquid in package
- Test time in weeks to years
- TPO ingress is under commercial conditions
- Measures the entire package
- TPO ingress under low oxygen stable conditions can be extrapolated to predict shelf-life
- Development and specification test



# Filled Package Barrier Testing

## Why?

- Polymers absorb liquids, odors and gases
- These absorbed materials usually act as plasticizers for the polymer
- Plasticizers change the physical and barrier properties of polymers
- Oxygen scavengers are often activated or accelerated by moisture from the package contents
- The temperature history and pressure from the contents may have an effect on the sealing and barrier properties
- Testing the package under the commercial-like conditions will give barrier values most like what they will be in commerce



# Benefits of Filled Package Barrier Testing

- Measures the oxygen concentration in the liquid, thus can be added to the oxygen measurements during filling to give TOP
- Can be directly compared to any other package type or size.
- Can be used to identify the activation and end of oxygen scavenger activity
- Can be used to determine package integrity by combining abuse testing with oxygen

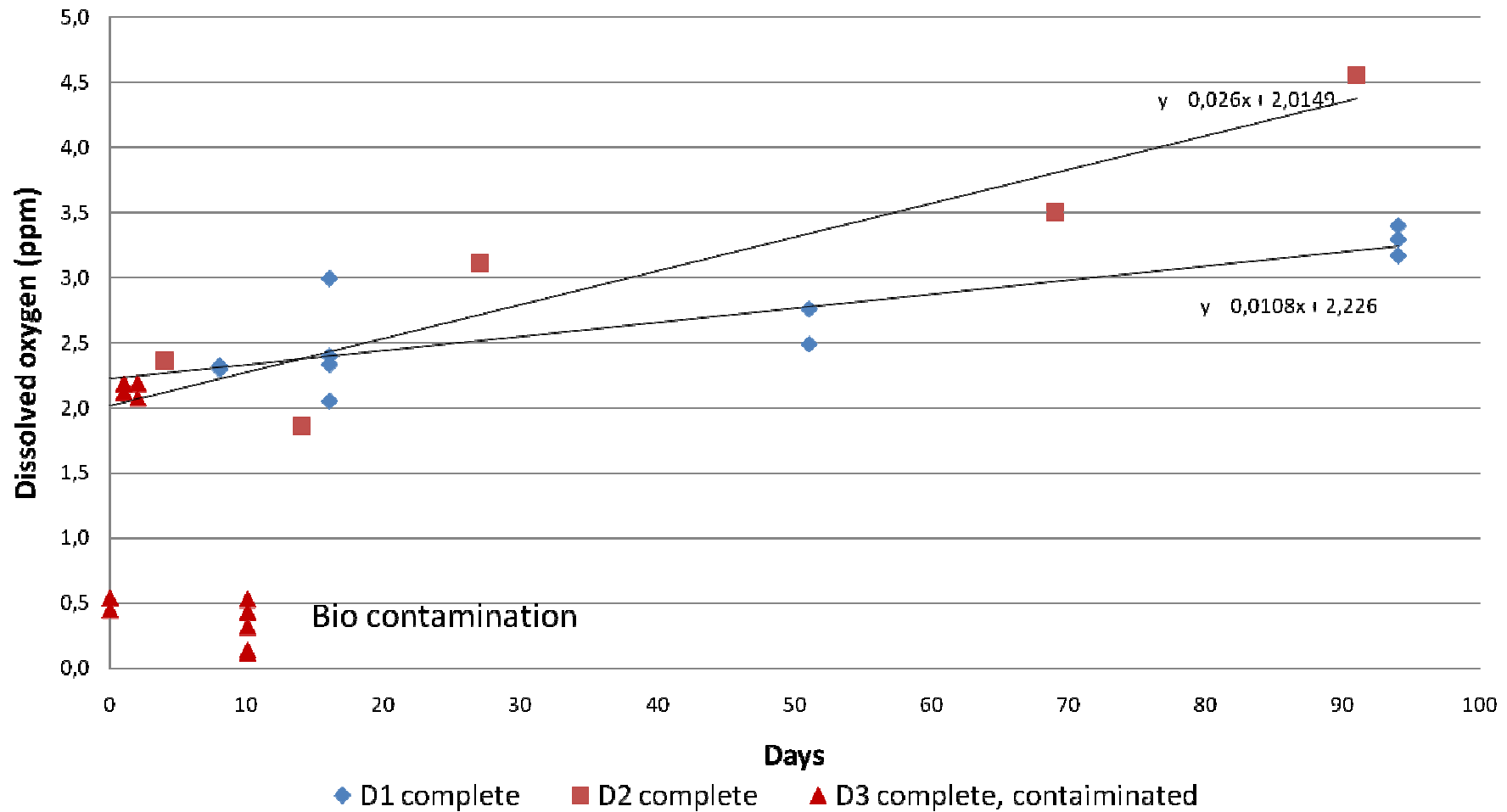
# BIB Filled Package Testing Requirements

