Designation: F2714 – 08 (Reapproved 2013)

Standard Test Method for Oxygen Headspace Analysis of Packages Using Fluorescent Decay[1]

This standard is issued under the fixed designation F2714; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure for determination of the oxygen concentration in the headspace within a sealed package without opening or compromising the integrity of the package.

1.2 This test method requires that chemically coated components be placed on the inside surface of the package before closing.

1.3 The package must be either transparent, translucent, or a transparent window must be affixed to the package surface without affecting the package's integrity.

1.4 As this test method determines the oxygen headspace over time, the oxygen permeability can easily be calculated as ingress per unit time as long as the volume of the container is known.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Summary of Test Method

2.1 Chemically coated components (dots) are affixed to the inside surface of the package to be tested.

2.2 The package is gas flushed to a reduced level of oxygen either manually or by subjecting the package to a filling operation.

2.3 A pulsing light source is directed through the package at the chemically treated dot (the package must be transparent, translucent or contain a window through which the light can pass).

2.4 The fluorescent response from the dot is monitored and the decay rate determined.

2.5 The internal oxygen content of the package is determined by comparing the measured decay rate to the decay rate observed with known oxygen concentrations.

3. Significance and Use

3.1 The oxygen content of a package's headspace is an important determinant of the packaging protection afforded by barrier materials. The package under test is typically MAP (modified atmosphere packaging) packaged.

3.2 Oxygen content is a key contributor to off-flavors and spoilage of various products, such as chemicals, food and pharmaceuticals.

3.3 The method determines the oxygen in a closed package headspace. This ability has application in:

3.3.1 *Package Permeability Studies*—The change of headspace composition over a known length of time allows the calculation of permeation. Since the headspace oxygen is measured as a percentage, the volume of the container's headspace must be known to allow conversion into a quantity such as millilitres (ml) of oxygen. The use of this approach to measure permeation generally applies to empty package systems only as oxygen uptake or outgassing of contained products could affect results.

3.3.2 *Leak Detection*—If the headspace contains more oxygen than expected or is increasing faster than expected, a leak can be suspected. A wide variety of techniques can be employed to verify that a leak is present and to identify its location. If necessary or of interest, a leak rate may be calculated with known headspace volume and measured oxygen concentration change over time.

3.3.3 *Efficacy of the MAP Packaging Process*—If the headspace oxygen concentration is found to be higher than expected soon after packaging, the gas flushing process may not be working as well as expected. Various techniques can evaluate whether the MAP system is functioning properly.

3.3.4 *Storage Studies*—As the method is non-destructive, the headspace can be monitored over time on individual samples to insure that results of storage studies such as shelf life testing are correctly interpreted.

[1] This test method is under the jurisdiction of ASTM Committee F02 on Flexible Barrier Packaging and is the direct responsibility of Subcommittee F02.40 on Package Integrity Test Methods.

Current edition approved Aug. 1, 2013. Published September 2013. Originally approved in 2008. Last previous edition approved in 2008 as F2714 – 08. DOI: 10.1520/F2714-08R13.

4. Discussion

4.1 Oxygen sensing based on fluorescence is well established. The typical indicators used are ruthenium complexes and porphyrins both of which are compatible with light emitting diodes (LEDs). In one oxygen sensitive coating, tris (4,7 biphenyl 1,10 phenanthroline) ruthenium chloride is used due to its stability, long lifetime, and strong absorption between 400 nm and 500 nm in the blue region of the spectrum. The absorption peak is compatible with high brightness blue LEDs or blue semiconductor lasers. The emission peak is at 600 nm in the red region of the spectrum and is detected by a photomultiplier tube or a photo detector to offer the flexibility of a large dynamic range and fast response time. The ruthenium complex is immobilized in a highly chemically resistant substrate.

4.2 The principle of fluorescence quenching is based on the excited state characteristics of a specific dye. Dynamic quenching is the transfer of energy from a fluorescent dye in its excited state to oxygen in the surrounding medium. The energy consumed by oxygen will be dissipated as heat after a short time and the whole process can repeat itself indefinitely without consuming oxygen.

