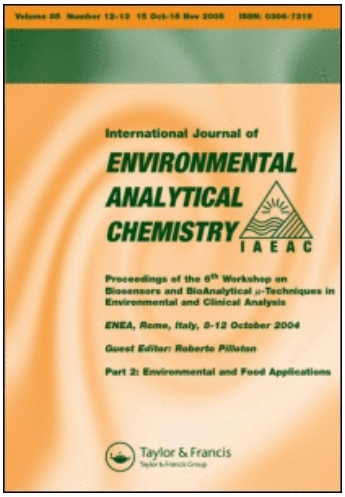

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DETERMINATION OF DISSOLVED ARGON AND NITROGEN IN WATER BY DIRECT AQUEOUS INJECTION GC-HID

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A gas chromatography-based automated method was developed for direct aqueous injection analysis of trace gases dissolved in water samples to support studies on air-water exchange processes of chemicals. Initial efforts were focused on the determination of dissolved gases such as Ar and N_2 because of their potential to serve as "tracer" species (or as "surrogates") for the air-water exchange process. Direct injection of water samples eliminated time-consuming sample preparation procedures and enabled short analysis cycles. The method employed a GC equipped with a helium ionization detector (HID) to achieve sensitivity sufficient for water analysis with direct injection of 10 µL water via a liquid sample valve. Analytes were isolated from the water matrix using a column switching technique prior to the separation and detection. Chromatographic separation of Ar, O_2 and N_2 was achieved with a long, 30-foot molecular sieve column. However, a short, 6-foot column combined with a chemical scrubber for O_2 was selected in order to ensure accurate quantitation of Ar and shorten the analysis cycle to 15 minutes. The precision for determination of Ar and N_2 was 1% RSD, with a method detection limit of ca. 30 µg/L Ar or N_2 in water and a linear range of ca. 2.5 orders of magnitude.

KEY WORDS: Aqueous injection, GC-HID, column switching, dissolved gases.

INTRODUCTION

Chemical contaminants are present in most natural waters and several hundred toxic chemicals have been detected in the Great Lakes.[1] Atmospheric deposition of chemicals to water, and volatilization from water to the atmosphere, can be significant processes influencing both media and generally contribute to determining the fate of environmental contaminants. For example, the contribution of atmospheric deposition to the total polychlorinated biphenyl (PCB) burden in the Great Lakes has been estimated to be as high as 90% for the upper lakes[2] and input from the atmosphere was considered the major source of PCB contamination of some central Ontario lakes.[3] It has also been suggested that Lake Ontario acts as a source to the atmosphere of some 185 kg/year of PCBs.[4] Therefore it is important to study the air-water exchange processes to improve our understanding of the environmental fate of a variety of chemicals. The fact that toxic organic contaminants, such as PCBs and other organochlorine compounds, are generally present at extremely low concentrations in natural waters presents a considerable challenge to the *direct, in-situ* investigation of their transfer across the air-water interface.

Therefore, it is fortunate that inorganic gases such as carbon dioxide, radon, helium (generally present at higher concentrations than environmental contaminants) can be used to model mass transfer of other chemicals across the air-water boundary.[5–7] Also, the Liss and Slater two-film resistance model[8], which was derived on the basis of observations with O_2, has been successfully used to model the air-water partitioning and intermedia transfer of synthetic organic chemicals (for example, PCBs) in the environment.[9–12] Similarly, Wanninkhof and other[13–15] have used sulfur hexafluoride, SF_6; nitrous oxide, N_2O; and methane, CH_4 as model compounds for investigating relationships existing between gas exchange, mass transfer velocities, wind speed, and other environmental or physical/chemical parameters.

From the preceding discussion it should be evident that substantial insight into air-water exchange processes can be obtained by observing the behaviour of inert gases such as Ar and N_2 dissolved in water.[16] These gases, which are present at higher concentrations than the synthetic organic chemicals, have the potential to serve as "trace" species (or as "surrogates") for other chemicals participating in the air-water exchange process. In order to follow the variation of such tracer concentrations in water, a fast, accurate and precise analytical method is required. Direct injection of water samples into the GC can eliminate time-consuming sample preparation procedures and enables short analysis cycles. Since the sample volume for direct injection analysis is limited, high sensitivity is necessary for the detector in such a GC system.

An automated method for direct aqueous injection analysis of trace gases dissolved in water has been developed, which employed a GC equipped with a helium ionization detector (HID) to achieve sufficient sensitivity. Water samples were directly introduced to the GC via a liquid sample valve. Analytes were then isolated from the water matrix using a column switching technique prior to the separation and detection.

