

A Third-Generation Electron Capture Gas Chromatograph System for the Analysis of Ozone-Depleting Chemicals in Flask-Air Samples.

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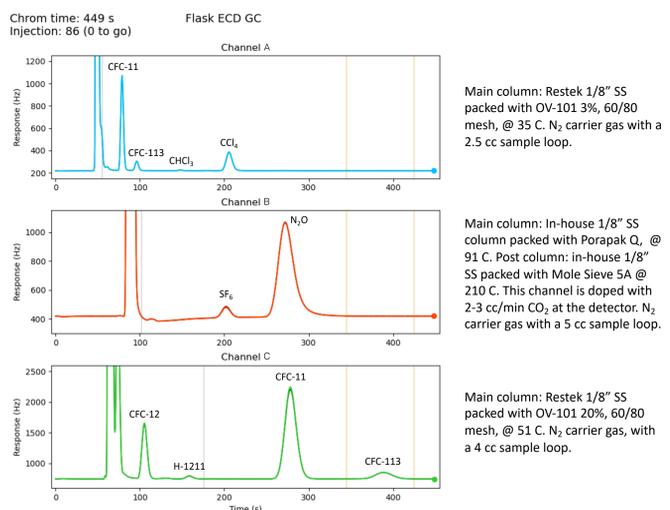


Abstract

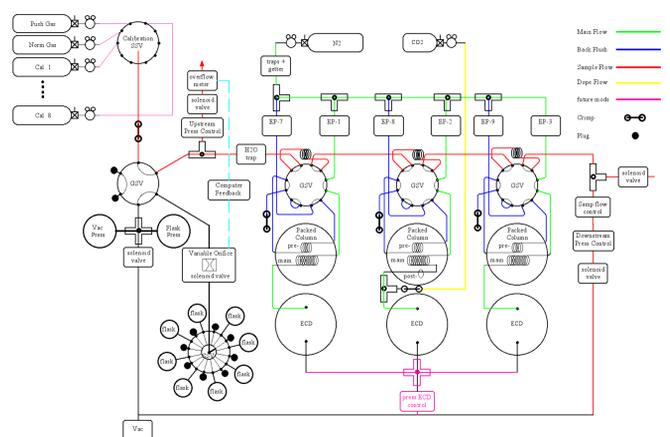
The HATS group of NOAA's Global Monitoring Laboratory (GML) has been measuring chlorofluorocarbons (CFCs) and other ozone-depleting, trace-level gases collected in stainless steel and glass flasks from a global network of field sites since the late 1970s. The original system in use at the program's inception was a gas chromatograph with electron capture detection (GC-ECD) for the measurement of CFC-11, CFC-12 and N₂O. The HATS flask program has expanded greatly since then to measure many more trace gases at many more sites using a variety of gas chromatograph systems outfitted either with electron capture detectors or with mass selective detectors. Recently, our second-generation GC-ECD system, colloquially known as "Otto", was retired after 25 years in operational service. This poster will introduce its successor: a 3-channel GC-ECD system ("FE3") centered around an Agilent 7890b gas chromatograph for highly-precise and accurate measurements of CFC-11, CFC-12, CFC-113, CCl₄, H-1211, CHCl₃, N₂O and SF₆. We will describe some of the unique design features that differentiate this system from its immediate predecessor. We will also show some comparisons between results from this new system and other systems within GML.

Chromatography

FE3 has redundant measures of CFC-11 and CFC-113 on channels A and C. However, the peaks on channel C, while generally less precise than those on channel A, have the advantage of being better separated and less prone to interferences from other small, nearby peaks that turn up intermittently, especially at certain sites that are characteristically more urban/continental. CHCl₃ is the smallest peak, but it has a large dynamic range that far outreaches its calibration curve.



Plumbing Diagram



Advances

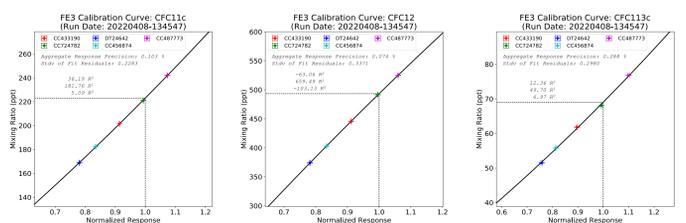
FE3's predecessor was developed in the early 1990's around a Hewlett-Packard 5890 GC. Otto pulled a vacuum on the sample loops between injections and flushed any remnants of the previous sample from the loops with a relatively high volume of new sample. Each of its chromatograms took 22 minutes to produce.

