5.1.4. GRAVIMETRIC STANDARDS

Calibration of Working Standards

In May 1999 the three-channel gas chromatograph system used to calibrate standards for the in situ monitoring program was replaced by a four-channel, custom-built GC. The four-channel GC is similar to the four-channel CATS instruments used for in situ monitoring at the observatories. The GC is operated under slightly different conditions compared to those at the observatories in order to optimize chromatography for cylinder calibration (Table 5.6).

The new four-channel instrument was compared to the old GC to ensure that the new GC would provide similar calibration results. For calibrations of ambient-level working standards, the new GC agreed to within 0.1% for N_2O, 0.4% for CFC-113, 0.5% for CH_3CCl_3, and 1% for CFC-11 and CCl_4. Initial tests revealed a 2-3% discrepancy for CFC-12. This experiment was repeated several months later, and the discrepancy could not be reproduced. Testing in December 1999 showed that the GCs agreed to within 0.2% for CFC-12. Following this CFC-12 experiment, the old three-channel GC instrument was retired. The four-channel GC is now used to calibrate working standards. Each standard is typically analyzed for 2 full days over a 2-3 week period (8-12 injections each day) (Table 5.7).

Preparation of Working Standards

Working standards for use with laboratory and in situ GCs continue to be filled at the C-1 site at Niwot Ridge, Colorado (40.04ºN, 105.54ºW, elevation 3013 m). Cylinders are filled using a three-stage, SA-6B compressor from Rix Industries (Oakland, California). Cylinders have occasionally been contaminated with trace amounts of unknown compounds that elute near CFC-11 and CFC-113 on the columns used in the CMDL in situ program. Contaminated standards have traditionally been associated with warm temperatures, while clean standards have been obtained during winter when ambient air temperatures are often below 5ºC. The contaminants are thought to result from outgassing of material from the piston rings of one or more of the compressor stages (Ray Weiss, personal communication, 1999). Outgassing may be more severe at higher operating temperatures. To reduce the operating temperature of the first stage of the compressor, the compressor was modified in order to allow a small amount of distilled, de-gassed water to be injected into the air stream just upstream of the first stage. Injection of water in this manner reduces the operating temperature of the first stage cylinder head from >100ºC to ~50ºC. Contamination is substantially reduced by injecting water at a rate of 10-20 mL min^{-1} (Figure 5.22).

TABLE 5.6. Configuration of the Four-Channel GC for Calibration of Working Standards

Channel	Column	Detector	Compounds Resolved
1	Porapak Q	Valco ECD	N_2O, SF_6
2	Unibeads 1s	Shimadzu ECD	CFC-12, CFC-11, halon-1211
3	OV-101	Valco ECD	CFC-12, CFC-11, halon-1211, CFC-113, $CHCl_3$, CH_3CCl_3, CCl_4
4	Poraplot Q	Shimadzu ECD	HCFC-22, CH_3Cl, CH_3Br

TABLE 5.7. Analytical Precision Typically Obtained for a Complete Calibration of a Working Standard on the Four-Channel GC-ECD

Compound*	Precsion (%)
N_2O	0.05
CFC-12	0.08
CFC-11	0.10
CFC-113	0.15
halon-1211†	0.2
$CHCl_3$	1.0
CH_3CCl_3	0.2
CCl_4	0.1
SF_6	0.8

*Calibration of HCFC-22, CH_3Cl and CH_3Br is only performed on the flask GC-MS instrument at this time.

†The calibration scale for halon-1211 is determined on the flask GC-ECD instrument. Halon-1211 calibration on the four-channel instrument is complicated by a co-eluting peak occurring on both channels 2 and 3.

Standards Preparation

A total of 66 natural-air standards were filled at Niwot Ridge during the 1998-1999 period. Fifty-eight of these were used by CMDL or related projects; eight standards were prepared for outside laboratories. A total of 10 gravimetric standards were prepared. Four were prepared for CMDL use, while 6 were prepared for outside laboratories.