EXPERIMENTAL SECTION

Sample introduction and water removal

The sampling/analysis flow for the system is illustrated in Figure 1. Three WP-series valves (Valco Instruments Co. Inc., Houston, TX) with air actuators were installed in the GC. Two of the valves (Part # VE206C C6WP, actuated by C33548/A60 helical actuators), both 6-port, employing interchangeable external sample loops, were utilised for injection of gas standards and liquid samples. The gas valve was equipped with a loop of 100 μL (VLW06C100) or 250 μL (VLW06C250). The liquid valve was equipped with a loop of 10 μL (VLW06C010) and was heated at 150°C to ensure sample vaporization. The 8-port valve (V208C C8WP), actuated by a C33592/A45 helical actuator, was used for switching the cut columns to allow the transmission of the analytes (Ar, O_2 and N_2), but prevent H_2O from being transmitted to the analytical column and the HID. A SSI Model 300 LC Pump (Scientific Systems, Inc., State College, PA) was used for delivery of water samples to the injection valve directly from a body of water or sample containers.

Two 3' × 1/8" HayeSep Q columns (60/80 mesh) were installed in the GC as the pre-columns (i.e. cut columns). One stream of helium carrying the analytes together with water flowed through cut-column A. While the analytes were carried into the analytical column in series with the cut column, water was retained by the cut column. Cut-column B was then switched in place of cut-column A before water broke through. This

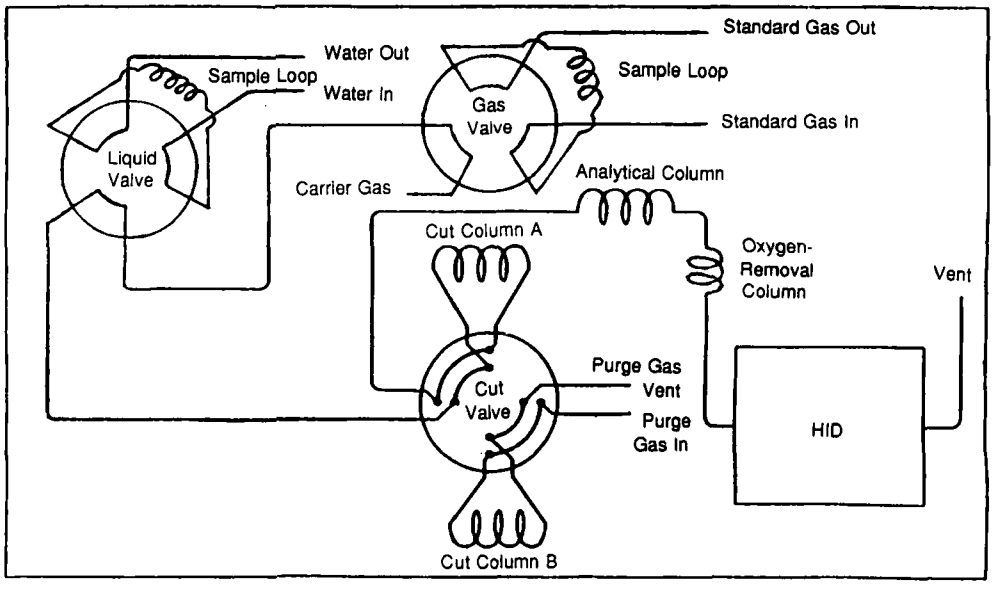

Figure 1 Sampling/analysis flow schematic.

prevented water from entering the analytical column and the HID, but allowed continuation of carrier gas into the analytical column and thus proper separation of the analytes by the analytical column. The water retained in cut-column A was back-flushed out of the column to a vent by a second stream of helium. Cut-column A was used only for sample injection (i.e. retaining water) and cut-column B was not exposed to water samples so as to minimize the possibility of contamination of the analytical column by water.

Separation and detection

The GC used was an Antek 3000 GC (Antek Instruments, Inc., Houston, TX) equipped with a helium ionization detector and a built-in helium purifier which was normally heated at 350°C. Five analytical columns were tested for separation of analytes. These included: a 6' × 1/8" molecular sieve 13X column, 60/80 mesh (Antek Instruments, Inc.); a 18' × 1/8" molecular sieve 5A column, 80/100 mesh, and a 30' × 1/8" molecular sieve 5A column, 60/80 mesh, both from Supelco Canada Ltd, Oakville, ON; a 6' × 1/4" Alltech CTR-III column (Part # 549062L) and a 6' × 1/8" Alltech modified CTR column, 60/80 mesh (C-5000 689936L) both from Alltech Associates Inc., Deerfield, IL. The CTR-III column consisted of two concentric molecular sieve columns: O_2 was removed from the inner column by a chemical scrubber and separated Ar and N_2 peaks eluted in sequence, followed by a combined Ar/O_2 peak and a N_2 peak, both of which eluted from the outer column. The modified CTR column was a single column packed with a mixture of molecular sieve and proprietary chemicals for removing oxygen.

