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Atmospheric Measurement Techniques
Discussions

Interactive comment on "A versatile, refrigerant-free cryofocusing-thermodesorption unit for preconcentration of traces gases in air" *by* F. Obersteiner et al.

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Some general comments: This manuscript describes the relatively simple design of a custom-designed preconcentration unit, which employs a Stirling cooler as the cold source for cryogenic preconcentration of trace atmospheric compounds. The basic design is common to several of their instruments, results of which have been published recently. The lack of need for an insulating vacuum chamber for these cold parts is an appealing characteristic as it greatly simplifies design, reduces cost and weight. The rapid analysis time that they have achieved also makes this a desirable field and laboratory instrument. The focus of the current manuscript is a detailed description and characterization common to these instruments, going beyond what was published

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in Hoker et al., 2015, Obersteiner et al., 2016 and Sala et al., 2014. The authors do present in-depth results of the chromatographic peak shape resulting from cryofocus and subsequent desorption of analytes. They also discuss results from analyte breakthrough tests and report some of their findings of system contamination.

I appreciated the depth of investigation of the ‘analyte residues’ issue. In such preconcentration methodologies, and at such low analyte mole fractions, these contamination issues can be a very difficult problem to investigate and rectify. So by sharing their observations, the authors are contributing to a knowledge base that may someday be useful in developing some remedies.

To add to the value of this residue investigation, I would like to see them include, for example in Table 4, which analyte contaminations they attribute to ‘carry-over’ from a previous sample, versus those derived from system hardware (e.g., outgassing of polymers, or desorption from surfaces), versus those derived from the carrier gas. In the text, they do allude to such finding with regard to a select set of analytes, but stop short of specification for each of the dozens of compounds listed in the table. Undoubtedly, there will be some analytes for which attribution is not readily discernible, but I would hope that they are able to elaborate with more useful details regarding more clear-cut cases.

Results from Table 4 present some difficulty in interpretation. For example, iodomethane shows a HayeSep D residue of 43.9%. This is, as defined in the caption, the ratio of the blank gas response to the preceding 1 L air sample, expressed as a percentage. The blank gas injection is defined as an injection of purified helium. From this information, we cannot deduce whether this high percentage is attributable to carry-over of analyte from the air injection into the subsequent blank injection, or if the carrier gas is contaminated with an iodomethane-like substance or if some hardware upstream from the adsorbent tube is outgassing or desorbing the contamination.

Further difficulty in interpreting table 4 stems from the precision limitation that they im-

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pose. The authors exclude analytes from Table 4 that show "...show poor precision $\geq$ 10%." With a 43.9% residue of unknown origin, how is a <10% precision justified for including iodomethane in this table? If this contamination comes from the carrier gas, and therefore might be assumed constant, one could correct responses accordingly, and obtain reasonable precisions and accuracies despite contamination. But carry-over requires a very different data work-up (e.g., modeling the carry-over). Some explanation is in order here. There are other examples, e.g., HFO-1234yf, chloroethane, tetrachloroethene, etc.

In reading the manuscript, it seemed odd to me that they omitted detailed analysis long-term reproducibility results, which for me is one of the principle 'bottom-line' results of characterization. The sharp, Gaussian-shaped peaks that they obtain are indeed a desirable trait of such an instrument. But in the intended applications of such an instrument, the value in the measurements comes from short-term repeatability and/or long-term reproducibility. For a repeatability example, in their aircraft application, what uncertainties might one expect in a vertical profile so that an observed altitude gradient was statistically discernible, or not? In a long-term monitoring application with flasks (i.e., their laboratory instrument), they present a favorable comparison with the AGAGE Medusa instrument at Mace Head, Ireland, for one compound, CFC-12 over one summer. But for characterizing long-term reproducibility suitable for such monitoring programs, one needs to demonstrate this on time-scales of a year or more to argue the potential for comparability and compatibility of datasets. The one brief comparison example falls short of proving the "highly accurate measurement results" that they claim, and it would be beneficial to see reproducibility results for all compounds for which they believe their instrument is suitable to measure.

