

5.2.2. IN SITU GAS CHROMATOGRAPH MEASUREMENTS

Radiatively Important Trace Species

The Radiatively Important Trace Species (RITS) project has ended. Table 5.5 outlines, for each station and data channel, the shutoff dates for the RITS equipment. Channel A measured N₂O, CFC-12 (CCl₂F₂), and CFC-11 (CCl₃F); channel B measured CFC-11, CH₃CCl₃, and CCl₄; and channel C measured N₂O. The RITS instruments continued to collect data until data from the replacement CATS instruments showed similar trends and equal or better precision. The precision for a particular chemical was determined as the standard deviation of the ratio of the responses of two calibration gases over an extended period of time (usually more than 1 month). Calibration gases are normally very stable for the species of interest.

TABLE 5.5. RITS Project Shutdown Schedule

Station	Channel*	Date and Time (GMT)
BRW	A, B, C	Feb. 17, 1999 (2100)
NWR	A, B, C	Aug. 7, 2001 (1900)
MLO	A, C	April 10, 2000 (2130)
	B	Dec. 18, 2000 (2030)
SMO	A, B	April 22, 2000 (0530)
	C	Sept. 30, 2000 (0000)
SPO	A, B	Nov. 30, 2000 (0200)

* See text for channel definitions.

Instruments associated with the CATS project, developed to replace the aging RITS instruments and add new measurement capabilities, continue to operate at the CMDL field sites. A CATS system was installed at NWR in October 2000. Table 5.6 shows the installation dates for the CATS instruments and the duration of the RITS-CATS comparisons.

A two-channel Hewlett-Packard 5890 GC-ECD used in the RITS project was refurbished for installation at Ushuaia, Tierra del Fuego, Argentina (TDF), as part of a cooperative venture with the Servicio Meteorologico Nacional de

TABLE 5.6. CATS Project Startup and Overlap Schedule with RITS

Station	Installation Date	Overlap with RITS (months)
BRW	June 16, 1998	8
NWR	Oct. 13, 2000	10
MLO	Sept. 29, 1998	18 [26]*
SMO	Dec. 4, 1998	17 [22]*
SPO	Jan. 30, 1998	34

*Months in brackets are for the one channel that continued to be operated after the others were turned off.

Argentina, sponsored by WMO. The TDF site is part of the WMO GAW program. This GC measures N₂O and SF₆ on the first channel and CFC-12, CFC-11, CFC-113, CH₃CCl₃, and CCl₄ on the second channel. A significant difference between this system and the previous RITS system is that nitrogen carrier gas with a CO₂ dopant is used on the N₂O-SF₆ channel as opposed to 5% CH₄ in argon (P-5). The use of CO₂-doped N₂ should (a) eliminate any CO₂ interference on the N₂O signal and (b) improve carrier gas quality (high-quality P-5 is difficult to obtain, particularly at remote sites).

The TDF GC system was installed on October 26, 2001, providing the first in situ CFC measurements in South America. Scientists from Argentina are interested in measuring CFCs because stratospheric chlorine from CFCs contributes to the formation of the Antarctic ozone hole. During vortex breakup, low-ozone events can occur over southern South America. Furthermore, while the total atmospheric chlorine burden is dropping [Montzka *et al.*, 1999; Elkins, 2000], CFC-12 is slowly increasing. Under the *Montreal Protocol on Substances that Deplete the Ozone Layer* [UNEP, 1987] and its amendments, developing countries can produce CFCs until 2010.

Mixing Ratio Calculation Methods

Over the past 3 years the RITS three-channel GC instruments at the CMDL baseline observatories have been replaced by four-channel GC instruments (CATS). In addition to the five trace gases measured by RITS instruments (N₂O, CFC-11, CFC-12, CH₃CCl₃, and CCl₄), CATS instruments measure SF₆, CFC-113, CHCl₃, COS, halon-1301, halon-1211, CH₃Cl, CH₃Br, HCFC-142b, and HCFC-22.