Calibration Scales

A summary of the calibration scales used in conjunction with measurements performed by the HATS group is reported here. Table 5.8 lists the year that each calibration scale was established. Table 5.9 lists the gravimetric standards and mixing ratios used to define each calibration scale. Factors that

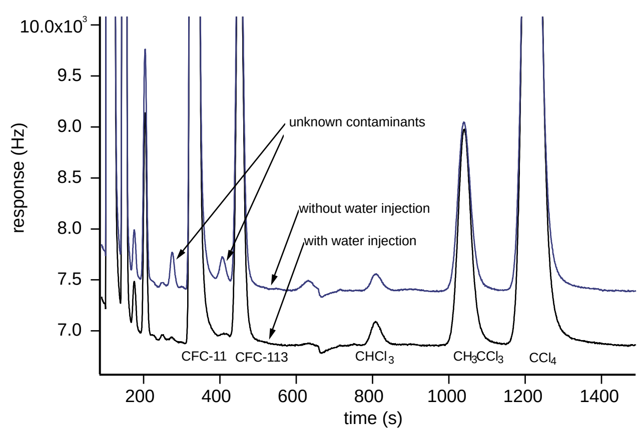

Fig. 5.22. Chromatograms of air samples from tanks pumped at Niwot Ridge, Colorado, with and without water injection (see text). The chromatogram (top) without water injection shows more contamination peaks.

TABLE 5.8. Reference Dates for HATS Calibration Scales

Compound	Year*	Reference‡
N_2O	1993	*Swanson et al*. [1993]
CFC-12	1997	*Butler et al*. [1998b]
CFC-11	1992	*Elkins et al*. [1993]
CFC-113	1993	*Swanson et al*. [1993]
CH_3CCl_3	1996	*Butler et al*. [998b]
CCl_4	1996	*Butler et al*. [1998b]
HCFC-22	1992	*Montzka et al*. [1993]
HCFC-141b	1994	*Montzka et al*. [1994]
HCFC-142b	1994	*Montzka et al*. [1994]
HCFC-134a	1995	*Montzka et al*. [1996b]
CH_3Cl	1996	*Butler et al*. [1998b]
CH_3Br	1996	*Butler et al*. [1998b]
CH_2Cl_2†	1992	*Spivakovsky et al*. [2000]
C_2Cl_4†	1992	*Hurst et al*. [1997]
$CHCl_3$†	1992	*Hurst et al*. [1997]
halon-2402†	1992	*Butler et al*. [1998b]
halon-1211	1996	*Butler et al*. [1998a]
halon-1301	1990	*Butler et al*. [1998a]
SF_6	1994	*Geller et al*. [1997]
H_2	1995	*Novelli et al*. [1999]
CO	1991	*Novelli et al*. [1991]

*Calibration scales are defined by a particular set of gravimetric standards (see Table 5.9). In some cases only a single standard is used. The year shown for each species refers to either the year during which the standards were prepared or the year in which a significant change in calibration scale occurred. Thus data reported prior to the year listed are associated with a different calibration scale than those reported in subsequent years.

†These species are measured by CMDL, but their calibration is defined only by an incomplete set of standards.

‡The reference listed for each species refers to a publication that describes a calibration change or a publication that includes recent results.

influence the number of gravimetric standards used to define a particular scale include the time-history of the measurements, the range of concentrations investigated, and the linearity of response (e.g., CFC-12 measurements were made over more extensive spatial and temporal scales than CH_3Br, thus a large number of CFC-12 standards were prepared over the years). All of the standards listed in Table 5.9 were prepared in 5.9-L or 29.5-L Aculife-treated aluminum cylinders (Scott Specialty Gases, Plumsteadville, Pennsylvania).

Examples of calibration response curves determined on the CATS GC instrument are shown in Figure 5.23. The uncertainty associated with the calibration curves (expressed as the standard error of the residuals) is typically 0.2-0.5%.