The HID had a cell volume of less than 200 µL, an ionization source of 190 mCi ^3H and a power supply capable of up to 1000 V dc in increments of 1 V. The detector temperature was usually 50°C and the column temperature was held isothermally at 50°C during most tests. The detector output signal was recorded by an HP 3393A integrator

interfaced to an HP PEAK96 data system installed on an IBM PC-XT computer. Ultra high purity (U.H.P., 99.999%) helium (Linde Division, Union Carbide Canada Limited, Toronto, ON) was used as the GC carrier gas. Another cylinder of U.H.P. helium was used as purge gas for the detector housing as well as to actuate the valves.

Standards and calibration

The following certified gas mixtures from Matheson Gas Products Canada, Whitby, ON, all with U.H.P. helium as the balance gas, were used as calibration standards: 9.10 ± 0.46 ppm Ar, 12.3 ± 0.6 ppm O_2 and 18.9 ± 1.0 ppm N_2; 12.0 ± 0.6 ppm Ar, 252 ± 5 ppm O_2 and 708 ± 14 ppm N_2; 1% Ar; 1% O_2 and 1% N_2; 12 ppm CH_4. Ambient air and U.H.P. Ar were also used. Calibration gases were delivered from cylinders to the GC gas valve through high purity regulators and clean copper tubing. A "normally-closed" Skinner valve (#B2DA1052, Honeywell Inc., New Britain, CT) was installed upstream of the gas valve, and was opened to flush and fill the sample loop but was closed before switching of the sample valve. This allowed the gas sample in the loop to equilibrate at ambient pressure prior to injection. Another approach for generation of gas standards for multilevel calibration was to use an exponential dilution flask (EDF)[17]. The glass, custom-made EDF was 32 mL in volume. The concentrations of test gases generated by the EDF were verified by comparison with direct introduction of certified gas standards to the GC-HID.

Data processing and system automation

Integration of individual analyte peaks was difficult because of upsets in the baseline caused by valve switching. The data quality was improved by using a PC based data system in conjunction with the HP 3393A integrator. Chromatographic data were stored by HP PEAK 96 software. Post-run re-processing, re-integration and re-plotting were then performed on previously poorly integrated data.

Automated operation was performed by using the GC as the central unit. The control block diagram is showed in Figure 2. The GC's 6 programmable methods and 8 programmable control outputs allowed overall system automation. Once the GC was properly programmed and a sequence was started, gas and liquid sample valves and the cut valve were controlled by programmable outputs #1, #2 and #3, respectively. Data acquisition was initiated by control output #5 (contact closure) and terminated by the internal "Timetable Stop" of the integrator at the programmed time. During routine, continuous operation, the GC was calibrated using the gas mixture from a calibration cylinder. The gas was allowed to flow to the sample valve when control output #6 activated an Archer 5 VDC Reed Relay which in turn permitted provision of a voltage of 110 v ac to actuate the solenoid valve. The gas flow was stopped to allow the sample in the loop to equilibrate at ambient pressure while a gas sample was injected onto the GC by the gas valve. The water sampling pump was turned on when a voltage of 5 V dc supplied by the GC control output #8 activated an Archer 5VDC Reed Relay. The pump delivered 2 mL of water from a sample vial to the GC sample loop at a rate of 1 mL/min for two minutes to ensure complete flushing of the sampling line and loop. The pump stopped before 10 µL of water was injected onto the GC by the built-in liquid sample valve.

