

TRACE OXYGEN IN GASES BY GAS CHROMATOGRAPHY

UOP Method 759-76

SCOPE

This method is for determining trace oxygen in gases. The lower limit of detection is 1 mol - ppm. High concentrations of argon will interfere with the analysis and raise the detectable limit.

OUTLINE OF METHOD

A reproducible volume of sample is injected into a chromatograph employing a molecular sieve column maintained at -78 C. Quantitative results are obtained from the area of the recorded oxygen peak by utilizing a factor obtained from the chromatogram of a blend of known oxygen or argon content.

APPARATUS

Chromatographic column, 1.5 m of 3/16-inch OD standard wall copper tubing filled with 20-40 mesh regenerated 5A molecular sieves

Flask, vacuum, wide neck, 1-pint capacity, Cat. No. S-34721B, Sargent - Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60076, or equivalent

Gas Chromatograph, equipped with a thermal conductivity detector which will give a minimum response of 13 sq mm/ppm of oxygen when operated at the stated *Operating Conditions*

Recorder, 1 mv, 1 sec, full - scale response

Sample inlet system, gas sampling valve, 8-port, equipped with a 15-ml sampling loop, Cat. No. L-208-8V, Dohrmann Division, Envirotech Corp., 1062 Linda Vista Ave., Mountain View, CA 94040, or equivalent

REAGENTS AND MATERIALS

Acetone, 99% minimum purity

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Calibration blend, see Calibration

Deoxygenation column, OXY-TRAP column, Cat. No. 4002, Alltech Associates, Inc., 202 Campus Drive, Arlington Heights, IL 60004, or equivalent

Dry ice

Hydrogen, chromatographic grade, oxygen free (see deoxygenation column, above)

Molecular sieves, Type 5A, Linde, 20-40 mesh, chromatographic grade. Available from Coast Engineering Laboratory, 13508 S. Normandie Ave., Gardena, CA 90249, or equivalent. Molecular sieves can be regenerated by heating them at 260 C for 2 hours while they are being purged with a slow flow of a dry inert gas.

PROCEDURE

Operating Conditions

Carrier gas	thermal conductivity
Carrier gas flow rate	60 ml/min
Detector type	thermal conductivity
Detector temperature	100 C
Column temperature	-78 C
Sample size	15 ml (gas)

Chromatographic Technique

Immerse the chromatographic column in a bath composed of an acetone - dry ice mixture and adjust the hydrogen carrier gas flow rate to 60 ml/min. When a stable recorder baseline has been established, securely connect the sample container to the sample valve with a short length of 1/8-inch OD metal tubing. Purge the sample loop with sample at a rate of approximately 50 ml/min for at least two minutes. Stop the sample flow and inject the sample. The oxygen will elute in approximately 20 minutes. Measure the area of the recorded oxygen peak by any acceptable technique. Argon, if present, will elute from the column in about 13 minutes, but nitrogen and other higher molecular weight compounds will not elute from the column at this temperature. Therefore, after several analyses have been completed, a loss of resolution and shortening of retention times will be observed. When this occurs, and at the end of each day, backflush the column either through the use of a backflushing valve or by simply reversing the column. While backflushing, heat the column to about 80 C with hot water to facilitate removal of the heavier components.

Calibration

Prepare or purchase a blend of nominally 100 mol-ppm oxygen in nitrogen. Obtain a chromatogram of this blend, as described under *Chromatographic Technique*, prior to each series of analyses, or at least once a day, and measure the area of the oxygen peak. Calculate the response factor relating the mol-ppm/unit of peak area for oxygen as follows:

$$K = P/A$$

where:

- K** = response factor for oxygen for a 15-ml sample volume
- P** = mol-ppm of oxygen in the blend
- A** = peak area for the oxygen

In the event that a proper calibration blend is not available, a temporary calibration can be made by substituting dry room air that contains nominally 9340 mol-ppm argon. Inject a sample of the room air, and obtain a peak for the argon. At the valley between the argon and oxygen peaks, switch off the filament current to protect the filaments from possible damage caused by the large amount of oxygen in the air. Determine the area of the argon peak, and multiply this area by a factor of 0.952 to adjust for differences in the thermal response between oxygen and argon. Calculate a response factor as previously directed.

CALCULATIONS

Calculate the mol - ppm of oxygen in the sample using the following equation:

$$\text{Oxygen, mol - ppm} = KS$$

where:

K = response factor, previously defined

S = peak area for oxygen

PRECISION

Based on 7 replicate determinations, the estimated standard deviation (esd) for oxygen at the 94 mol - ppm level was calculated to be 4.86.

Duplicate results by the same operator should not differ by more than 16.8 mol - ppm (95% probability) at the stated level.

TIME FOR ANALYSIS

The elapsed time for one analysis, including the running of a blend, is 0.83 hour. The labor requirement is 0.33 man - hour.