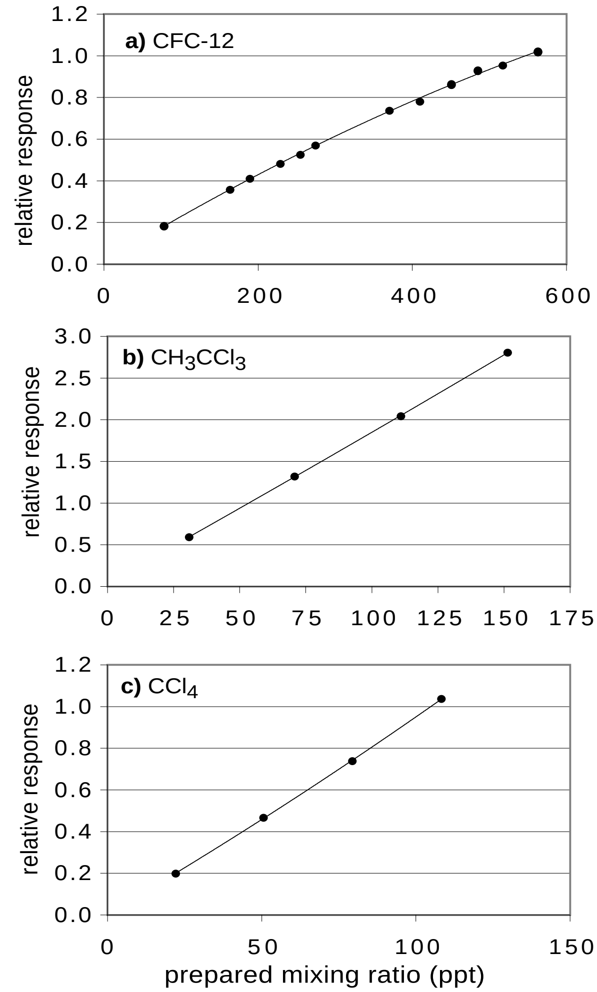

Fig. 5.23. Sample calibration curves for CFC-12 (a), CH_3CCl_3 (b), and CCl_4 (c). Each filled circle represents the response of a gravimetric standard relative to a working standard. Solid lines are second-order polynomial fits to response data.

The number of gravimetric standards used to define scales for N_2O and SF_6 will be expanded in the near future. A number of standards with N_2O and SF_6 mixing ratios near ambient levels will be prepared. The addition of numerous standards at near-ambient concentrations will enable high-precision maintenance of the scales over time.

TABLE 5.9. Gravimetric Standards Used to Define Calibration Scales for the HATS Group

Compound	Cylinder Number	Prepared Gravimetric Concentration
N_2O	*ALM-38408	96.2 ppb
	*ALM-26738	172.0 ppb
	*ALM-26743	331.0 ppb
	*ALM-26737	359.9 ppb
	*CLM-30135	801.1 ppb
CFC-11	*ALM-38408	25.5 ppt
	*CLM-2431	49.5 ppt
	*ALM-38417	80.9 ppt
	*CLM-2482	69.2 ppt
	*ALM-26735	75.16 ppt
	*CLM-2413	136.3 ppt
	*ALM-26743	288.2 ppt
	*ALM-26737	313.6 ppt
CFC-12	*CLM-2426	77.8 ppt
	*CLM-2431	163.5 ppt
	*CLM-9015	189.2 ppt
	*CLM-2482	228.8 ppt
	*CLM-9041	274.4 ppt
	*CLM-9018	370.3 ppt
	*CLM-2413	450.7 ppt
	*CLM-9038	646.9 ppt
CFC-113	*CLM-2482	19.1 ppt
	*CLM-2413	37.5 ppt
	*†ALM-26735	48.0 ppt
	†ALM-26738	48.0 ppt
	*†ALM-26743	82.8 ppt
	*†ALM-26737	90.0 ppt
CH_3CCl_3	*†ALM-52792	30.9 ppt
	*†ALM-52788	70.8 ppt
	*†ALM-59967	111.0 ppt
	*†ALM-52811	151.4 ppt
CCl_4	*†ALM-52792	22.1 ppt
	*†ALM-52788	50.6 ppt
	*†ALM-59967	79.4 ppt
	*†ALM-52811	108.3 ppt
SF_6	*CLM-7506	3.1 ppt
	*CLM-7519	23.2 ppt
	*CLM-7494	60.6 ppt
	*CLM-7503	107.6 ppt
CH_3Br	†CLM-7490	5.3 ppt
	†ALM-62626	5.3 ppt
	†ALM-39771	25.6 ppt
CH_3Cl	†ALM-39971	1024 ppt
HCFC-22	†ALM-26738	105 ppt
	†ALM-26743	145 ppt
	†ALM-26735	105 ppt
	†ALM-38417	111.6 ppt
	†ALM-26737	158 ppt
HCFC-141b	†ALM-39758	5.0 ppt
	†ALM-39744	25.5 ppt
	†ALM-39749	51.3 ppt
HCFC-142b	†ALM-39758	5.0 ppt
	†ALM-39744	25.4 ppt
	†ALM-39749	51.1 ppt
HCFC-134a	†CLM-8952	5.44 ppt
	†CLM-9036	10.22 ppt
halon-1211	*†CLM-9039	3.02 ppt
	*†CLM-9024	5.41 ppt
halon-1301	*†CLM-2416	95.4 ppt
	*†FF-30071	6.08 ppb
halon-2402	†ALM-26748	47.5 ppt
CH_2Cl_2	†ALM-26748	122.0 ppt
C_2Cl_4	†ALM-26748	157.0 ppt
$CHCl_3$	†ALM-26748	141.0 ppt

*These standards are used to define the calibration scales associated with GC-ECD instruments.
†These standards are used to define the calibration scales associated with GC-MS instruments.