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Note

Determination of traces of nitrogen and argon in oxygen by a simple gas chromatographic method

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Industrial oxygen used in the steel industry may contain traces of nitrogen and argon. The concentration of nitrogen must be below 1000 ppm otherwise the steel can show weakness or brittleness. The accurate determination of the nitrogen concentration in industrial oxygen is therefore important. For other purposes it may also be interesting to be able to measure higher nitrogen concentrations in O_2. Direct gas chromatographic (GC) separation of nitrogen and oxygen is possible on molecular sieve 5A with katharometer detection, but not when the nitrogen concentration is at the ppm level because the huge oxygen peak overlaps the later eluting nitrogen peak. Argon elutes with oxygen on molecular sieve 5A. On Chromosorb 102 (pellicular SiO_2) the elution sequence is nitrogen, oxygen and then argon. This separation has to be carried out at very low temperature ($-78°C$). This is not very practical, especially for routine analyses. At room temperature, nitrogen and oxygen are not separated on Chromosorb 102. Gas analysis in general was thoroughly discussed in a Varian special edition by Thompson[1]. The special case of the determination of nitrogen and argon was described in 1959[2], and more recently by Karlsson[3] using hydrogen as carrier with BTS catalyst and molecular sieve 13X as packing material. We find that the conditions for introducing the sample are critical and must be described more clearly, and that other column materials are preferable. We also prefer helium as carrier gas because with hydrogen the water uptake of the separating column changes retention times (as mentioned by Karlsson) and thus adversely affects reproducibility of peak area measurements with the katharometer detection used.

EXPERIMENTAL

The GC instrument was a Varian 1400 fitted with a micro katharometer. The detailed set-up for the analytical method to determine nitrogen and argon is shown in Fig. 1.

Several oxygen-absorbing chemicals were evaluated. Some commercial materials had batches with good performance but some of the same brand failed to absorb all the oxygen in the samples. RSL-Fixox is a material specially selected for the purpose of the described analysis (RSL, Eke, Belgium or Alltech, Deerfield, IL, U.S.A.). To activate the RSL-Fixox, the column is mounted in the GC oven and connected to an empty stainless steel column led out of the oven. The oven tempera-

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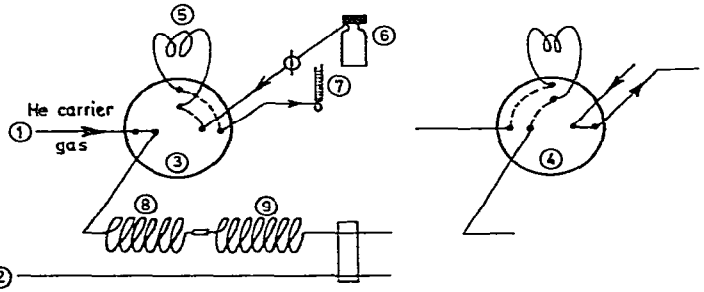

Fig. 1. Instrumental set-up for trace analysis of N_2 and Ar in O_2. Varian 1400 gas chromatograph with micro katharometer. 1 = Helium carrier gas at a flow-rate of 18 ml/min; 2 = helium reference gas at a flow-rate of 18 ml/min; 3 = six-port Valco 7000 HPLC sample loop injector in load position; 4 = six-port Valco 7000 sample loop injector in injection position; 5 = sample loop (*ca.* 2 ml) in stainless steel of *ca.* 50–60 cm × 3.2 mm O.D.; 6 = lecture bottle of calibration gas or unknown; 7 = soap bubble flow-meter; 8 = stainless-steel column (1 m × 0.62 cm I.D.) filled with RSL-Fixox; 9 = stainless-steel column (3 m × 0.62 cm I.D.) filled with molecular sieve 5A.

ture is raised to 250°C and hydrogen is passed through for *ca.* 2 h at 30 ml/min. Water vapour is a reaction product. The end of activation can be ascertained accurately when no more water is eluted (mirror test!). RSL-Fixox shrinks somewhat during this activation step and it is generally necessary at this stage to add some packing to fill the column completely. The oxygen-absorbing column has to be regenerated in the same way when the Ar/N_2 peak ratio of the reference gas sample starts to increase. The advocated RSL-Fixox column (100 × 0.62 cm I.D.) can absorb *ca.* 0.5–0.6 g of oxygen. Regeneration is however needed after every 20 analyses in the conditions as described.