Both RITS and CATS instruments are calibrated using two calibration tanks that are sampled alternately along with ambient air. One calibration standard (C1) consists of a mixture of 90% ambient air and 10% synthetic ultrapure air. The other standard (C2) is 100% ambient air. The sequence of sample injections is C1, A1, C2, A2, where A1 and A2 are ambient air samples obtained at two different heights on the sampling tower. Each sample chromatograph is 30 minutes in length; thus the full sequence takes 2 hours. Both RITS and CATS in situ measurement programs have utilized several different methods to compute the trace gas concentrations in air samples bracketed by two calibration samples. This section focuses on the difficulties involved in these calculations. A new algorithm, designed to minimize problems associated with calibration tank changes and uncertainties in the assignment of calibration tank mixing ratios (see section 5.2.3), is presented here.

One-point method. The simplest method of calculating mixing ratios is to use only one calibration tank as a reference measurement:

$$\chi_a = \frac{R_a}{R_c} \chi_c \quad (1)$$

where R_a is the ECD response of the air sample, R_c is the ECD response of the calibration sample, χ_c is the known mixing ratio of the calibration sample, and χ_a is the mixing ratio of the air sample. The one-point method can be plagued by nonlinearities in chromatography and detector

response (Figure 5.16). Compounding problems occur

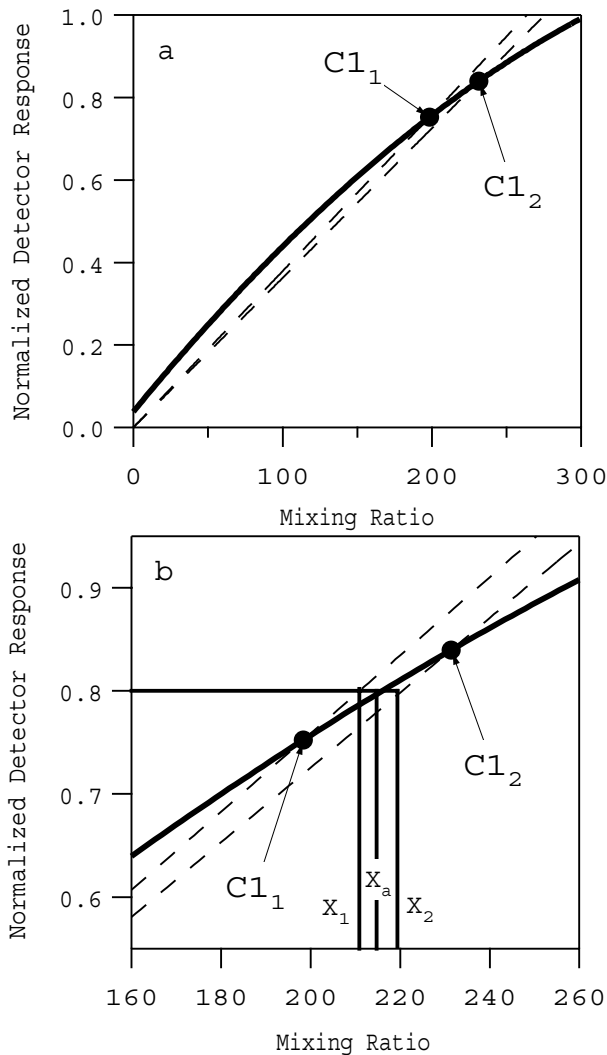


Fig. 5.16. Estimates of mixing ratio by the one-point method. Plot (a) is full scale and (b) is expanded. Both plots demonstrate the potential problems that can occur with only a single calibration measurement. The nonlinear response curve (solid) is the normalized response to a known quantity of a particular molecule (in arbitrary units). The one-point method uses a single measurement of an assigned mixing ratio (C₁) and assumes a linear response (dotted lines). For an ECD with a nonlinear response, a calibration error will occur if the air sample and calibration gas have significantly different responses. The solid vertical lines (X₁, X₂) correspond to the mixing ratios calculated for a response of 0.8 using two different calibration standards (C₁ and C₂). The middle vertical line (X_a) is the actual mixing ratio if the response curve is known.