For routine operation, the system was programmed in 6 steps. Method #1 controlled injection of a certified gas standard for calibration. The remaining 5 methods

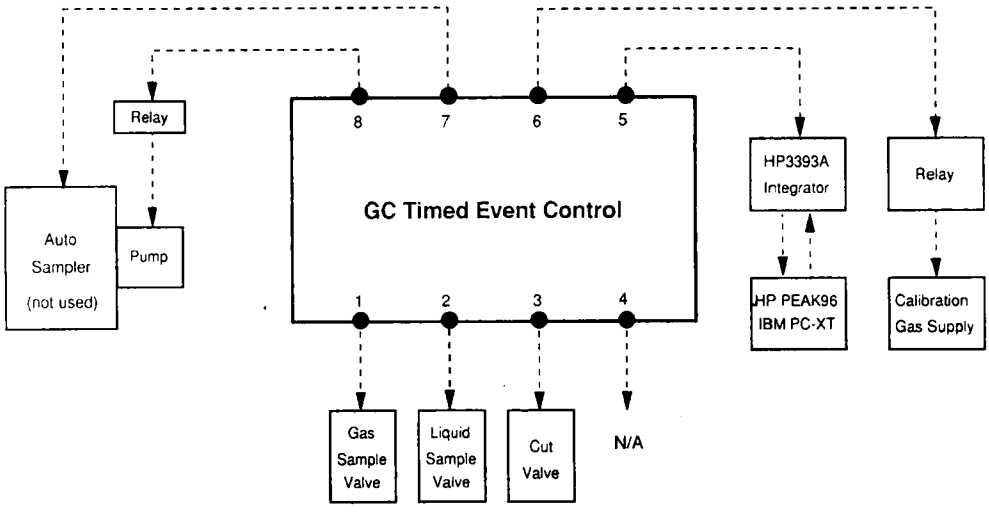

Figure 2 Automation block diagram.

commanded injection of water samples. At the end of each method the next method was called and the last method (Method #6) recalled Method #1. Therefore, a cycle included a calibration and 5 sample analyses. Cycles with more frequent calibration were possible. The automated system was able to provide un-attended analyses at intervals of 15 minutes, for ca. 100 water samples and appropriate number of gas standards. The maximum water sample number (100) was limited by the need to re-condition the analytical and oxygen-removal columns.

RESULTS AND DISCUSSION

Selection of analytical column

The 6-foot molecular sieve 13X column was first used for confirmation of the HID sensitivity using a CH_4 gas standard. It was not able to resolve Ar from O_2 on this column. The 18-foot molecular sieve 5A column also failed to achieve this separation. A longer (30-foot) column was used. Figure 3 demonstrates the separation of the three target analytes by the 30-foot column after proper conditioning (300°C overnight). The column temperature was 32°C and the carrier flow rate was 25 mL/min. Better resolutions could be achieved with lower column temperatures, but that would require even longer analysis cycles. Also, the requirement for cryogenic operation would complicate the instrumentation.

The porous layer open tubular (PLOT) columns are rapidly gaining popularity.[18,19] They have significant retention to the permanent gases and light organic compounds, which leads to their application in the separation of these compounds without the inconvenience of subambient temperature operation.[19-21] A Molsieve 5Å PLOT column can provide baseline resolution of Ar and O_2.[19] However, PLOT columns were not used in this work due to 1) that the GC used is designed for packed columns and certain instrumental alterations were required to adapt to the PLOT columns which are capillary or megabore columns, 2) that the separation of Ar and O_2 provided by the Molsieve 5Å

