A System for Monitoring Gases in Constant-Volume Atmospheres

A constant volume system is described which permits continuous monitoring of variations in atmospheric gases of packaged, stored food. Repeated gas sampling is possible, and the system is maintained free of external contamination. The system is especially useful for monitoring radioactive headspace gases or those of samples containing pathogenic bacteria.

Modified Atmosphere storage can increase the shelf life of foods packaged in gas impermeable containers. Manipulation of the gas content in the container has improved shelf life (Ogilvy and Ayres, 1951; Salunkhe and Wu, 1974; Kader, 1980), reduced or modified the microbial flora (Gottlieb, 1971; Gill and Tan, 1980), and provided some control over the appearance of foodstuffs (Clark and Lentz, 1973; Taylor and McDougall, 1973; Rikert et al., 1957b). A recent article by Finne (1982) reviewed the history and current research into modified atmosphere storage of foods.

Quantifying changes that occur in gas composition of the atmosphere of a package during storage are of major importance to the complete understanding of this subject. In the past, many techniques used for modified atmosphere packaging research did not permit repeated sampling from the same package. A large number of packages were required to obtain sequential measurements, and a replicate was sacrificed with each sample. More often, sequential observations were not made and only initial and final atmosphere compositions were studied.

A system combining a silicone septum with a flexible barrier bag was used by Seideman et al. (1979a,b) and Hoermann (1980). This pseudo-constant-pressure system approached isobaric conditions and was useful for the analysis of beef packaged in modified atmospheres. It allowed for multiple gas samples to be taken from a single experimental unit, reducing the number of replicates required for a sequential study. However, the volume of the package was difficult to measure accurately over the course of an experiment. Several observers (Baran et al., 1969; Seideman et al., 1979a,b; Hoermann, 1980) reported noticeable volume losses in flexible pouches containing beef, further complicating the experiment.

A constant-volume system with multiple sampling capabilities would eliminate the need for accurate volume measurements and provide additional information about modified atmosphere packaging. Some researchers (Rikert et al., 1957a; Taylor and MacDougall, 1973) have used a sealed metal can as a constant-volume vessel. The metal container had to be pierced to obtain a sample, which destroyed the system. If the pressure in the container was lower than atmospheric pressure, it was difficult to obtain the sample without contamination from atmospheric gases caused by the pressure differential. Visual monitoring of the foodstuff was not possible and important observations may have gone unnoticed.

An improvement over the sealed metal can using a modified vacuum desiccator was developed by Rikert et al. (1957b). Sequential sampling and visual inspection of the product were possible. However, in this system, no mechanism was available to adjust the pressure precisely, to allow for sampling at atmospheric pressure, or to readjust the system pressure after the sampling operation.

The purpose of this communication is to introduce a constant-volume, hypobaric container for use in modified and controlled atmosphere packaging studies which can be sampled repeatedly during storage, protects the sample and its contiguous atmosphere from contamination, and allows for precise manipulation of pressure in the container during the experiment.

APPARATUS

The system consists of a vacuum desiccator similar to the one described by Rikert et al. (1957b) but with important modifications (Figure 1). Three glass nipples were sealed into openings in the lid of the desiccator that serve as "ports" into the chamber. High-vacuum stopcocks were attached to two of the openings (ports A and B), and the third opening (port C) was covered with a rubber serum bottle stopper (Fisher Scientific, Houston) to provide a septum.

The vacuum port on the top of the vessel was connected by a short length of vacuum tubing to a Firestone valve (Ace Glass, Inc., Vineland, NJ). Port A was attached to a manometer with a section of vacuum tubing. Port B was enlarged on the inside of the desiccator lid to form two annular rings to facilitate the airtight fitting of a round, pretested, latex balloon. The system is easily fabricated by a glass blower with standard materials and methods.

DISCUSSION

Studies involving constant volume modified atmosphere systems are rare, primarily because of the difficulties in obtaining sequential samples, in maintaining constant pressure before and after sampling, and in obtaining accurate volume measurements using conventional techniques. This proposed system has several features that alleviate these problems. The Firestone valve facilitates efficient evacuation and refilling of the reaction vessel. The manometer attached to a separate port allows for precise monitoring of the internal pressure in the desiccator and permits uniform evacuation and refilling of the vessel. It is possible to observe pressure changes and to adjust the pressure during the experiment.

The flexible latex membrane provides relatively convenient sample procural without danger of contamination from the outside atmosphere. The pressure in the chamber can be brought to external pressure by opening the valve (port B) and allowing the balloon to inflate. The sample can be drawn into a gas-tight syringe through the septum (port C) without creating an influx of the external atmosphere around the needle and into the vessel. Once the sample is obtained a vacuum source is attached to the stopcock (port B) and air removed from the balloon until the original pressure is reached.

