Supplementary Information (SI) for Analyst.

Supplementary Information

Improving the Resolution of Permanent Gas Analytes Using Solvent Gas in Gas Chromatography

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1. Experimental Details:

GC operations: The instrument used to conduct the studies was an Agilent 7820A Gas Chromatograph equipped with a 30 m Carboxen 1010 PLOT column. Split injection, with a split ratio of 4:1, was used. In a typical experiment, a total of 500 μL of a mixture containing solvent gas and sample gas was injected manually using an air-tight syringe. Typical temperature programming was as follows: Isothermal conditions at 35°C held for 4.5 minutes before ramping at a rate of 40°C/min to a final temperature of 225°C and held for an additional 5 minutes. Ramping conditions held at 35°C for 1 minute before ramping at a rate of 40°C/min to a final temperature of 225°C and held for an additional 5 minutes. Inlet temperature was maintained at 200°C for both conditions. A thermal conductivity detector (TCD) was used to measure the elutes.

Surface modification of stationary phase: Surface modification was performed by injection of a quantity (200-1000 μL) of CO_2 (g) into the column without temperature ramping, held at 35°C for approximately 15 minutes. The analyte sample was then injected for analysis.

He pulse experiment: The He band passing through air was performed by first an injection of 30 μL of air followed by an injection of 500 μL of helium after a delay of 20 seconds. Oven temperature was maintained at 35°C.

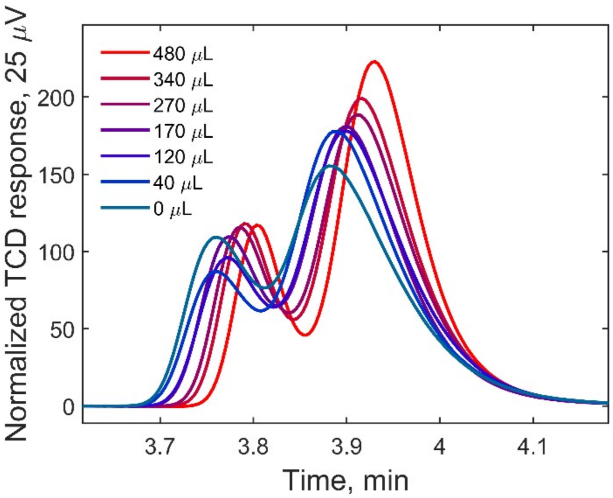

Figure S1. Various amounts of helium added as solvent gas to sample of air and argon. Total volume of injection was held constant at 500 μL, with 20 μL of air, varied amounts of helium as listed in legend, and the remaining volume filled with argon.

2. Van't Hoff Model:

The Van't Hoff equation for an ideal thermodynamic model of column-solute interactions can be written as:

$$\ln k = \frac{G_H}{RT} - \frac{G_S}{R} + \ln 4\phi \tag{1}$$

Where k represents the retention factor which is dependent on the column-solute interactions. G_H and G_S represent the enthalpy and entropy, respectively, of the column-solute interaction thermodynamics. R is the ideal gas constant and T is thermodynamic temperature, while ϕ is the adsorbed gas film thickness relative to the internal diameter of the column (unitless).[1]

Since the observed retention time is dependent on the retention factor, k, the time at the maximum of the N_2 and O_2 bands were used as a proportional measurement of the retention factor. Due to this approximation, enthalpy and entropy values obtained from the Van't Hoff linear fitting may not represent the true enthalpy and entropy of the column-solute interaction. However, by comparing the thermodynamics of N_2 and O_2 injection with and without solvent gas, some valuable information can be extracted.

The evaluation of the enthalpy for the N_2 Van't Hoff equation reveals subtle differences between the conditions with and without solvent gas. The slope corresponds to $C\frac{G_H}{R}$, where C is some correction for the approximation of using retention time (t_r) instead of the retention factor, k. In the case of N_2 alone versus the slopes of N_2 with CO_2 and H_2 as the solvent gases, only small variation is found (+0.91% change for CO_2 and -0.99% change for H_2). With such small deviation of enthalpy, it is assumed that the thermodynamics of the N_2-column interactions are unaffected by the additional solvent gas. This assumption relies on the insignificant effect of adsorbed CO_2 on the sorption thermodynamics of N_2. This may be rationalized by considering the N_2-CO_2 interaction is likely much less substantial than N_2-column interactions, as well as the fast separation of N_2 from CO_2, which means the resultant retention time relies mostly on the column. Additionally, the N_2 interaction with the column will be consistent despite higher occupancy of the sorption sites by CO_2, assuming mostly monolayer adsorption.