when the calibration tank is replaced with a new tank with different assigned concentrations. Because the one-point method approximates the actual ECD response with a straight line with a zero intercept, a change in the mixing ratio of the calibration tank (χ_c and R_c) results in a different slope used to approximate the ECD response (Figure 5.16a). This can lead to discontinuities in the atmospheric record when the true ECD response is nonlinear. Small errors can

occur even when two calibration tanks are used (i.e., mixing ratio is determined as the mean of two one-point calculations).

Two-point method. The results of both calibration tanks together can be used to calculate mixing ratios by approximation of the ECD response with a straight line with a nonzero intercept (Figure 5.17):

$$\chi_a = \frac{(R_a - R_{c1})(\chi_{c1} - \chi_{c2})}{R_{c1} - R_{c2}} + \chi_{c1} \quad (2)$$

where R_a is the ECD response of the air sample, R_{c1} is the ECD response of C1, R_{c2} is the ECD response of C2, χ_{c1} is the known mixing ratio of C1, and χ_{c2} is the known mixing ratio of C2. Improvements in accuracy, compared with the one-point method, can sometimes be obscured by precision problems associated with the two-point method. Random noise in both measured quantities R_{c1} and R_{c2} can affect the slope and intercept. Averaging calibration tank responses over short time periods can improve precision. Changing calibration tanks can also lead to discontinuities in the atmospheric record when the two-point method is used, because different segments of the nonlinear response curve are encountered as calibration tanks with different mixing ratios are used. This is particularly true for trace gases with strong tropospheric trends (such as CH_3CCl_3).

In addition to difficulties associated with nonlinear ECD response, the accuracies of both the one-point and two-point methods are dependent on the accuracies of the mixing ratios assigned to the calibration gases (χ_{c1} and χ_{c2}). To address these issues, a new method that utilizes the thousands of routine measurements made of each calibration tank during normal operation was developed. The method

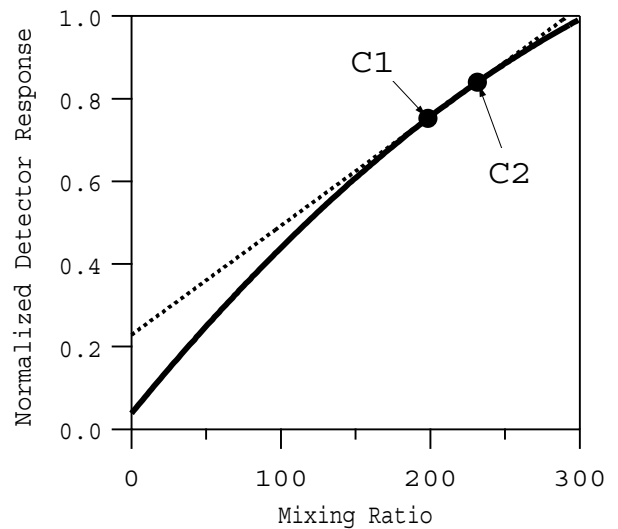


Fig. 5.17. Estimates of mixing ratio by the two-point method. This method utilizes two calibration tank measurements (C1 and C2) to approximate the response curve (solid) with a straight line (dashed).

can be used to adjust assigned calibration tank concentrations (within specified uncertainties) to provide a self-consistent set of calibration standards and minimize discontinuities in the atmospheric time series.