For reproducible results it is important to rinse the sample loop sufficiently (*e.g.* 30 sec at 50 ml/min) and to keep the sample gas rate constant.

To fill the sampling gas pressure cylinders they were coupled via a three-way valve to a gas pressure line. Evacuating and filling the cylinder three times by appropriately manipulating the valve then ensures correct sampling. A minimum pressure of 0.2 kg/cm^2 was required in our case.

The separation of nitrogen and argon is better at room temperature than at 30°C. We prefer the latter temperature, however, because this is easier to control in a closed oven with a heated detector. In the Varian 1400 with micro katharometer, used for the present work, 30°C is obtained normally with the oven fan on and the detector at 230°C.

RESULTS AND DISCUSSION

To determine nitrogen and argon concentrations a reference gas sample —in our case 99.7% O_2, 0.2% Ar (2000 ppm) and 0.1% N_2 (1000 ppm)— is injected three times, and then the unknown sample is also injected three times. The peak heights or peak areas are measured (manually or with an electronic integrator) and the amounts of nitrogen and argon in the unknown are calculated. The Ar/N_2 peak ratio can vary as a function of the current intensity through the bridge. Best results on the Varian 1400 with micro katharometer were obtained with a bridge current of 250 mA.

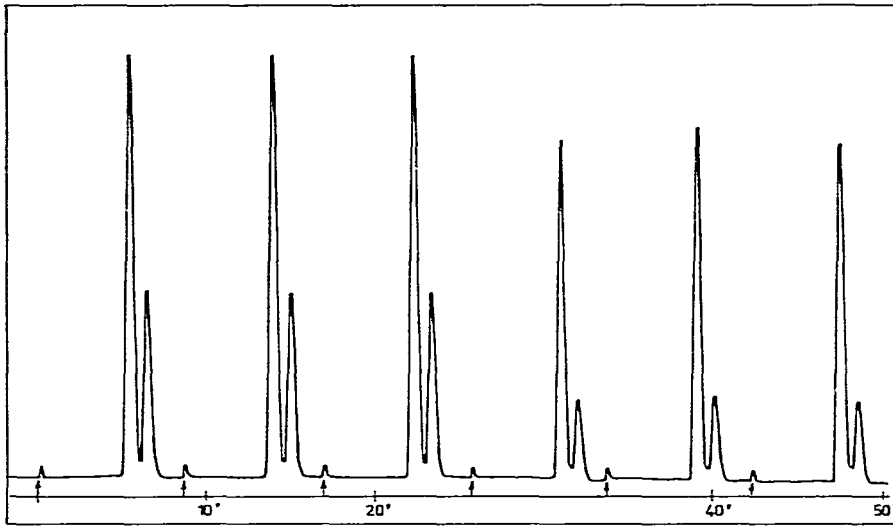

Fig. 2. Chromatograms obtained with calibration gas (first three injections) and with an unknown (second group of three) at 30°C. First peak Ar, second peak N_2. Total time 50 min.

An example of such an analysis is shown in Fig. 2. Typical results based on peak height measurements are as follows:

Calibration gas. Ar: 137.5; 137.2; 137.2; $\bar{x}$, 137.3; σ, 0.12%; N_2: 59.5; 59.7; 60.2; $\bar{x}$, 59.8; σ, 0.60%.

Unknown gas sample. Ar: 107.0; 109.0; 107.0; $\bar{x}$, 107.7; σ, 1.07%. Result: 1583 ppm; N_2: 26.5; 27.0; 26.2; $\bar{x}$, 26.6; σ, 1.52%. Result: 461 ppm.

The standard deviation can easily be kept below 1.5%. It is obvious that the same method could be used to determine nitrogen and argon in other oxygen-containing samples, such as air.

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