

Interactive comment on “Dynamic Solution Injection: a new method for preparing pptv-ppbv standard atmospheres of volatile organic compounds” by K. J. Jardine et al.

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Response to Reviewer 1

We greatly thank reviewer 1 for recognizing some of the advantages of the Dynamic Solution Injection (DSI) method for the generation of VOC standard atmospheres presented in this manuscript and for the helpful suggestions of how to make our manuscript better. Our responses to each comment are below.

Comment 1 Based on the description and data presented in the article, DSI definitely seems to be a valid method for producing dynamic gas phase standards of VOCs at
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mixing ratios relevant to ambient atmospheric studies. Especially in the category of cost and simplicity, this calibration method seems attractive (depending on the cost of the liquid pump).

Response 1 The cost of the liquid pump is roughly the same price as a single high quality mass flow controller commonly used with compressed gas standards and permeation/diffusion tubes (cost of liquid pump was \$2,700 in January, 2010).

Comment 2 The claims of accuracy made in the manuscript, and in particular the claim that the DSI method is more accurate than using CG standards and PTs is not conclusively supported by the data presented. The observed discrepancy when calibration curves are compared between standards prepared using DSI versus CG standards and PTs cannot necessarily be attributed to the latter methods. The fact that responses for the CG and PT methods are lower than those for DSI suggests VOC losses in the calibration system; however, there are other possibilities. Accuracy issues associated with making dilute solutions of the VOCs listed in table 1 could lead to the observed discrepancies. Especially when these solutions were produced by delivering volumes as small as 5 μL . If this was accomplished using a GC syringe, the error could be large. Poorly calibrated or misused mechanical action micropipets can also lead to large volume errors.

Response 2 We agree that preparing solutions (using a GC syringe) could result in additional errors for the DSI technique which we did not take into account. If our article is accepted for publication, we will change the following:

Materials and Methods Change: “Each solution was prepared by diluting 5.0 μL each of an authentic, neat liquid standard (Sigma-Aldrich) in 100 ml of the appropriate solvent to produce concentrations in the range of 0.22 to 0.89 mM.”

To: Using a 10 μL GC syringe and a 100 mL volumetric flask, each solution was prepared by diluting 5 μL each of an authentic, neat liquid standard (Sigma-Aldrich) in 100 ml of the appropriate solvent to produce concentrations in the range of 0.22 to 0.89

mM.”

Abstract Change: “This implies that concentration measurements of some VOCs may be overestimated using permeation tubes and/or compressed gas cylinders for calibration.”

To: “These differences suggest VOC losses in the permeation tube and compressed gas calibration systems but may also be related to other errors including permeation tube oven temperatures and VOC solution concentrations used in the DSI technique.”

Change: “Because of its high accuracy and precision, small size, low cost, and simplicity, we conclude that the Dynamic Solution Injection method will be of great use to both laboratory and field VOC studies.”

To: “Because of its small size, low cost, and simplicity, we conclude that the Dynamic Solution Injection method will be of great use to both laboratory and field VOC studies.

Conclusion Change: “Dynamic methods for the generation of low concentration gas standards are preferred due to the minimization of wall effects, but the current techniques (permeation and diffusion tubes) can suffer from low accuracy that can change over time, long calibration times, high costs, low compound availability, and difficulties preparing complex mixtures.”

To: “Dynamic methods for the generation of low concentration gas standards are preferred due to the minimization of wall effects, but the current techniques (permeation and diffusion tubes) can suffer from long calibration times, high costs, low compound availability, and difficulties preparing complex mixtures.”

Change: “The flexibility and versatility of the DSI system stems from the fact that liquid calibration solutions containing complex mixtures of VOCs can be used to generate a wide range of gas-phase concentrations with high accuracy and precision.”

To: “The flexibility and versatility of the DSI system stems from the fact that liquid calibration solutions containing complex mixtures of VOCs can be used to dynamically

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generate a wide range of gas-phase concentrations.

Change: “These results suggest that for some compounds, permeation tubes and compressed gas cylinders generate lower concentrations than initially certified. This would result in an overestimation of VOC concentrations in air samples by up to a factor of 2. This may be due to loss processes that are difficult to characterize including absorptive losses in gas cylinders, chemical decomposition processes in permeation tubes, and changes in permeation tube membrane properties over time.”

To: “Among other possibilities, these results may be due to absorptive losses in the gas cylinder, chemical decomposition processes in the permeation tubes, possible discrepancies in permeation rates determined gravimetrically and actual compound permeation rates, and errors in the permeation tube oven temperature used relative to the temperature used by the manufacturer for certification. However, errors associated with volumetrically preparing the VOC solutions used in the DSI system could also contribute to the observed discrepancies.”

Comment 3 Another possible issue could be with the permeation tubes. The manuscript does not state how the permeation rates were determined, which can have a large effect on the calculated mixing ratio of the final standard gas.

Response 3 Permeation tubes used in this experiment were purchased commercially from Kintek Laboratories (www.kintek.com) with permeation rates determined gravimetrically and not with a GC technique. In the new manuscript, we will change the following. Change: “For acetone, ethanol, and α -pinene, National Institute of Standards and Technologies (NIST) traceable permeation tubes (KIN-TEK Laboratories, Inc.) placed in a temperature controlled permeation chamber (VICI Valco Instruments Co. Inc.) with 100 sccm of UHP nitrogen flowing through was used to generate known concentrations of acetone (456 ppbv), ethanol (579 ppbv), and α -pinene (313 ppbv).”

To: “For acetone, ethanol, and α -pinene, gravimetrically certified permeation tubes (KIN-TEK Laboratories, Inc.) placed in a temperature controlled permeation chamber

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(VICI Valco Instruments Co. Inc.) with 100 sccm of UHP nitrogen flowing through was used to generate known concentrations of acetone (456 ppbv), ethanol (579 ppbv), and α -pinene (313 ppbv)."

Comment 4 In several places, the manuscript states that the DSI method is field portable relative to other calibration generation methods such as CG and PT methods. The DSI method, as with the other methods, requires a dilution gas. In the field, the dilution gas is usually a tank of compressed zero air or UHP nitrogen. The authors should be more explicit in what they intend when they say 'field portable'.

Response 4 We will make the following changes to the manuscript to explain what we intend when we say "field portable".

Conclusion Change: "Another major advantage of the DSI technique is the low consumption rate of the purified dilution gas. Unlike diffusion and permeation tube methods where the calibration gas concentrations are achieved by dilution with high flow rates of UHP N₂ or zero air, the DSI technique utilizes a constant 1.0 slpm of dilution gas."

To: "The DSI system is more field portable relative to other calibration techniques due to its small size (pump: 2.0 in x 2.3 in x 7.1 in) and weight (1.7 kg with all components). It eliminates the need for bulky temperature controlled permeation/diffusion tube ovens and compressed gas VOC cylinders. Like conventional methods, the DSI method requires a dilution gas, but the flow rate is low (1.0 slpm) and could easily be generated in the field from ambient air using a small catalytic converter/pump system. Because many VOCs will oxidize in permeation tube ovens at elevated temperatures, it is not possible to use air as the carrier gas through permeation chambers. Therefore, the DSI VOC calibration method could potentially operate free of compressed gas cylinders."

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