Statistical ratio method. The CATS GCs make continuous measurements of each calibration tank every day, about 12 injections per day. Over the lifetime of the calibration tank (usually 9 to 12 months) nearly 4000 separate measurements of each calibration tank can be made. Several comparisons of one calibration tank to another (Figure 5.18) can be used to adjust the assigned mixing ratios such that the effects of calibration tank changes are minimized.

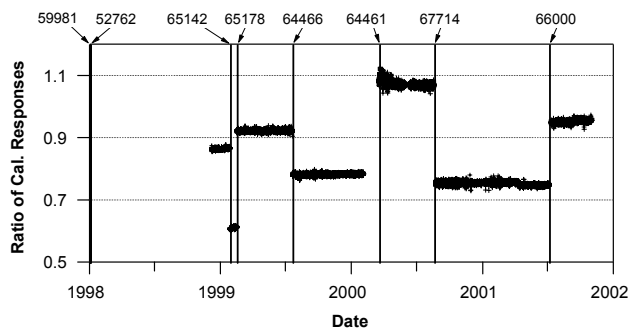


Fig. 5.18. Response ratio (C1/C2) for CH_3CCl_3 at SMO for different pairs of calibration standards. Calibration tank changes are shown as vertical lines identified by cylinder number along the top of the figure.

A two-step procedure is used to establish a self-consistent set of calibration tank mixing ratios. The first step takes advantage of the fact that the mean response ratio of calibration tanks is functionally related to the assigned calibration tank values:

$$B_{ij} = f(\chi_{cl,i}, \chi_{c2,j}) \approx m \left(\frac{\chi_{cl,i}}{\chi_{c2,j}} \right) + b \quad (3)$$

where B_{ij} is the response ratio of the i^{th} C1 tank to the j^{th} C2 tank, $\chi_{cl,i}$ is the assigned concentration for the i^{th} C1 tank, and $\chi_{c2,j}$ is the assigned concentration for the j^{th} C2 tank. The ratio B_{ij} can vary between 0.5 and 1.1 depending on the growth rate of the compound analyzed and when the calibration tanks were prepared. Plotting the measured mean calibration tank ratios (B_{ij}) versus assigned concentration ratios creates an effective ECD response curve (Figure 5.19a) that can be fitted with a least-squares regression line. The line represents a long-term average ECD response for a particular molecule. If the chromatography is stable over the period of all B_{ij} measurements, the linear fit can be used to calculate air concentrations and estimate errors. The functional relationship is nearly linear for all compounds measured by the CATS instruments. Problems arise in the linear