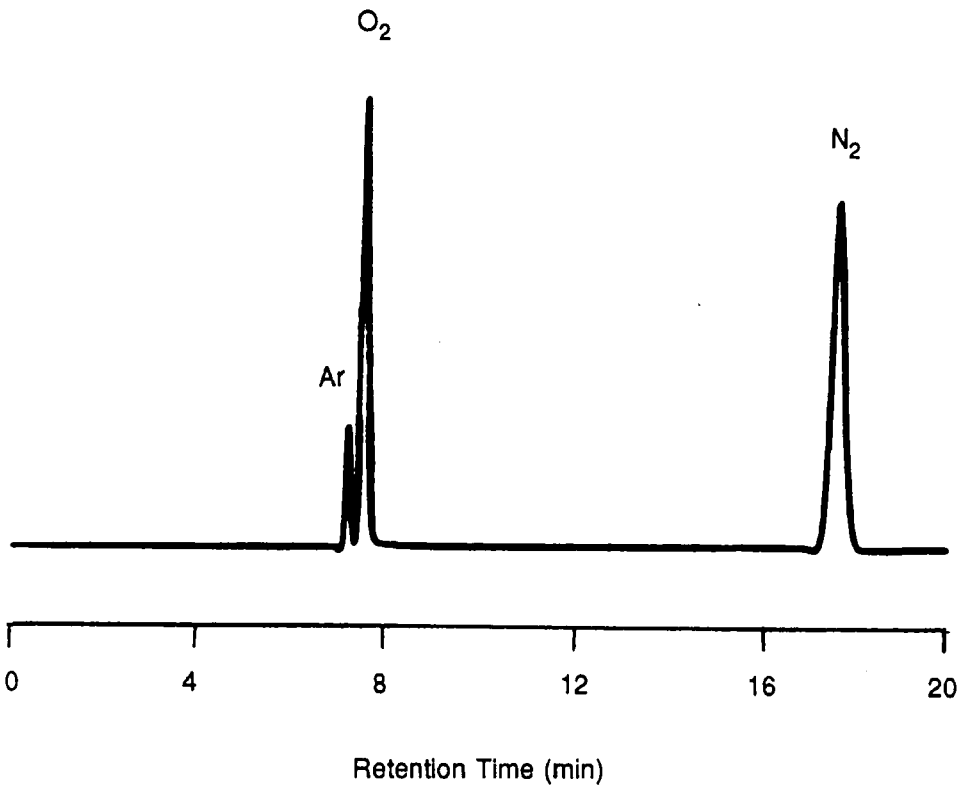

Figure 3 Resolution of a 30' molecular sieve 5A column.
Detector temperature: 60°C; Column temperature: 32°C; Injector temperature: 150°C; He purifier temperature: 350°C; He flow rate: 25 mL/min; HID voltage: 425 V.

PLOT column is similar to that by a packed molecular sieve column as demonstrated in Figure 3, although the analysis time (3 minutes) of the PLOT column is much shorter than the packed one, and 3) that the column combination discussed later would have served out purposes. An additional way to achieve separation of Ar and O_2 is to convert O_2 into H_2O, which could be readily separated from Ar and N_2.[16,22] However, water would cause severe damage to the HID.

The Alltech CTR-III column was designed to provide faster analyses of fixed gases. Figure 4 demonstrates the analysis of a water sample at a column temperature of 50°C and with a carrier flow rate of 40 mL/min. While the analytical cycle was short (< 10 minutes) and sensitivity was adequate for Ar determination, the large N_2 peak closely following the Ar peak might interfere with Ar quantitation. A longer (than 6 feet) CTR-III column, if available, could resolve this problem. However, an additional problem of the CTR-III column with respect to this application was the need of relatively high total carrier flow rates (> 30 mL/min). It was observed that at such high flow rates the HID response polarity could be reversed or variable in certain concentration ranges, causing problems in quantitation. This is discussed further in the later section on HID response polarity.

The modified CTR column (alone) was unable to achieve separation of Ar and N_2 but did permit efficient removal of O_2 from the sample. Therefore, this modified CTR

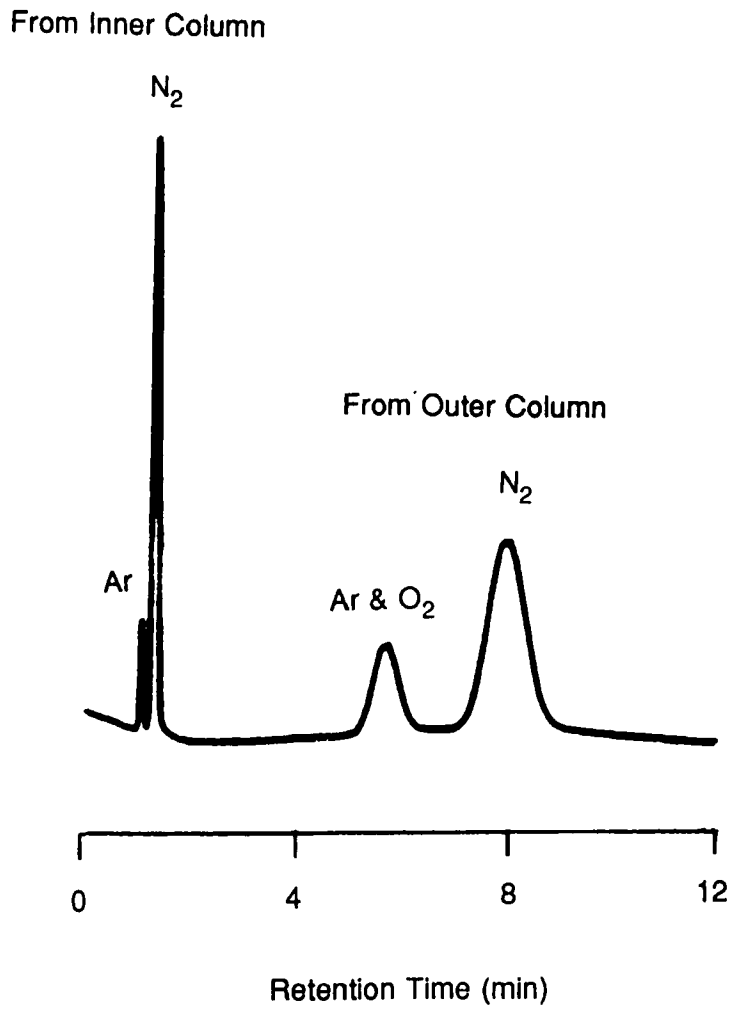

Figure 4 Separation by the CTR-III column.
Detector temperature: 60°C; Column temperature: 50°C; Injector temperature: 150°C; He purifier temperature: 350°C; He flow rate: 40 mL/min; HID voltage: 425 V.