- Inert liquid – water, ethanol, non-oxidizable acid
- Liquid must be toxic to bio growth
- Low and consistent initial oxygen levels, at least  $<0.50$  ppm (mg/l), ideally  $<0.05$  ppm
- Instrument/measurement method must work with all bag types (clear, translucent, foil, etc.) without modifying the package



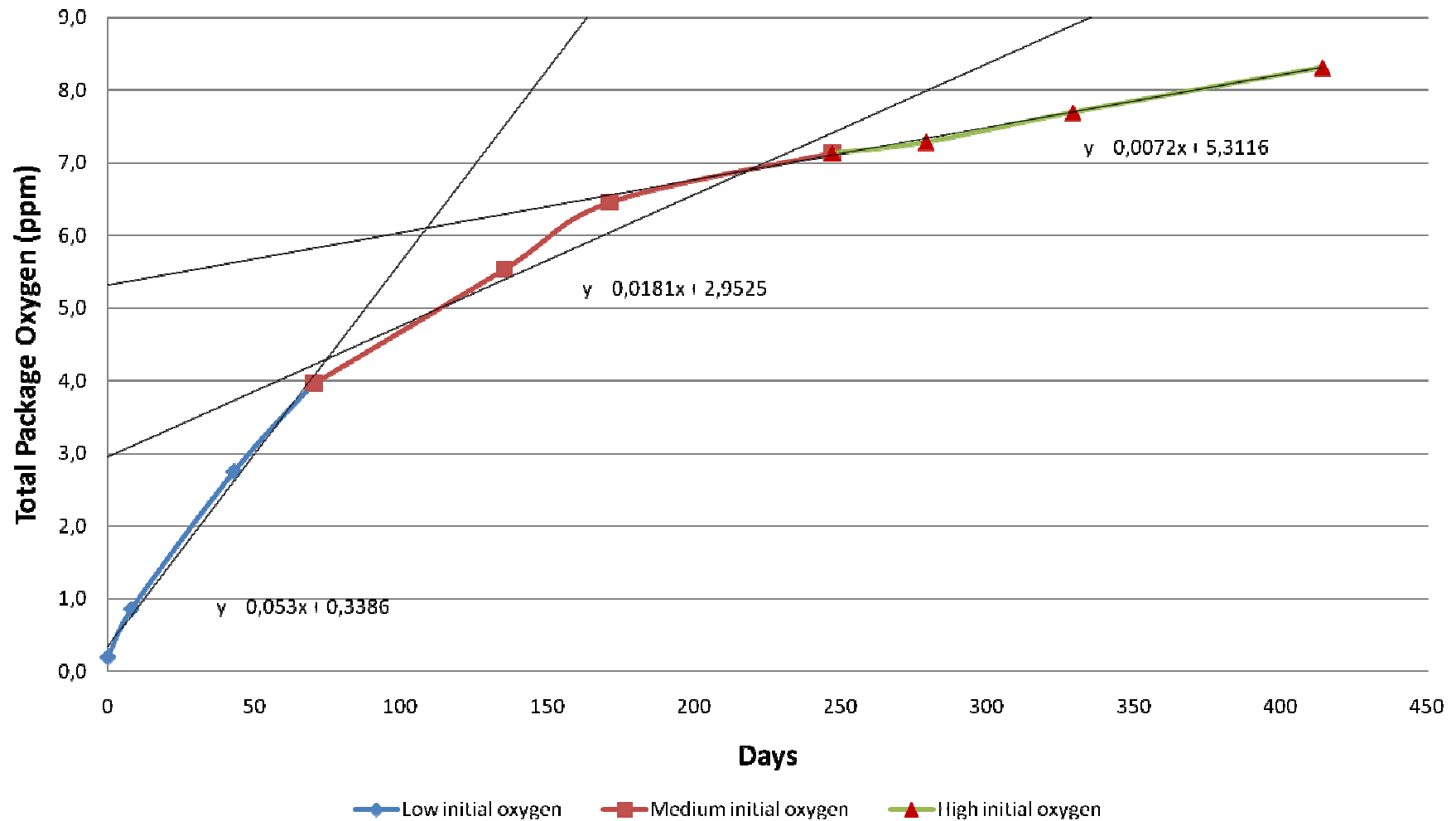


## Repeated Tests of Different Lots of the Same Bag & Tap Illustrates the lot to lot variation and a problem due to bio-contamination