Considering that the thermodynamics are likely to remain unchanged, the measured change in the y-intercept must correspond to the film thickness change, as the intercept is represented by: $-C\frac{G_S}{R} + \ln 4\phi$, with some correction factor for entropy, where the variable of interest is ϕ. Equating $C\frac{G_S}{R}$ between the slopes of N_2 obtained without and with solvent gas, the relative change in the adsorbed film thickness of N_2 can be evaluated by:

$$b_1 - b_2 = \ln\frac{\phi_1}{\phi_2} \qquad (2)$$

Where b is the intercept determined by the plots in Figure S2. In this case, the film thicknesses which are compared by the ratio of $\phi_1:\phi_2$, correspond to the thickness of N_2 only. When comparing the intercepts of N_2 without solvent and N_2 with CO_2 solvent gas, an approximately 4% decrease in the N_2 film thickness is observed for the latter case. Therefore, the CO_2 acts to compete with surface sites, effectively decreasing the observed N_2 film thickness. On the other hand, we see that the film thickness of N_2 increases by approximately 2% when H_2 is used as the solvent gas. The results of such analysis are summarized in Table S1.

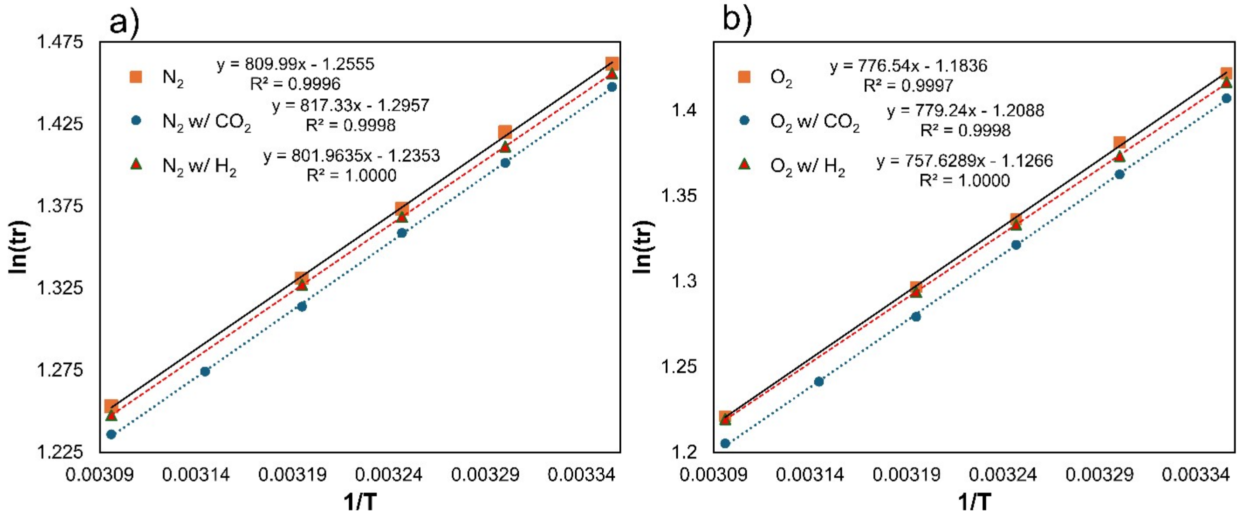

Figure S2. The Van't Hoff plots using the dependence of retention time on temperature to extract enthalpic and entropic information, linear fitting results included subset into each plot next to corresponding legend entry. The measurements with solvent gases were performed with co-injection of the mixture of 20 μL of air sample and 480 μL of solvent gas.

Table S1. Summary of Van't Hoff equation (equation 1 and 2) fitting results. Relative film thickness compared to results obtained without solvent gas.

