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Note

Analysis of dinitrogen–nitrogen oxide mixtures employing direct vacuum line–gas chromatograph injection

KENNETH A. PEARSALL and FRANCIS T. BONNER*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794 (U.S.A.)

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Recent work in this laboratory[1,2] has often concerned heterogeneous reaction systems in which some or all of the reactant or product species N_2, NO and N_2O are present in the gas phase, and the reliability of our stoichiometric, kinetic and thermodynamic measurements therefore depends critically upon the methods employed for containment, handling and analysis of such gas mixtures. While we have successfully used a combination of standard inert gas deaeration and high vacuum techniques in the preparation and handling of these systems in isolation from the atmosphere, we have found it essential to eliminate standard hypodermic gas sample withdrawal and gas chromatographic (GC) injection methods, at the analytical stage. To illustrate this necessity: a 1973 paper on the reduction of nitrous acid by iron(II) reports that NO, N_2O and N_2 are produced in this reaction at pH 5 in acetate buffer[3]. The measurements were carried out under a helium atmosphere, and analyses were done by GC employing syringe withdrawal and injection. The proportions of N_2 were reported to be in the range 8.5–28.1% of total product gas under the conditions employed. However, we have subsequently demonstrated[4,5] conclusively that N_2 is *not* a product of Fe(II) reduction of nitrite at pH 5, specifically under conditions identical to those described in ref. 3. We are forced to conclude that the N_2 product reported there had its origin in the atmosphere.

While errors of the magnitude cited in the previous paragraph can be reduced by the use of improved syringes (*e.g.*, locking, low dead volume), atmospheric N_2 background cannot be eliminated entirely in GC by port injection. If NO is present in the mixture, the presence of atmospheric N_2 background will also indicate error due to the ready oxidation of NO to NO_2. Because of the seriousness of these problems in our program, we have developed a vacuum line–GC interface which permits introduction of gas samples directly from high vacuum conditions to a gas chromatograph, and eliminates the use of syringe sampling and injection altogether. We do not claim unique originality for the system and methods we have developed, but have found them so successful and valuable in meeting the needs of our research that we believe it worthwhile to offer this description for the benefit of others who may face similar or related analytical problems.

A detailed diagram of the vacuum line–GC interface is shown in Fig. 1. All stopcocks are 2-mm bore, high vacuum; stopcocks A and B are pressure-high

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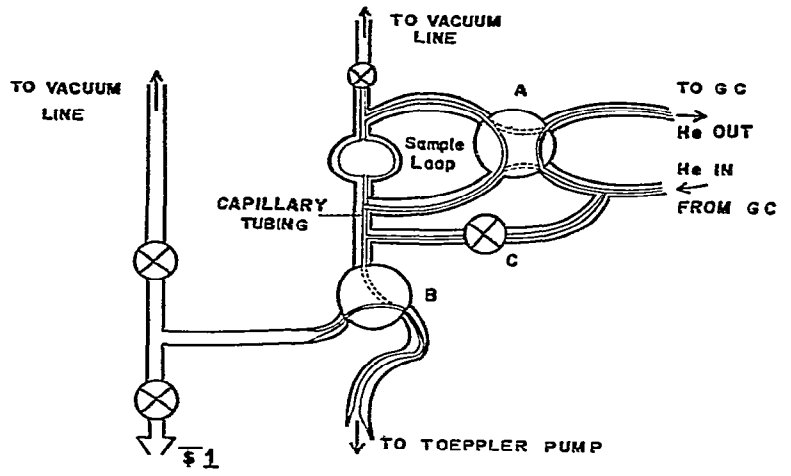

Fig. 1. Gas chromatograph–vacuum line interface.

vacuum, spring loaded types with 2-mm capillary tubing (special order; Eck and Krebs, Long Island City, NY, U.S.A.). Analyses are currently conducted using a Hewlett-Packard 5712A dual column instrument with a column switching valve (special option). One of the two helium carrier lines is rerouted from its flow controller to the interface, and from there to the column switching valve. Using the appropriate valve position, the interface can thus be connected to either GC column; the other column is simultaneously connected to a functional injection port. (In a previously used configuration a Varian 920 single column instrument was modified by inserting the interface between the flow controlling needle valve and the injection port. In this configuration, the injection port could be routinely used for the column conditioning that is required for NO analysis.)

The sample to be analyzed, contained in a sample bulb, is attached at standard taper joint 1. After appropriate pumping the sample is transferred by Toeppler pump to the sample loop. Stopcock C is then opened for 2–4 sec to equalize sample loop and carrier gas pressure. Four-way stopcock A is then turned through 90° for 2–5 sec, allowing carrier gas to entrain the major portion of the sample and carry it into the gas chromatograph. The sample loop is then pumped out in preparation for the next sample injection.