## Example of Oxygen Ingress Rate as a Function of Oxygen Concentration in Package

### Low initial oxygen concentration is critical to accurate results



# Interpreting TPO Ingress Data

- Absorption from the package
- Oxygen Ingress Rate
- Bag ingress vs. Tap/gland ingress
- Oxygen scavenger activity
- True oxygen ingress when scavengers are used

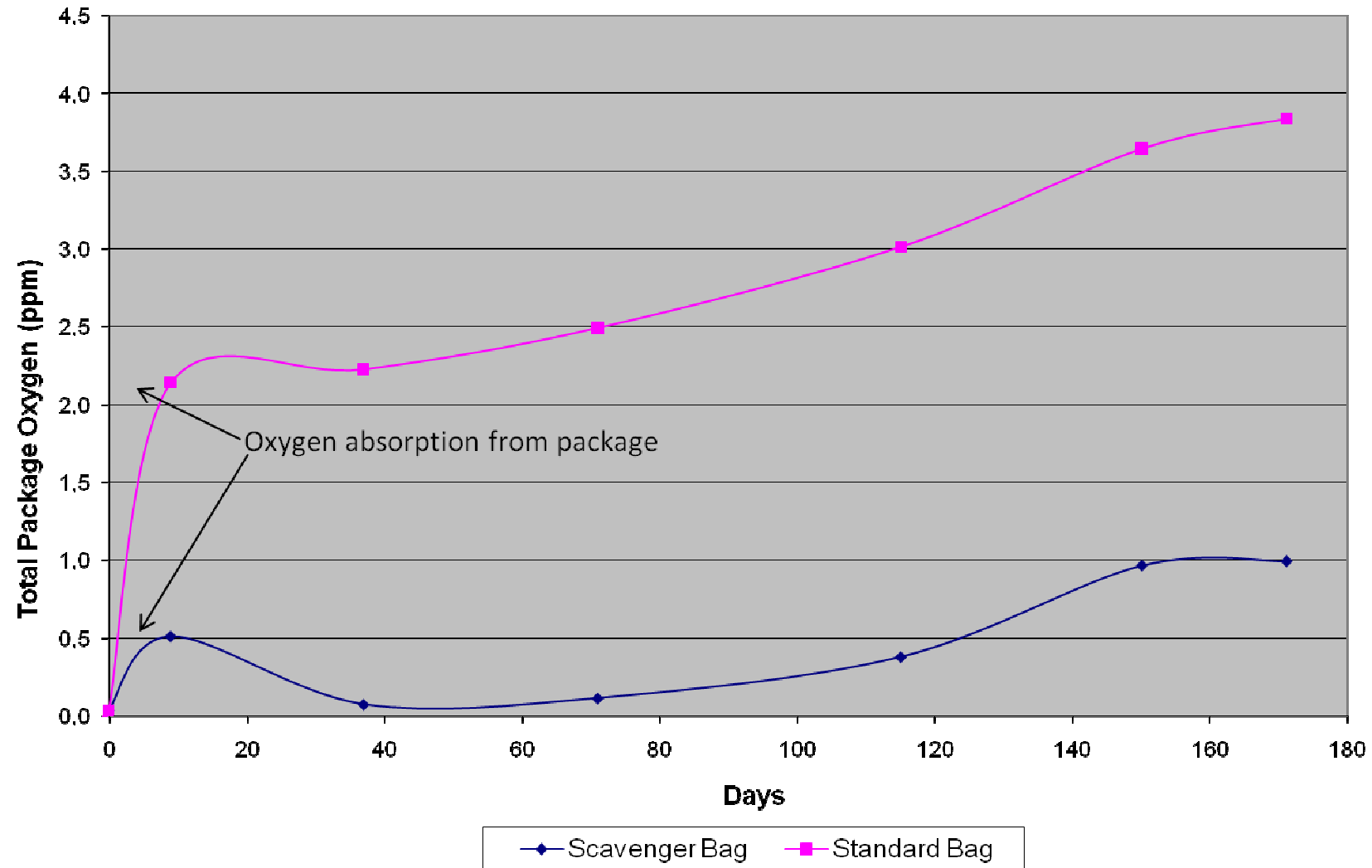


# Oxygen Absorbed from the Package

- While conducting oxygen ingress tests we have observed a sharp increase in the oxygen concentration over the first week, then it stabilizes to a slower ingress rate
- This has also been observed in plastic bottles
- We have observed dissolved oxygen and TPO increase between 0.07 to 2 mg/liter in the first week due to absorption
- This does add variability to any test
- Minimizing this would require material and construction changes but could significantly improve the shelf life of the wine