Experiment	**Slope**	**Intercept**	**Relative film thickness of adsorbed N_2 or O_2**
N_2	809.99	-1.255	1.0000
N_2 with CO_2	817.33	-1.2957	0.9601
N_2 with H_2	801.96	-1.2353	1.0199
O_2	776.54	-1.1836	1.0000
O_2 with CO_2	779.24	-1.2088	0.9751
O_2 with H_2	757.63	-1.1266	1.0587

3. Competitive Isotherm Explanation:

The adsorption of Ar on the column surface in the presence of He can be estimated using a competitive isotherm model described by the following equation

$$\theta_{Ar} = \frac{K_{eq}^{Ar} p_{Ar}}{1 + K_{eq}^{Ar} p_{Ar} + K_{eq}^{solv} p_{solv}}, \qquad (3)$$

where the fractional coverage of argon, θ_{Ar}, depends on the partial pressures of argon and the solvent gas, p_{Ar} and p_{solv}, respectively, and the adsorption equilibrium constants of argon and solvent gas on the column surface, are K_{eq}^{Ar} and K_{eq}^{solv}, respectively. At low temperature (e.g., 35 °C), the adsorption of Ar on the column is assumed to be appreciable.[2] Upon the injection of He, the Ar molecules adsorbed on the column surface desorb with the increase of the partial pressure of He (p_{He}), leading to the improvement of resolution. However, the He pulse experiment presented in Figure 2b does not substantially improve the separation efficiency, suggesting the importance of co-injection of He (solvent gas) and analyte air. The adsorption of Ar exhibits a nonlinear dependence on p_{He} (eq. 3, Figure S3). In the process of He pulse injection, the He band has time to mix with the carrier gas of Ar, lowering p_{He}. The effective surface coverage of Ar goes from ~0% at p_{Ar} = ~0% (i.e., p_{He} = 100%) to ~40% at p_{Ar} = 20% (i.e., p_{He} = 80%). Since a small amount of Ar mixing with He could greatly increase Ar coverage on the column surface, the He pulse experiment fails to improve the resolution. On the other hand, the co-injection of helium and analyte takes advantage of the high $p_{He}$when He is undiluted by Ar, producing a better separation efficiency. Another possible contribution to the narrowing of analyte peaks is the reverse diffusion caused by imbalanced interdiffusion between carrier gas and solvent gas. Numerical calculations of the Maxwell-Stefan diffusion equations suggest that reverse diffusion of carrier gas could provide a narrowing effect on the analyte by focusing the band over time rather than broadening (Section 4, Figure S4 and S5).

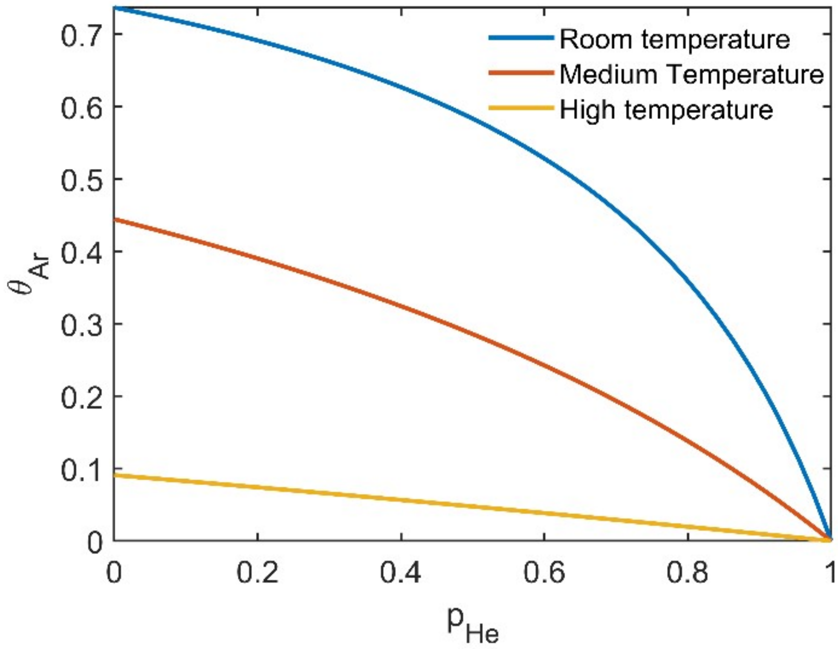

Figure S3. Surface coverage of argon in response to the change of partial pressure of helium carrier gas in different “temperature” scenarios, calculated from the competitive isotherm adsorption (equation 3). The K_{eq} values used were 0.0001 for He and 2.8, 0.8, and 0.1 for the room temperature, medium high temperature, and high temperature equilibria of Ar, respectively.