Extensive measurements were carried out to determine the optimum time of opening of stopcock A, the percentage of sample entrained, analytical reproducibility, sample pressure dependence of reproducibility and possible gas mixture fractionation in the loop. Successive analyses for N_2O were found reproducible within 0.2%, NO within 0.4% and N_2 0.6% for several samples at the same pressure in the loop, and also at different pressures within the range 20–200 Torr (*ca.* 3–30 μmole of total sample). At pressures within the range 2–20 Torr (*ca.* 0.4–3.0 μmole) reproducibility is within 2% (N_2O) and 4% (NO). 60–70% of the sample entrained in 10 sec was found to be entrained within the first 3 sec, hence 2–5 sec was selected as operating range, and is the condition yielding the reproducibility figures given above. Pressure equalization reduces the initial pressure pulse peak from the detector and sharpens

the N_2–NO separation. Sudden expansion into capillary tubing was found to cause slight fractionation of light and heavy gases, but as long as relatively slow Toeppler pumping is employed to transfer gases into the sample loop (1–2 min) no fractionation is observed. Overall analytical accuracy was assessed to be of the order of, or somewhat better than 2% for NO and N_2O and 4% for N_2 in the 3–30 μmole range.

This system has the advantages over other vacuum line–GC interfaces known to us that it is relatively simple in design, not expensive, and easy to operate; after preparation only one stopcock need be turned to introduce a sample into the gas chromatograph. Its main disadvantage is that it cannot effect quantitative transfer of a sample into the gas chromatograph; while it is thus useful for obtaining relative results, absolute results require the use of internal standards. For this purpose we initially employed CO_2, whose properties were found generally satisfactory except for the strong disadvantage, to our work, in its sharp dependence of solubility upon pH. We now use CF_4 exclusively as internal reference, and find its properties entirely satisfactory for our needs.

In order to determine the partial pressures of individual component gases, detector/integrator response has been carefully calibrated, using all binary combinations of N_2, NO and N_2O with CF_4 in mixtures of known composition, prepared by weight. Successive samples of several such standards were analyzed, and relative sensitivity factors then calculated and averaged.

The column material employed, Porapak Q, initially retains some NO and it is therefore necessary to condition it in advance of an NO analysis; a routine consisting of three successive injections of NO in amount at least five times larger than anticipated in a sample was found to provide adequate conditioning. After these increments have been introduced at 2-min intervals, the column remains conditioned indefinitely if NO-containing samples are introduced at intervals of 10–15 min.

This system was operated initially with a Varian Model 920 gas chromatograph with a Porapak Q column (12 ft. × 1/4 in.), thermal conductivity detector (TCD) at 150°C, output integrated by a Hewlett-Packard 3373B digital integrator, column temperature 30°C and helium carrier gas flow-rate 50 ml min^{-1}. In its current operation we employ a Hewlett-Packard 5712A gas chromatograph with Model 3380S reporting integrator, Porapak Q column (18 ft. × 1/8 in.) (35°C), TCD (200°C), helium carrier flow-rate 20 ml min^{-1}. Connection between the stainless steel carrier gas line and the glass interface is accomplished with Swagelok fittings using Viton O-rings.

The general level of analytical comfort afforded by the present system lies in the micromolar range with an estimated lower limit at about 0.1 μmole. While this range is entirely adequate for our current needs, the sensitivity could be greatly extended if necessary by a change in the detector system. Similarly, the retention times of N_2 and NO are not widely separated in the current configuration (see Fig. 2), and while the resolution of these peaks is adequate for our current needs it could be improved by an increase in column length, and hence analysis time, or by the use of a divided stream technique, employing a parallel molecular sieve column specifically to improve N_2–NO resolution.

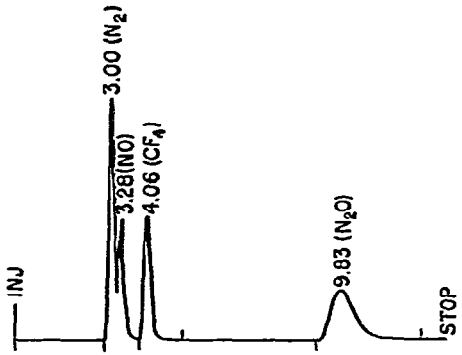

Fig. 2. Typical gas chromatogram. Retention times in minutes. Combining integrated areas and measured sensitivity factors this sample is found to contain 46.9% NO, 19.4% N_2O, 22.9% N_2 and 10.8% CF_4

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