## Examples of BIB Oxygen Ingress with Initial Oxygen Absorption from the Package

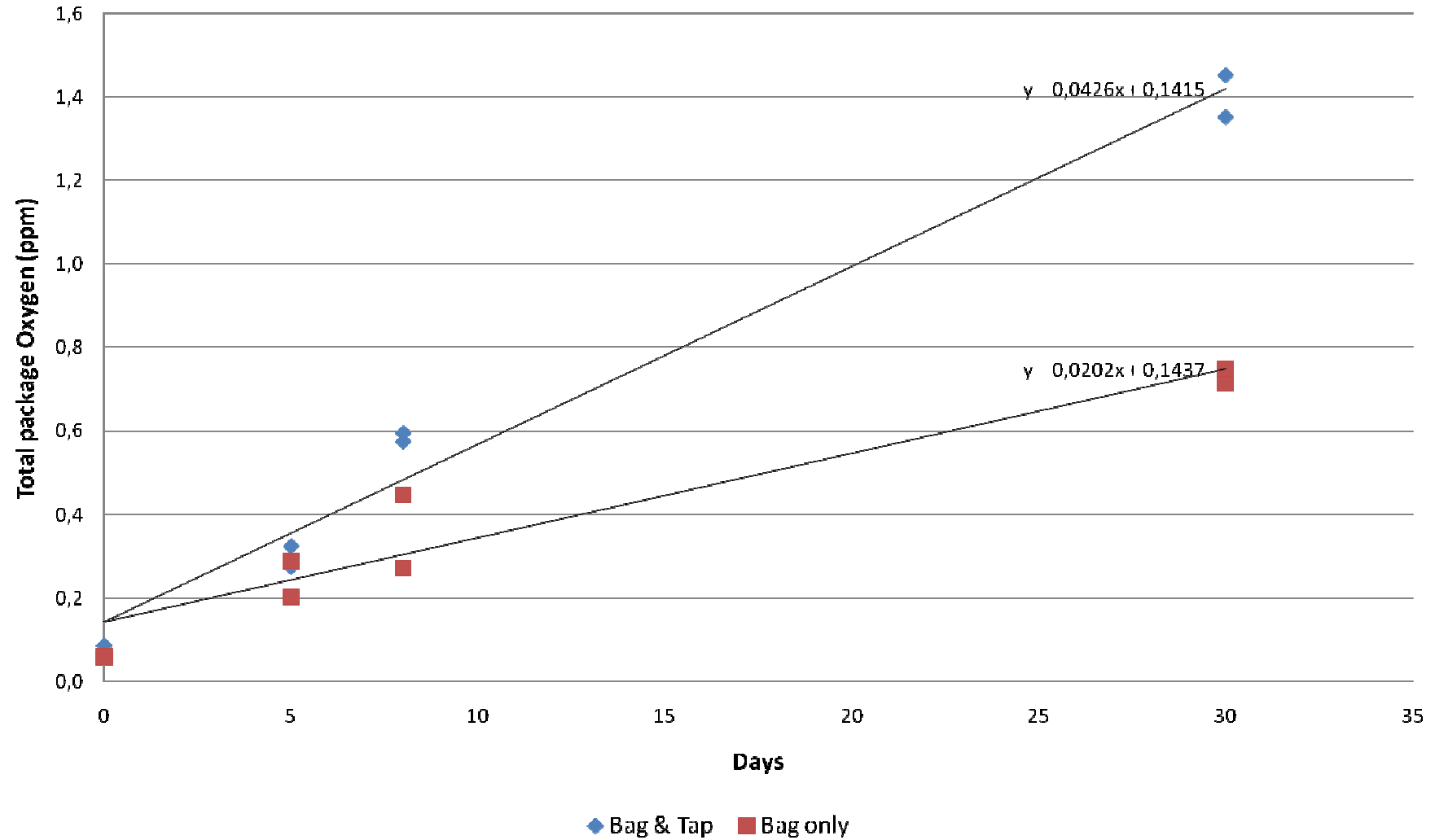


# Oxygen Ingress per Component

- Tests are run on the complete package for overall complete package oxygen ingress performance
- Earlier tests were carried out by applying a foil seal over the gland in place of a tap, but this allowed increased ingress through the gland walls.
- Bags made without glands are filled, heat sealed and tested for bag oxygen ingress performance
- Oxygen ingress for the gland and tap is obtained by subtracting the bag ingress from the complete package ingress.