4. Maxwell-Stefan Diffusion Modelling for Reverse Diffusion

Maxwell-Stefan Diffusion Modelling - The basis of the calculation was performed using a modified version of the Matlab script written by Scott Rowe.[3] The conditions were then predicted up to 6 seconds of equilibration assuming an initial width of the ternary "injected" gas of 6.89 cm which approximates the length of 500 μL injection volume of gas in the GC liner (4 mm ID x 8 cm). Gas flow and movement were not considered during the calculation except to determine the approximate equilibration time. The model calculates a mixture of nitrogen, helium, and argon diffusing from the middle into pure argon surroundings in a 1-dimensional calculation. The ratio of N_2:He was varied to imitate the injections performed experimentally, in which nitrogen was held in a constant quantity, while helium and/or argon were premixed with nitrogen to keep the volume of N_2 was held constant at 30 μL and the total volume held constant at 500 μL.

The physical effects of helium and hydrogen mixtures were explored using numerical calculations of the Maxwell-Stefan diffusion equations under conditions analogous to the co-injection scenario in the injector. Nitrogen was used as the analogue of air, in which changing fractions of N_2:He with constant volume was assumed by backfilling with argon. Since the scope of this work is only to gain insight into the band narrowing mechanism in the inlet, the injected ternary gas mixture of varying N_2:He backfilled with argon was modelled in only a 1-dimensional diffusion condition. In this scenario, it is assumed that the gas mixture is filling the liner of the GC across the diameter, while the only diffusion direction is longitudinal.

For the case of ternary diffusion, the Maxwell-Stefan equations can explain the observed non-Fickian diffusion, where concentration gradients do not predict the direction of the diffusion.[4]

This diffusion can be predicted via the binary coefficients of each gas involved, which were taken from NIST gaseous diffusion standards[5] calculated at the inlet temperature setting of 200°C. The resident time of the injected gas in the liner is approximately 3 seconds before entering the column. Gas flow and movement were not considered during the calculation except to determine the approximate equilibration time. Under these conditions, which resemble the true inlet conditions, nitrogen is expected to concentrate in the center of the “injected” gas (Figure S4, S5).

The “uphill diffusion” of nitrogen may offer a reasonable explanation for the band focusing effect, which is observed in the case of hydrogen and helium solvent gases. This focusing effect is heavily reliant on the carrier gas, as the diffusion of the solvent gas with the carrier gas must be fast, while diffusion of the analyte with the carrier gas must be substantially slow enough to notice this effect. When working with permanent gases, these combinations will be limited primarily to slower carrier gases (Ar, N_2, CO_2) and fast solvent gases (H_2 and He). However, noticeable improvements in the band widths and resolution can easily be obtained without the need to alter the column or chromatographic method.