column was used only as an O_2 remover and a molecular sieve 13X column (6' × 1/8") ahead of the modified CTR column was used for separation (Figure 1). The combination of these two columns provided adequate separation of Ar and N_2 and removal of O_2 (Figure 5a), and was selected for further testing. It was understood that information on O_2 was lost but it was considered acceptable with respect to the purpose of this exercise, since the behaviour of the *inert* gases (Ar and N_2) was of our primary concern.

Isolation of analytes from water matrix

The time at which the pre-columns switched was very critical to the success of the method. Switching too early cut off analytes but, if too late, the risk of water transfer to

the analytical column occurred. Furthermore, sufficient time was needed to allow complete purge of water from the cut column. At 50°C and a helium flow rate of 11 mL/min, water retention in the cut column was ca. 4 minutes while that of air was less than 0.6 minutes. Different times (0.5, 0.6, 0.7, 0.8 and 0.9 minutes) for cut columns switching after injection were tested and 0.8 minutes was selected since it allowed complete transmission of analytes to the analytical column. A purge time of at least 10 minutes was necessary.

With a "fore-flushing" scheme, incomplete purge of water from the cut column was possible even with prolonged purging time. Although the majority of water could be purged out of the pre-column within a certain time, unnoticeable, trace amounts of water might still be retained and later transmitted to the analytical column, causing accumulation of water in the analytical column and thus its deterioration. GC resolution was noticeably reduced after continued extensive use of the system for water analysis. An increase in purge time could solve this problem but also lengthen the analysis cycle considerably. Higher cut column temperatures could speed up the elution of water but this required construction of a separate, temperature-controlled block for the cut columns. Therefore, the "back-flushing" approach was tested. The water retained by the cut column was back flushed from the column, eliminating the chance of water being transmitted to the analytical column. This approach proved to be satisfactory and was used in subsequent tests. Figure 5b shows the analysis of a 10-μL water sample. The