The desiccator assembly provides further advantages. Visual monitoring of the stored food is possible. The vessel is completely sealed and can be heat sterilized, making it suitable for use in research involving pathogenic bacteria or radioactive materials. Moreover, the unit can be placed in a negative-pressure hood for additional safety. Although the modified desiccator is of relatively simple design, its unique features greatly facilitate constant-volume, hypo-

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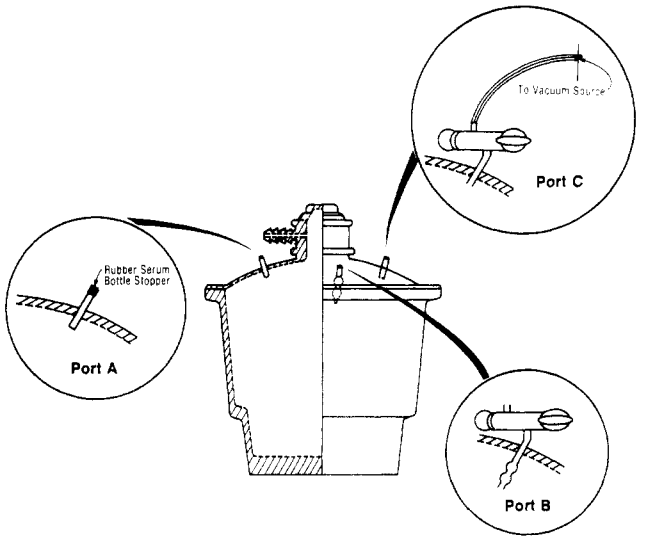

Figure 1. Desiccator modified for gas analysis.

baric, modified atmosphere storage and testing of foods.

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Identification and Quantitation of 6-Hydroxy-1,2,3,4-tetrahydro-β-carboline in Alcoholic Beverages

A gas chromatographic–mass spectrometric method was used to identify and quantitate 6-hydroxy-1,2,3,4-tetrahydro-β-carboline (6OHTHBC) in beer. The concentration of 6OHTHBC varied between 33 and 235 nmol/L and was not a function of the alcoholic content of the beer.

6-Hydroxy-1,2,3,4-tetrahydro-β-carboline (6OHTHBC) is a tricyclic indole derivative which is formed by a Pictet–Spengler reaction involving serotonin (5-hydroxytryptamine, 5-HT) and formaldehyde. The formation of such tetrahydro-β-carbolines occurs readily under physiological conditions (Whaley and Govindachari, 1951) and produces substances which can function as neurotransmitters and/or neuromodulators (Buckholtz, 1980). Furthermore, acute and chronic administration of tetrahydro-β-carbolines to rats has been reported to significantly alter ethanol consumption (Geller et al., 1973; Myers and Oblinger, 1977). Recently 1-methyl-1,2,3,4-tetrahydro-β-carboline and 6-hydroxy-1-methyl-1,2,3,4-tetrahydro-β-carboline have been identified and quantitated in various foods and alcoholic beverages (Beck and Holmstedt, 1981; Beck et al., 1983). In light of their pharmacological activity and potential role in alcoholism, we undertook the analysis of 6OHTHBC in alcoholic beverages, which is the subject of this communication.

EXPERIMENTAL SECTION

Materials. 6-Hydroxy-1,2,3,4-tetrahydro-β-carboline (6OHTHBC) 5-hydroxytryptamine and glyoxylic acid by the method of Vejdelek et al. (1961). The deuterated internal standard was prepared by the exchange labeling procedure of Elliott (1975). The procedure involved dissolving 100 mg of 6OHTHBC in 10 mL of ^2H_2O and 5 mL of ^2HCl (38% in ^2H_2O) and refluxing for 1 h. The reaction mixture was lyophilized to dryness, and labile deuterium atoms were exchanged by repeated dissolving in H_2O and lyophilization. This procedure gave a mixture of dideuterated–pentadeuterated molecules; however, the major species and the one monitored in this study was 6OHTHBC-$^2H_4$. The positions of deuterium atom labeling have not been established. 5-Hydroxytryptamine creatinine sulfate and 5-methoxytryptamine were obtained from Sigma Chemical Co. (St. Louis, MO), dichloromethane (CH_2Cl_2) was from E. Merck (Darmstadt, West Germany), and pentafluoropropionic anhydride (PFPA) was from Massanalys AB (Bromma, Sweden). All other chemicals were of analytical purity.

Sample Preparation. A 1.0-mL aliquot of each alcoholic beverage was added to acid-washed (dichromate–sulfur acid), silanized, glass tubes containing a solution (150 μL) of 6OHTHBC-$^2H_4$ (110 pmol), semicarbazide (4.5 mmol), ascorbic acid (0.5 nmol) and EDTA (0.05 nmol). Semicarbazide was added to control for the artifactual formation of 6OHTHBC during the sample workup. Its

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