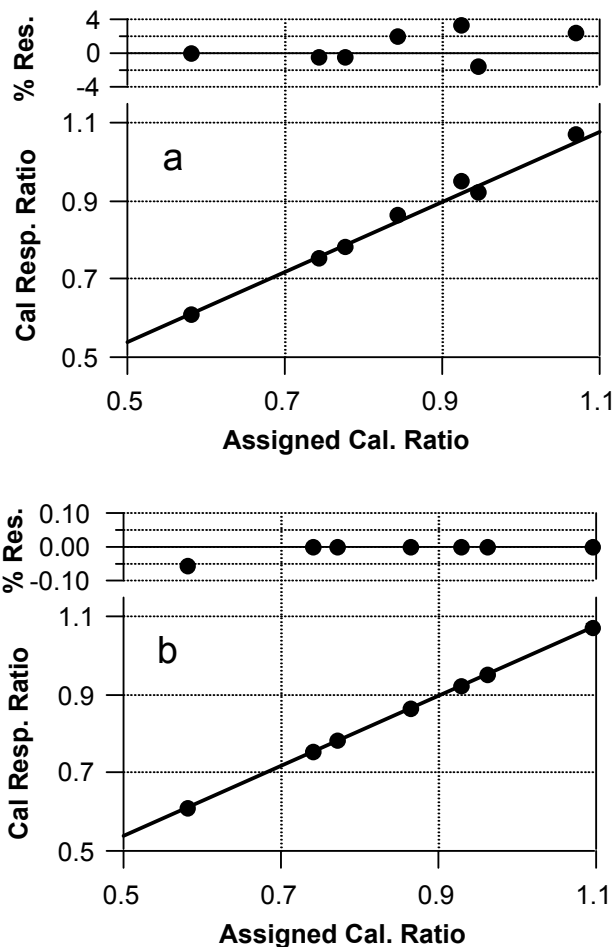


Fig. 5.19. (a) Mean response ratio for CH_3CCl_3 at SMO plotted against the ratio of assigned CH_3CCl_3 concentration for each calibration tank pair. A linear least-squares fit through the calibration tank ratios (solid line) is used to compute an average effective response curve. Residual differences are plotted at the top of the graph and demonstrate the magnitude of errors associated with a calibration tank change. (b) Mean response ratio as in (a) except that calibration tank concentrations have been adjusted to minimize the residuals.

representation when there are chromatographic problems, such as co-eluting compounds and ECD response curves that show relatively large nonzero intercepts. For current tropospheric mixing ratios of all species measured by CATS instruments, equation (3) seems to provide a good estimate for the effective response curve.

Once the slope and intercept of the effective response curve are known, uncertainties in the assigned calibration tank mixing ratios can be incorporated:

$$B_{ij} = m \left(\frac{\chi_{cl,i} + \sigma_{cl,i}}{\chi_{c2,j} + \sigma_{c2,j}} \right) + b \quad (4)$$

where $\sigma_{c1,i}$ is the possible uncertainty associated with the i^{th} C1 and $\sigma_{c2,j}$ is the possible uncertainty associated with the j^{th} C2. A numerical algorithm is used to iteratively adjust all $\sigma_{c1,i}$ and $\sigma_{c2,j}$ to minimize the residual difference (Figure 5.19b). The adjustments to the calibration tank values are constrained by the estimated uncertainties on the assigned values (section 5.2.3). For most compounds the adjustments are less than 0.5% of the ambient mixing ratio.

Equation (4) can be rewritten in terms of χ_a to yield two equations to compute atmospheric mixing ratio using the optimal values of $\sigma_{c1,i}$ and $\sigma_{c2,j}$:

$$\chi_a = (\chi_{c1,i} + \sigma_{c1,i}) m \left(\frac{R_{c1,i}}{R_a} - b \right)^{-1}, \quad (5)$$

$$\chi_a = (\chi_{c2,j} + \sigma_{c2,j}) \frac{1}{m} \left(\frac{R_a}{R_{c2,j}} - b \right). \quad (6)$$

If both calibration tanks are in operation, the average of equations (5) and (6) is used. Atmospheric mixing ratios calculated with the statistical ratio method tend to be more precise than with the two-point method and are more accurate than the one-point method. The gain in precision comes from use of the average response curve rather than estimation of a response curve from each sequence of measurements, as in the case of the two-point method.

Figures 5.20 and 5.21 illustrate the differences between results from the two-point method and from the statistical ratio method. Figure 5.20a shows discontinuities in the mixing ratio for CH_3CCl_3 at SMO calculated with the two-point method. These discontinuities are the result of rapidly changing atmospheric CH_3CCl_3 mixing ratios, and calibration tanks that have widely varying CH_3CCl_3 relative to the atmosphere. The CH_3CCl_3 data shown in Figure 5.20b were calculated with the statistical ratio method. These data clearly represent a continuous time series. The missing data seen prior to the 64461 calibration tank change correspond to a period in which the C2 tank (65178) was emptied before the arrival of its replacement. Even though the ratio of calibration tanks cannot be used for this period, the statistical relationship used to derive equations (5) and (6) is still valid. In this case the atmospheric mixing ratio can be calculated with equation (5) without having to rely on the one-point calculation method. The CFC-11 data from BRW shown in Figure 5.21 do not show large discontinuities associated with calibration tank changes. However, application of the statistical ratio method reveals a possible downward trend in CFC-11 concentration (Figure 5.21b) that is not apparent in data computed with the two-point method (Figure 5.21a).