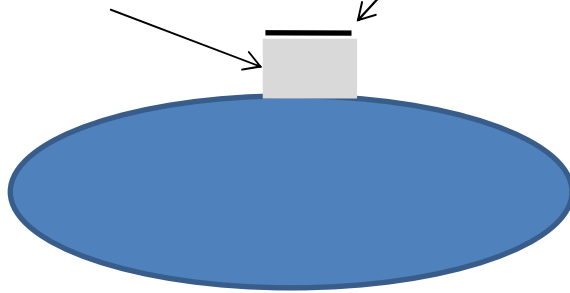
## Oxygen Ingress Comparison of a Generic Bag with Tap versus Bag Only



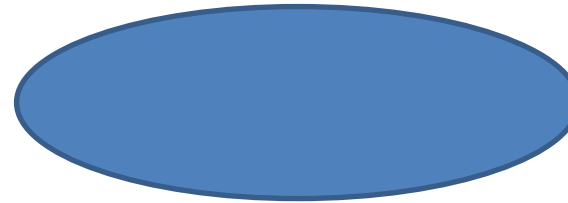
# Bag Configurations Tested

Oxygen Ingress  
through gland wall

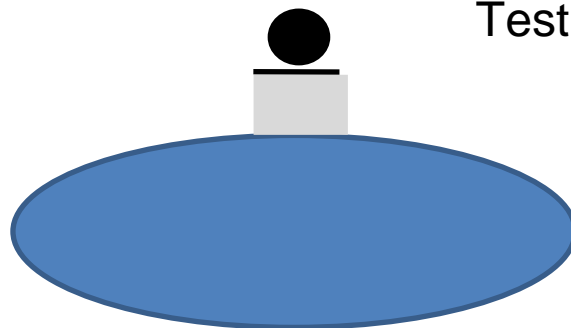
Foil seal



Earlier Bag Only Test



Current Bag Only Test



Complete Bag, Gland & Tap



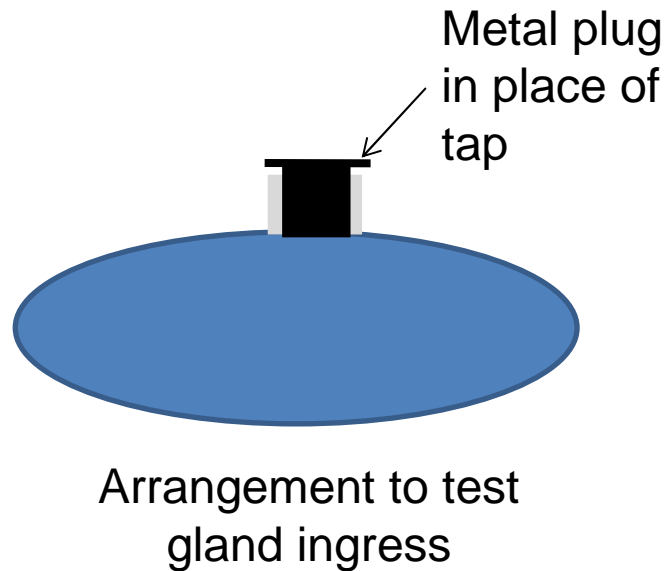
# Oxygen Ingress of Package Components

These are values for a specific bag, gland & tap. The results may change drastically from one manufacture and/or material to another.

Component	TPO ingress (mg/liter/day for 3 liter bag)
Bag, gland & tap	0.0426
Bag	0.0202
Gland & tap	0.0224
Absorption from bag	0.07