Another component of characterization that they authors appeared to have overlooked is the potential for CO2-induced artifacts. The methodology appears to offer little in terms of mitigating the presence of this atmospheric constituent that is a million times more abundant than their target analytes. They do make the point that they do not

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attempt analysis of analytes which elute under the CO2. On their 20 mg of adsorbent, chilled to -80 C or -120 C, they need to show that the co-adsorption of CO2 does not adversely affect adsorption and/or desorption of their analytes. Consider that a 1-L sample of ambient air has order 0.4 ml STP of pure CO2, enough gas to fill a 50 cm length of their 1 mm I.D. tubing. While it is unlikely that they have quantitative adsorption of all the CO2, we aren't given any evidence that sufficient CO2 does not remain to disrupt the desorption of the other analytes and/or disrupt the sensitivity of the detector. In instruments in which no CO2 mitigation is performed, I have observed the co-desorption of CO2 to cause peak width and shape changes in certain co-adsorbed analytes. I have also observed short-term MS detector response reduction due to injection of CO2-containing samples, with subsequent 'rebound' in sensitivity with CO2-free samples. An experiment that the authors could perform to examine this detector issue is to sequence injections of CO2-containing and CO2-free air-like mixtures mixed in with injections of a reference standard gas. If the amount of injected CO2 is having an effect on the reference gas sensitivity, it will be apparent when the sample preceding the reference contained or did not contain CO2.

Table 2 and corresponding text present unbelievably precise chromatographic retention times, given that this represents 112 injections of various samples. Are these the correct units? Taking CFC-11 for example, 0.006%/100*7.25s*60s/min yields 0.19s standard deviation for the CFC-11 retention time. Also, if the fourth column truly is a variance, then the units would be the square of the measurement units, i.e., sec(sup)2. Same applies to line 25 of page 13, where the units would be sec(sup)2.

Retention times vary over time scales on the order of a week in such instruments due to several factors. First, their retention times should vary inversely with ambient pressure. Their electronic pressure control (EPC) of their gas chromatograph references atmospheric pressure such that as ambient pressure increases, the chromatographic pressure gradient between EPC and the absolute vacuum of the detector increases, causing retention time to decrease. Another run-to-run variable is the flow resistance of the gas in the heated adsorbent tube. Figure 3 illustrates quite large temperature oscillations during desorption. Are these oscillations really so reproducible that the gas viscosity is identical in each run?

The authors are commended for making the substance breakthrough experiments. However, their conclusions regarding “quantitative trapping” (e.g., page 11, line 8) are only valid if one assumes that the instrument is linear in response, an assumption for which no evidence is provided. For example, the greater than 100% response ratio of ethyne may be attributable to “memory effect” as they claim, but the 0.3% to 1.4% ‘residue’ for ethyne listed in table 4 does not support the observed 109% ‘breakthrough result’ reported in table 2. There are more definitive tests for characterizing breakthrough, several of which are described in the 1999 thesis work of Dr. Brian Greally from the University of Bristol, UK. Use of the technique of varying the volume of sample gas is one method to examine system non-linearities, but this must be accompanied by a confirming technique such as analysis of a suite of air-like gases of differing analyte mole fraction.

Specific comments:

The authors refer to their micro-packed adsorbent tube as a ‘sample loop’, which I find an unusual use of the term. The use of the term ‘sample loop’ in the general literature usually refers to an open tubular device which is used to measure the sample volume, typically by pressure measurement under fixed temperature and volume assumptions. I would suggest using a more common terminology for their adsorbent tube.

Pg. 3, line 9: LN2 and Ar used for cooling in these kinds of instruments are not typical examples of ‘refrigerants’, but of cryogens. Refrigerants undergo expansion (cooling) and subsequent recompression cycles.

Pg. 4, line 28: “self-written control software” should be changed to “custom-written” or similar.

Pg. 10, line 19: "…strips the air of its most abundant constituents…" makes it sound like you are preconcentrating N2, O2, etc., and not the trace target compounds.

Pg. 14, line 16: "In general, most of the detected analyte residues are most probably caused by system contaminations (HFCs from fittings, solenoid valve membrane etc.) …" By 'solenoid valve membranes, are you referring to those in the EPCs?

Table 4 caption: Why is it that some analytes that show large residues, e.g., iodomethane at 43.9% for HayeSep D, are included in this table when the caption states that those that "…show poor precision $\geq$ 10% were excluded?"

Figure 4 caption and elsewhere: "n-propane" should be simply "propane".

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