4.3 The ruthenium complex is excited with blue light from an LED. Short pulses of blue light from the LED are absorbed by the ruthenium complex. In the absence of oxygen, the ruthenium complex will emit light in the red region of the spectrum. The average time between the absorption of the blue photon and the release of the red photon is called the fluorescence lifetime. The fluorescence lifetime of the ruthenium complex is about 5 µs. However, if oxygen is present, the fluorescence is quenched. This occurs when oxygen molecules collide with the excited ruthenium molecules. During the collision, energy is transferred from the ruthenium to the oxygen, preventing emission. This process is called dynamic quenching, and it results in a decrease in the fluorescence lifetime proportional to the oxygen partial pressure. The fluorescence lifetime will decrease from 5 µs in an oxygen free environment (for example, nitrogen) to 1 µs in ambient air (see Fig. 1). The most important aspect of using quenching for oxygen detection is that neither the oxygen nor the sensor is consumed during a measurement.

5. Interferences

5.1 The presence of certain interfering substances in the headspace may, in theory, give rise to incorrect readings. Normal headspaces in empty or filled packages have not been found to be problematic. Relative humidity in that headspace also has shown to not cause interferences.

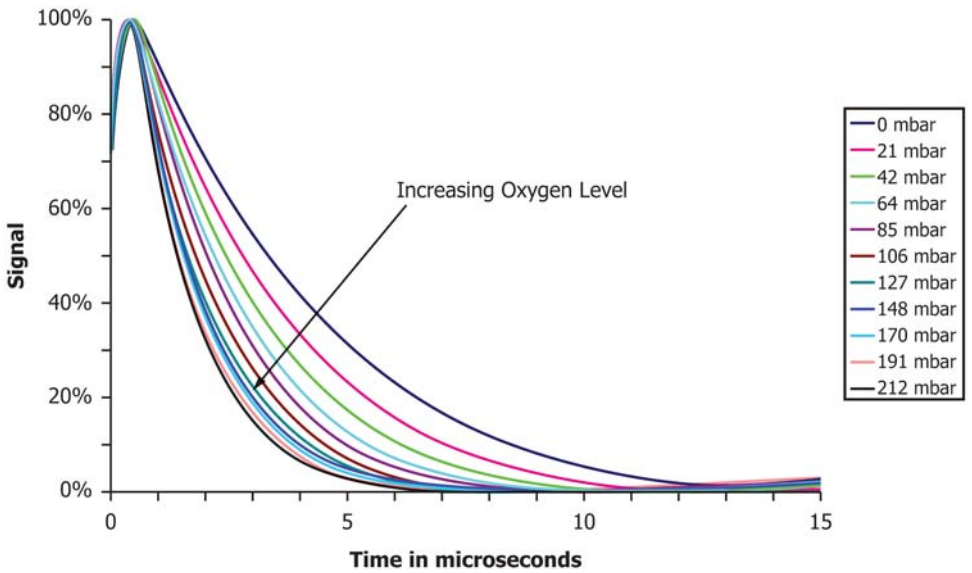
5.2 The temperature of the package, when tested, needs to be measured.

5.3 It is recommended that calibration, described below, of the chemically treated dots be conducted on packages containing known oxygen concentrations as close to the level to be experienced in actual tests. If the calibration is carried out at levels far different than actual levels, the results may shown less precision than predicted in the precision and bias statement below.

6. Apparatus

6.1 *Chemically Treated Components (aka "dots")*—Coated substrates of glass or flexible clear plastic have been found to be satisfactory. A fluorescent dye polymer is deposited on one side of the substrate.

6.2 *Adhesive* is used to attach the non-coated side of the dot to the inside of the package. Silicone rubber adhesive has been shown to be satisfactory. Other adhesives and double-sided tape will work as well. No adhesive has yet been identified which interferes with the fluorescence of the dye as long as the adhesive is sufficiently translucent.



NOTE 1—The fluorescent lifetime lies between 1 µs and 5 µs.

FIG. 1 Relative Fluorescence Signals (I/I_0) after Illumination of a Short Blue Pulse, Quenched by Different Oxygen Pressures in Air of 20°C