# Proposed Test Configuration to Determine Ingress Through the Gland versus the Tap



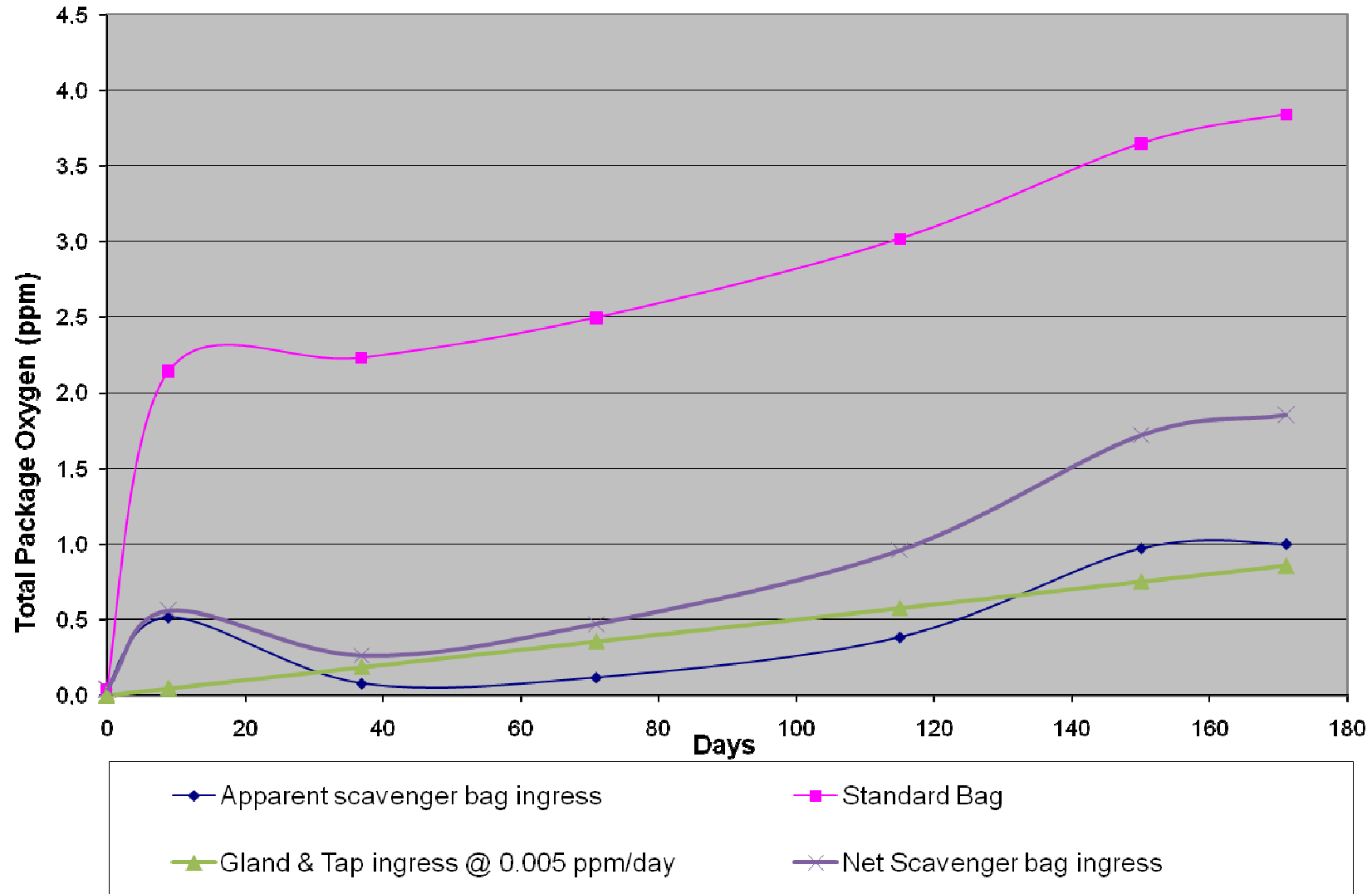
- A stainless steel plug machined to the plug dimensions of the tap would be used in place of the tap for testing
- The resulting ingress would be from the bag and gland under conditions similar to when the tap is inserted
- A comparison to the bag only test would give the ingress through the gland
- A comparison to the total package ingress would give the ingress through the tap