The application of the statistical ratio method is new to the HATS in situ program and may undergo further enhancements. For example, the two-point method may be preferred during periods when chromatography is noticeably different from the statistics upon which the method is based. However, with each additional working standard, the entire data record could change significantly when the statistical ratio method is applied. A future improvement might be to use equation (2) in conjunction with the estimated $\sigma_{c1,i}$ and $\sigma_{c2,j}$ for these periods.

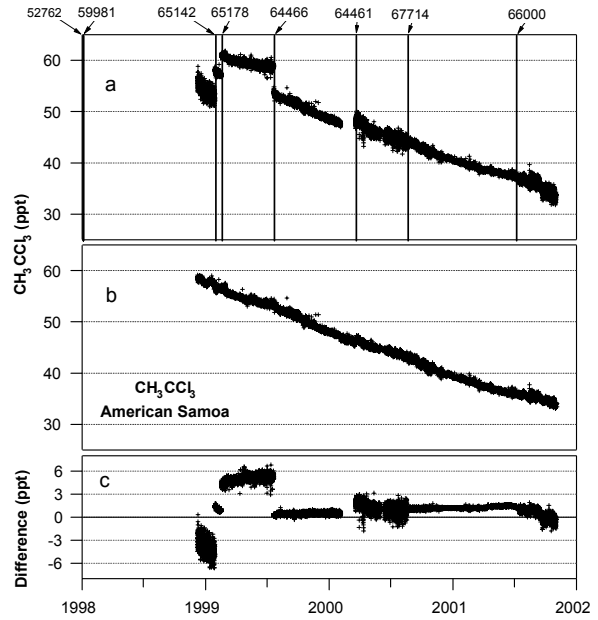


Fig. 5.20. CH_3CCl_3 data from SMO computed with two different methods: (a) the two-point method and (b) the statistical ratio method. The difference between methods (a) and (b) is shown in (c). Note that many of the discontinuities in (a) are absent in (b). Calibration tank changes are shown as vertical lines identified by cylinder number along the top of (a).

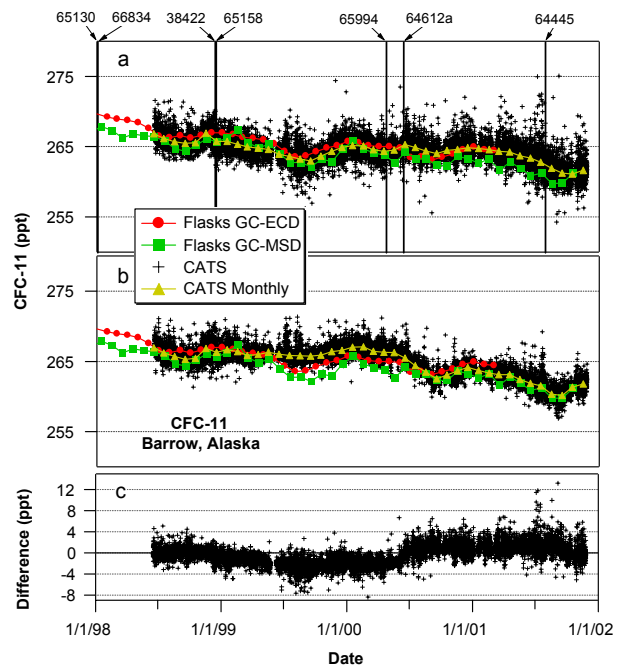


Fig. 5.21. CFC-11 data from BRW, as in Figure 5.20. Also included are data from flasks analyzed on GC-ECD (red) and GC-MSD (green) instruments, and monthly mean values from the CATS instrument (yellow). Although discontinuities are not apparent in (a), the statistical ratio method (b) dramatically improves precision.