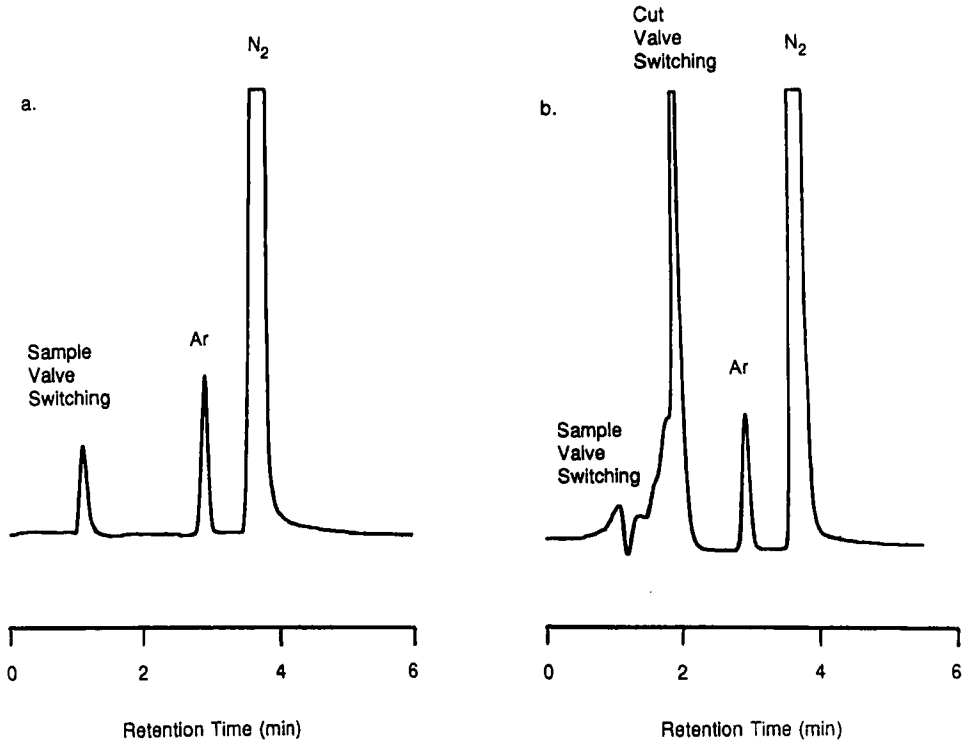

Figure 5 Gas chromatography with a 6' molecular sieve 13X column and a modified CTR column. Detector temperature: 50°C; Column temperature: 50°C; Injector temperature: 150°C; He purifier temperature: 350°C: He flow rate: 11 mL/min; HID voltage: 375 V. (a) Air sample, (b) Water sample.

peak at ca. 2 min. was caused by cut valve switching. Baseline upsets before this peak were caused by water injection.

HID response polarity

In principle, any analytes with ionization potentials below the energy states of helium metastables should be ionized in the HID cell via Penning ionization and thus cause an increase in ionization current.[23] The variation of the detector ionization current is then used as the measure of analyte concentration change in the carrier gas. Neon is the only permanent gas which is not ionized because of its higher ionization potential than the helium metastables. Its presence may result in a decrease in ionization current due to quenching of helium metastables. However, the helium ionization detector's performance is far more complicated and, as a consequence, some analytes other than neon can cause either increase or decrease in ionization current or both. The HID responses may be either positive or negative or bipolar, depending on the type and/or concentration of analytes, the purity and flow rate of carrier gas, and the detector design and operation conditions.[24] Unfortunately, the target analytes of this study are among the list of substances exhibiting such complex response characteristics. Reversal of detector response polarity was observed during some tests.

In this work, the major controllable factor found to affect the response polarity was the carrier gas flow rate. Table 1 shows the relationship between the flow rate and response polarity. A polarity change-over for Ar response occurred at flow rates between 32 and 40 mL/min: responses were positive at helium flow rates less than 32 mL/min and negative at flow rates higher than 40 mL/min. The change-over range might depend on the type of analyte, its concentrations and other operating parameters. To allow proper separation and quantitation of the analytes with greater carrier gas flow rates, the column temperature (32°C) used in this test was lower than normally used (50°C). However, the polarity change-over was also observed at other column temperatures. The behaviour of this particular HID excluded the use of columns requiring relatively high flow rates, such as the 1/4" CTR-III column. The helium flow rate selected for the operation of the column combination of the modified CTR and oxygen-removal columns was 11 mL/min.

Table 1 Effect of carrier gas flow rate on HID response polarity.

He flow rate (mL/min)	*Ar response (Area counts)*	*N_2 response (Area counts)*
50	Negative	Bipolar
40	Negative	83456
32	3754	186333
25	7269	367884
12	30499	1023672

Detector temperature:	40°C
Column temperature:	32°C
Injector temperature:	150°C
He purifier temperature:	350°C
HID voltage:	400 V

100 μL gas mixture (12 ppm Ar, 252 ppm O_2, 708 ppm N_2)

Detection limit and linearity

Although volume mixing ratios (e.g. %, ppm and ppb) are normally used for characterization of gas-phase concentrations, it would be more convenient to express calibration in terms of mass injected. This is because gas solubilities in water are usually expressed in terms of mass per unit volume and in this particular application gas-phase calibration was to be used for quantifying the analytes in water samples. The calibration curve for Ar was linear up to ca. 160 ng Ar injected (250 μL loop). The smallest amount injected was 0.4 ng and by extrapolation the minimum detectable amount was ca. 0.25 ng (S/N = 3). The linear range fully covers the anticipated amount of Ar (ca. 3 to 7 ng) dissolved in a 10 μL water sample.

The N_2 calibration curve was linear up to ca. 135 ng, with a minimum detection limit of ca. 0.33 ng. The amount of N_2 dissolved in 10 μL water is ca. 100 to 200 ng, close to or even beyond the upper linear limit of the system for N_2. Therefore, precautions should be taken for N_2 calibration if a 10 μL water sample is to be analyzed. A smaller sample volume (e.g. 5 μL) can be used to ensure that the amount of N_2 injected remains in the linear range, if relatively higher concentrations of N_2 is found in the samples.

System stability and precision

The system stability was examined by replicate, continued analyses of an Ar standard over a 400-h period. A dramatic downward trend of the system sensitivity during the first 48 hours of operation and a slowdown of this trend after that period were observed. After one week the system stabilized and daily drifts in sensitivity were less than 5%. It should be noted that the columns were conditioned at 250°C for 24 hours immediately before the system was used for analysis. In fact, if the HID was disconnected from the columns during, and until 48 hours after, column conditioning at a high temperature, the dramatic change in system sensitivity was not observed.