# Oxygen Scavenger Containing Bags

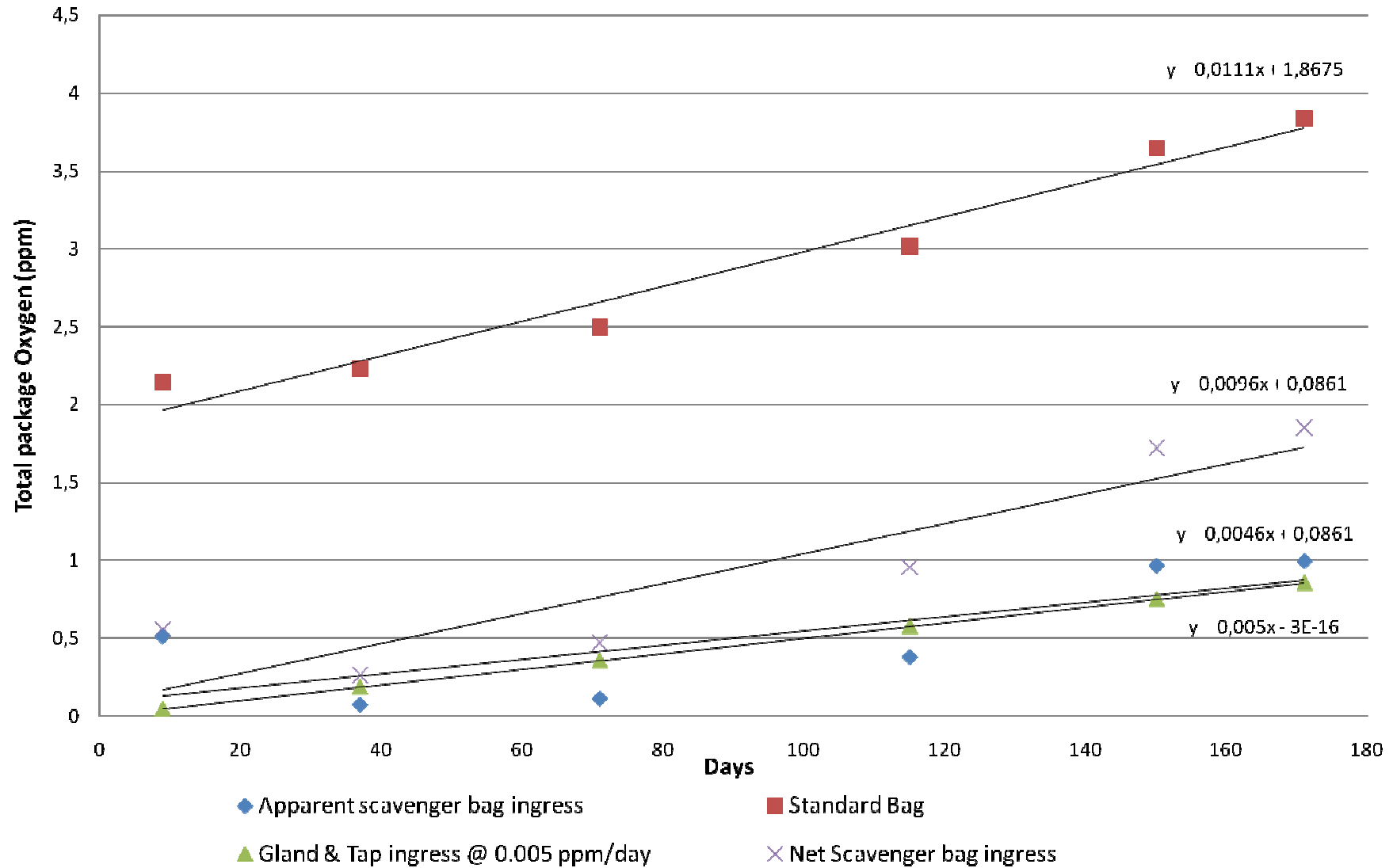
- Oxygen scavengers often require some time (hours to days) to activate and establish a steady state
- Scavengers can react with oxygen inside the bag, competing with the wine
- At some point in time the scavenger will be completely reacted and oxygen will start to accumulate in the bag (or reacting with the wine when in commerce)
- Oxygen ingress through the tap and gland can travel through the water and react with the scavenger in the bag, under commercial conditions that oxygen will react with the wine
- Tap and gland ingress must be determined on an inert bag then added to the scavenger bag ingress.



## Standard versus Oxygen Scavenger BIB TPO Ingress Scavenger Apparent and Actual/Net Ingress



## Net Oxygen Ingress for Oxygen Scavenger Containing BIBs



# Oxygen Scavenger Package Ingress

Package Components	TPO ingress (mg/liter/day for 3 liter bag)
Apparent scavenger bag ingress	0.0046
Gland & Tap ingress (from inert bag test)	0.005 (estimated, this gland and tap was not actually tested)
Calculated net scavenger bag ingress	0.0096
Reference standard complete BIB	0.0111