The sample loading system utilized by FE3 takes advantage of new techniques developed by Dr. Fred Moore for the HATS group's new StratCore analysis system. A small volume of sample is pushed through the sample loops at a gentle, well-controlled pace of 30 cc/min. This results in laminar flow through the plumbing without turbulent mixing, and a clean displacement of the gas in the sample loops at the start of the load process. Injections that alternate background air with zero air show no detectable evidence of hysteresis from one injection to the next. Each injection of flask air on FE3 uses ~40 std ccs of sample volume and runs in only 7.5 minutes. The savings in time and sample usage allow for 4 injections from a single flask per hour when alternating with a normalizing reference. This has led to substantial improvements in analysis precision and efficiency.

Calibration

Otto alternated flask sample injections with samples from two reference standards. One standard was unaltered background air. The other was background air diluted by about 10% with "zero air" (a standard mixture of N₂, O₂, and Ar scrubbed of other impurities). The idea was to bracket the flask samples with standards samples of similar concentration, but with enough separation to interpolate - or mildly extrapolate - the value of an air sample along a localized, two-point calibration line. This method suffered from stability issues tied to measurement noise, and also from accuracy issues related to analytical biases unique to each standard. Both issues were greatly magnified when the two standards were insufficiently separated in value. Because of this, and also because of the occasional tendency for an unstable reference peak to drift in value over time, a great deal of post-processing work was performed to compensate.

FE3 takes a different approach by generating calibration curves fitted to the responses of five reference standards normalized by an undefined, background reference. The standards nominally range in value from ~75% of background up to ~110%. Experiments to rederive the calibration curves are run every 1-2 weeks to track any significant changes in instrument response. These curves are then used to compute mixing ratios for the flask samples that are run in the interim. Flask samples must be normalized by the same background reference used to normalize the standards during a calibration run. This approach dramatically mitigates the calibration issues noted above, and it conserves valuable standards gases at the expense of the undefined normalizing reference.

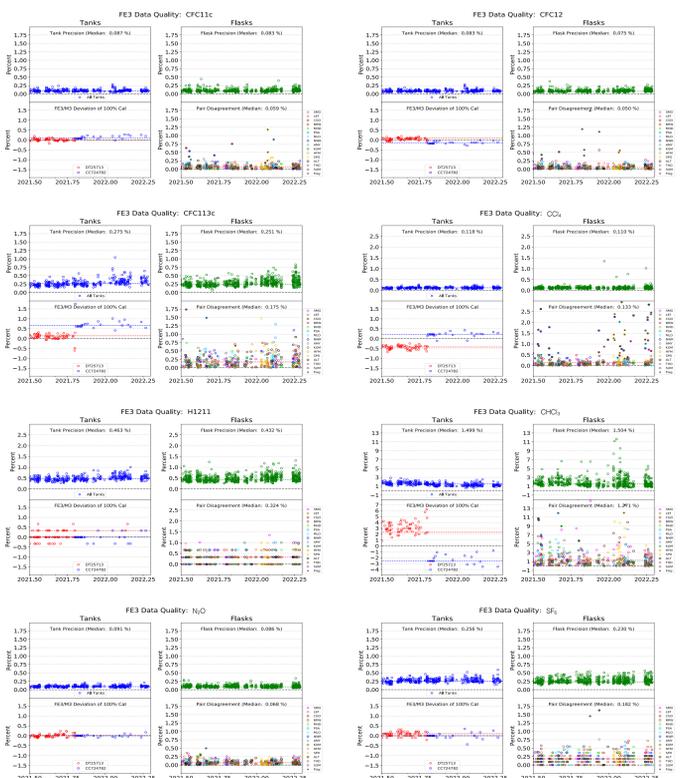


Precision

Precisions are similar for reference gas injections and flask sample injections across all peaks. These are better than 0.1% for CFC-11, CFC-12, and N₂O, ~0.1% for CCl₄, ~0.25% for CFC-113 and SF₆, ~0.5% for H-1211, and ~1.5% for CHCl₃.