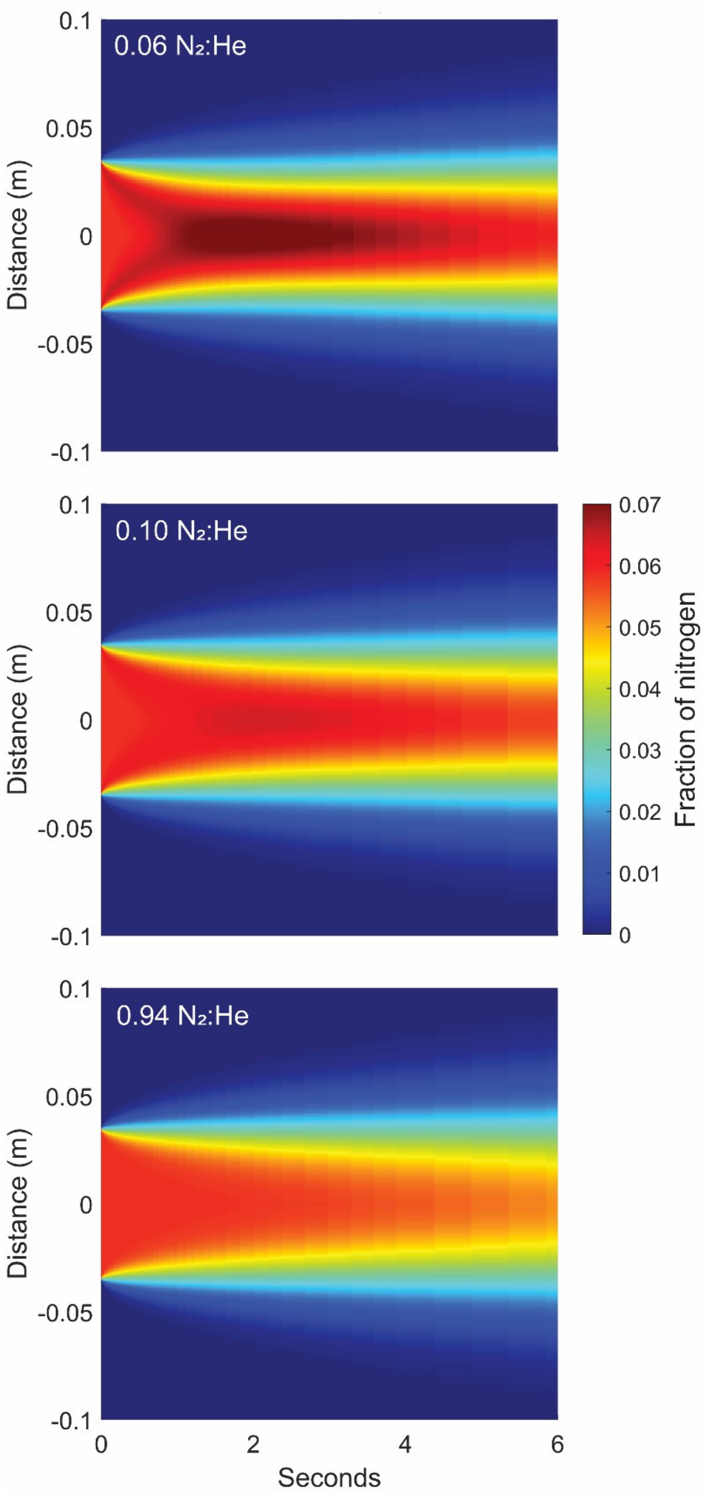

Figure S4. Modeling results of nitrogen, helium, and argon mixture diffusing into pure argon. Legend indicates the ratio of N_2:He. The volume of N_2 was held constant at 30 µL and the total volume was held constant at 500 µL by premixing with Ar. Low ratio indicates more helium added.

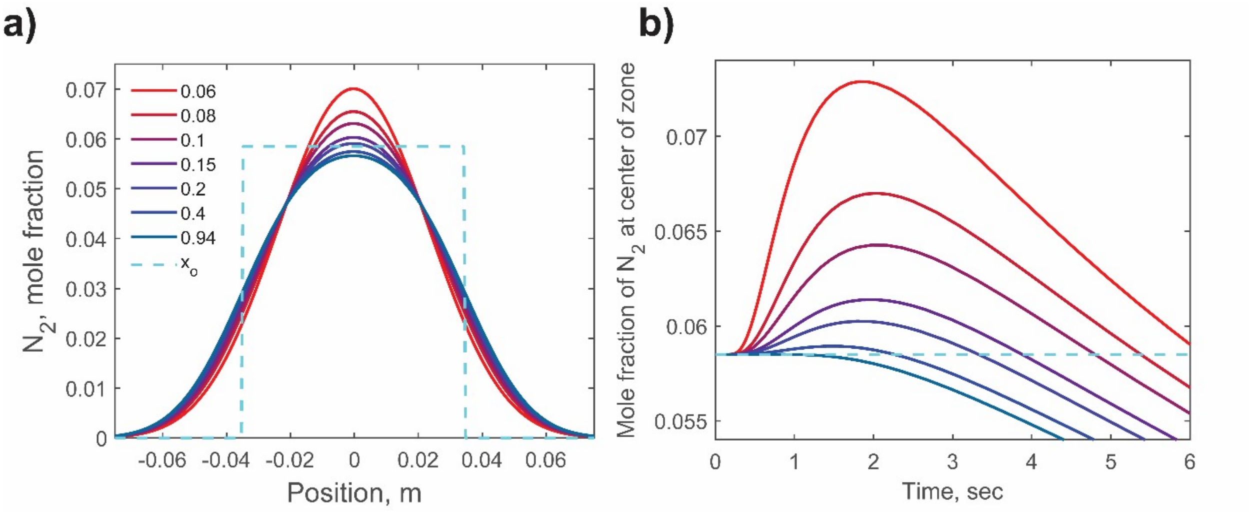

Figure S5. a) Cross-sections showing the mole fraction of nitrogen distribution after 3 seconds of diffusing under different N_2:He ratios. b) Mole fraction of nitrogen at the center of the distribution over time under different N_2:He ratios. Legend indicates the ratio of N_2:He. Low ratio means more helium added. The colors of the plots in both (a) and (b) are coded for the same N_2:He ratios. The dashed, light blue line indicates the starting mole fraction of nitrogen for reference.

References

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