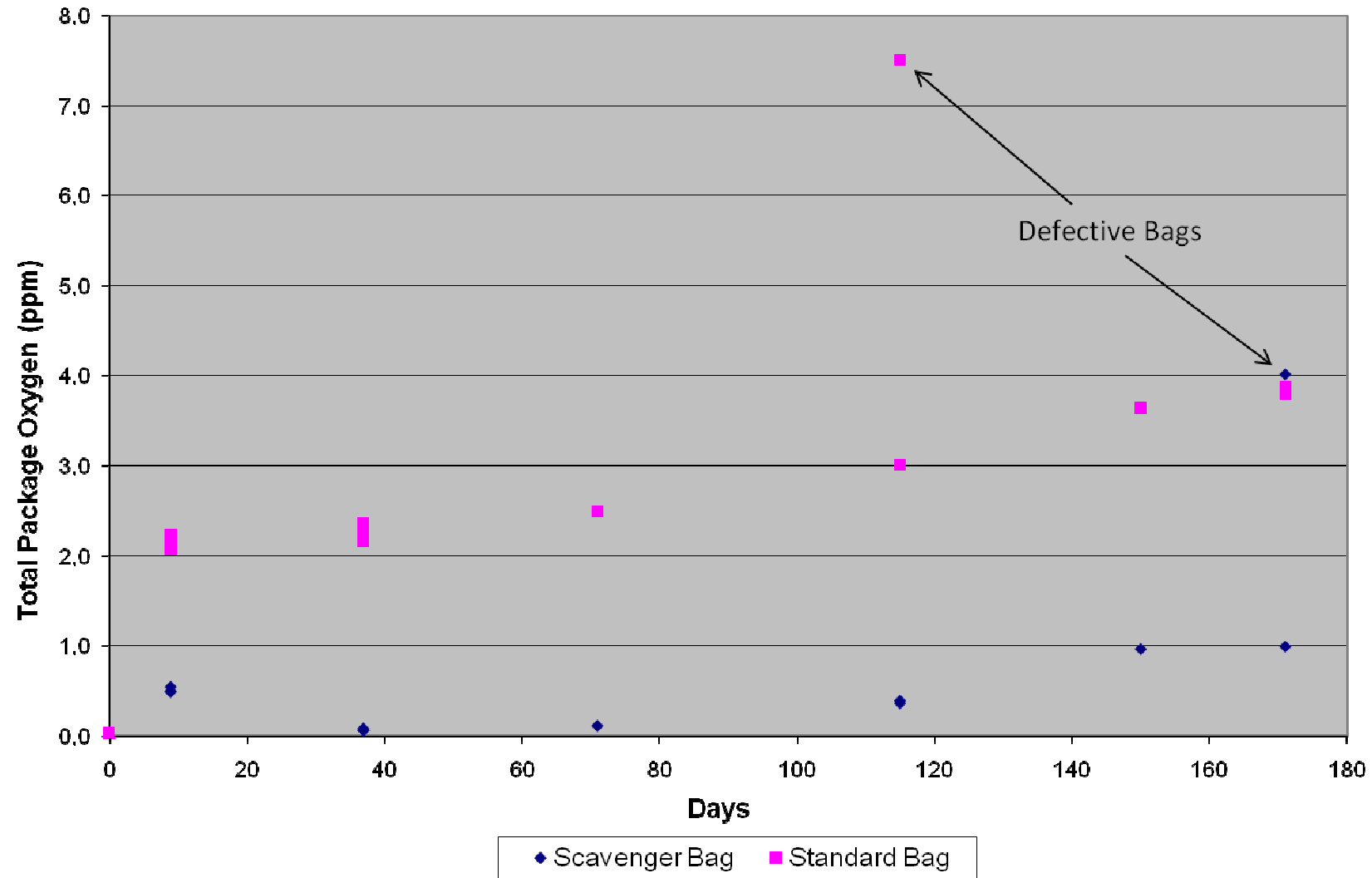


# Detection of Package Failure

- Ability to detect microgram per liter changes in oxygen level allows detection of the smallest defect in the package
  - Screwcaps that do not leak can have extremely poor barrier properties due to “micro” wrinkles in the gasket
  - Long before bags leak due to stress cracking oxygen levels increase as air gets in through the minute cracks in the film
- As data is collected, packages with unusually high oxygen levels indicate a problem with the package



## Bag-in-Box Oxygen Ingress Test





# Conclusions

- When using this method it is critical to fill bags at low and consistent oxygen levels
- This method does determine the total amount of oxygen gets into the bag after the bag is filled
- Variations of the test determine the ingress through the various components
- Further work may lead to a reliable early detection of package failure by stress cracking
- Stress cracking may be a function of water and ethanol exposure in addition to physical abuse



# Suggestions for the Industry

- BIB packages can now be characterized by the following parameters
  - Initial oxygen absorbed from the package
  - Total oxygen ingress
  - Bag oxygen ingress
  - Gland oxygen ingress
  - Tap oxygen ingress
- Manufactures can improve any component and quantify the degree of improvement on the complete package
- It is highly probable the shelf-life of wine or any other beverage packaged in BIB will be improved by working to minimize both oxygen ingress and flavor scalping as both work to reduce or change original flavors