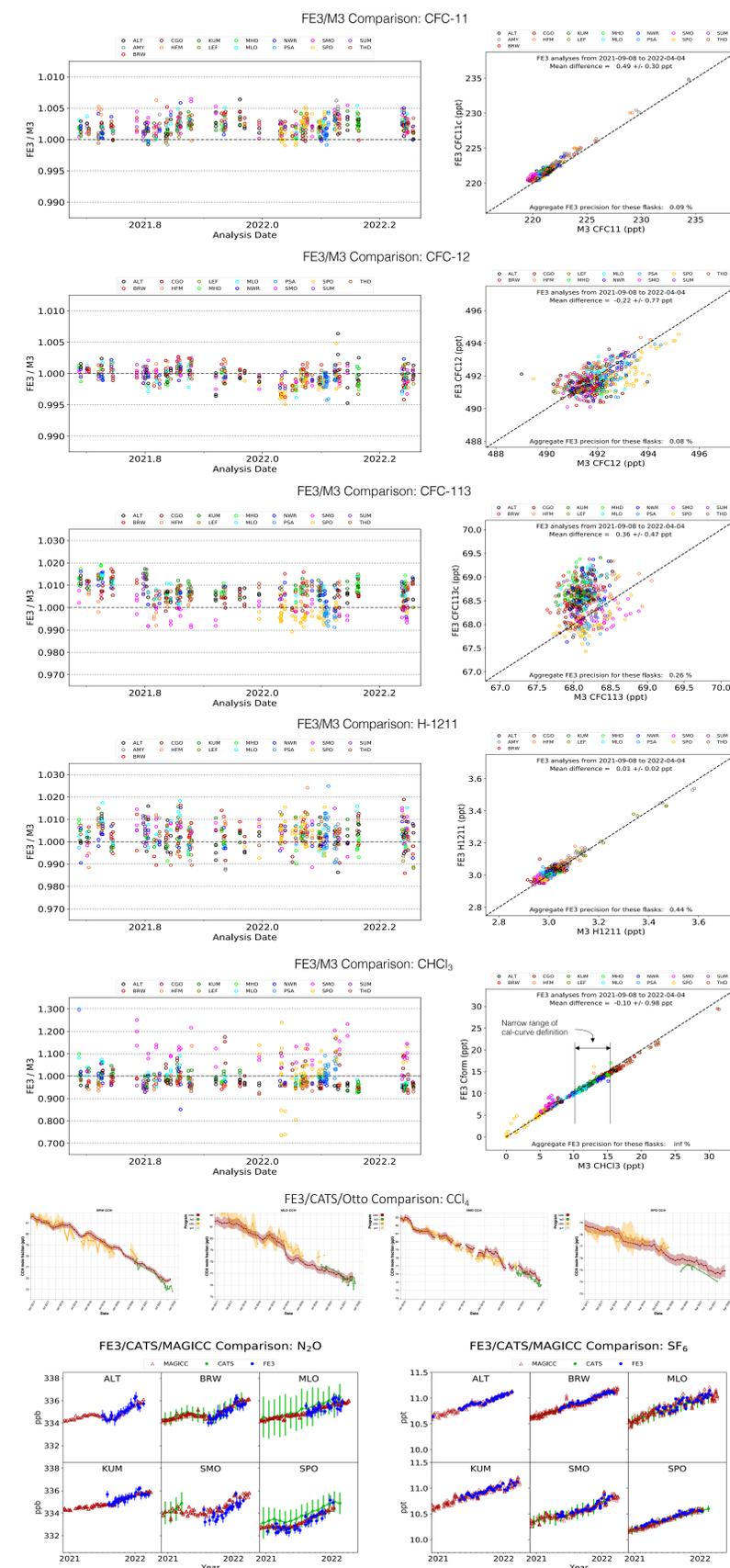
Samples are collected in two concurrently-filled flasks, and the results from each are compared for QC purposes. When the results disagree, a sample pair is flagged. In each of the 4-panel plots below, the lower right panel gives a feel for how many pairs are rejected for disagreement. The high proportion of CCl₄ samples rejected mostly stems from a known loss issue for samples collected in stainless steel flasks at dry field sites (dry samples collected in glass flasks are largely immune). [Note: discrete vertical steps observed in the plots below (see H-1211, e.g.) are the result of an excessively rounded storage format.]

The lower left panels give an indication of the potential analytical bias that can be associated with each reference gas. The 100% background standard used to generate calibration curves was swapped out in the autumn of 2021. These panels show the ratio of the value computed by FE3 during each calibration run to the value assigned to the standard by a GCMS system known as "M3". In effect, these panels reveal the lack of fit between the background standard FE3 response and the calibration curves derived by FE3.



Accuracy

In the plots below, FE3 measurements are compared to the results from four other systems operated by GML scientists. M3 is a GC-MS system designed for the analysis of flasks samples in Boulder and is operated by GML's HATS group (Dr. Stephen Montzka). It cryogenically pre-concentrates a defined sample volume using liquid nitrogen in order to boost detector signals and provide the desired measurement precisions. CATS systems are stand-alone, in-situ GC-ECDs located in the field at five sites. They are also operated by GML's HATS group (Geoff Dutton) and have an atmospheric sampling frequency of one per hour, although monthly means are used for the comparisons. MAGICC is a system operated by GML's CCGG group (Dr. Ed Dlugokencky) that measures SF₆ from flasks by GC-ECD and N₂O by Tunable Infrared Laser Direct Absorption Spectroscopy. Finally, Otto was the GC-ECD that preceded FE3. Only the comparisons to M3 are direct comparisons of measurements from shared flask samples. With CATS, MAGICC, and Otto, each measured sample is unique, so the results are presented in time series form from a subset of common field sites.



Thanks to Ed Dlugokencky and GML's Carbon Cycle and Greenhouses Gases division for usage of their MAGICC data.