The pooled relative standard deviations (RSDs) were used for assessment of the method precision. The pooled RSDs are calculated from pooled standard deviations (SDs) which are given by:

$$SD = \sqrt{\frac{\Sigma D^2}{2N}}$$

where D is the difference of two consecutive analyses (i.e. a duplicate measurements) and N the number of duplicate measurements. The method precision for gas injection analysis was demonstrated using 100 repeat, consecutive analyses of a gas standard. The pooled RSDs for Ar and N_2 were both around 1%. Analytical precision of 1% was also achieved with this approach for 100 consecutive water analyses, enabling determination of greater than 2% variation of Ar and N_2 concentrations in water.

Continuous use

Figure 6 demonstrates the concentrations variations of Ar and N_2 in water contained in a 500-mL beaker and exposed to ambient air. The water was drawn to the sample valve by the LC pump and recycled back to the beaker. The dropping process of water from the

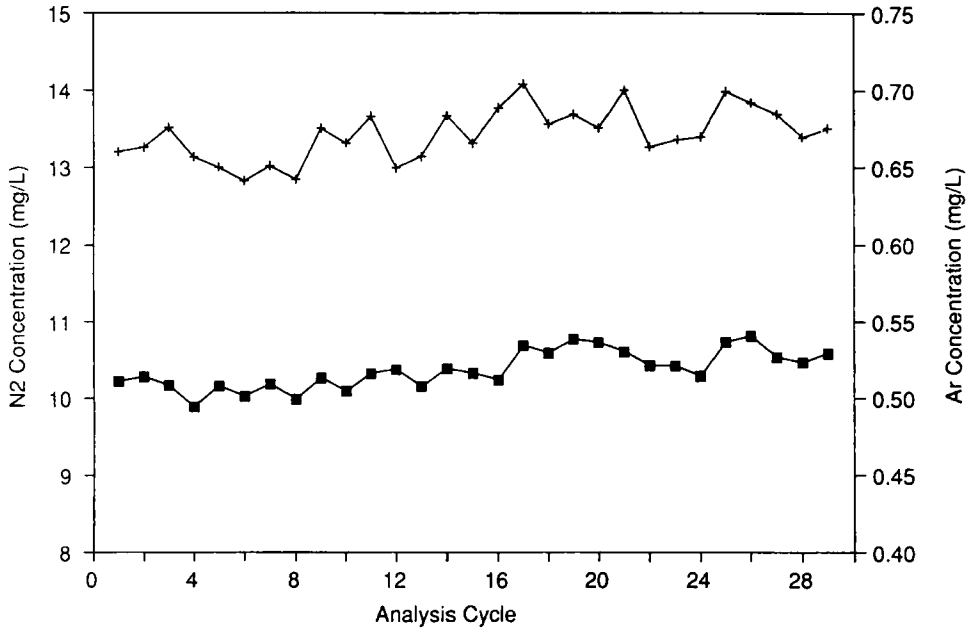

Figure 6 Variation of argon and nitrogen concentrations in water exposed to ambient air. ■ - Ar, + - N_2.

valve outlet to the beaker provided exposure of water to ambient air. The concentration corresponding to each cycle was the average result of the five water analyses conducted in the cycle and were calibrated against the average of the standard responses before and after the five water analyses. The concentrations of Ar and N_2 determined by the system agreed well with the solubilities listed in the Handbook of Chemistry and Physics.[25]

The analytical and oxygen-removal columns were deactivated normally after 100 to 150 water analyses. This was not observed for analyses with gas injections only. The resolution of Ar and N_2 was reduced and O_2 broke through the remover, possibly due to CO_2 or H_2O poisoning of the molecular sieve column and saturation/poisoning of the oxygen-removal column. This necessitated reconditioning of columns at 250°C for 24 hours with 20 mL/min of helium, with the HID disconnected from the columns and sealed. This "heating with helium purge" approach restored the column performance.

The other way for regeneration of the oxygen-removal column was to pass hydrogen through the column at 120°C for 1 to 2 hours. This approach proved to be more cumbersome, because it required separate conditioning of the analytical column and the oxygen-removal column. Also, in order to avoid contamination of the system by impurities in hydrogen, the oxygen-removal column had to be disconnected from the system during regeneration. In doing so, some safety precautions should be considered, i.e. venting the hydrogen properly to avoid potential explosion hazards.

Acknowledgements

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