NOAA Data Report ERL PMEL-45

DEPARTMENT OF COMMERCE ★ UNITED STATES OF AMERICA

WOCE 1991 CHLOROFLUOROCARBON STANDARD INTERCOMPARISON REPORT

J. L. Bullister
F. Menzia
D. P. Wisegarver

Pacific Marine Environment Laboratory
Seattle, Washington
July 1993

noaa NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION / Environmental Research Laboratories

NOAA Data Report ERL PMEL-45

WOCE 1991 CHLOROFLUOROCARBON STANDARD INTERCOMPARISON REPORT

J. L. Bullister[1]
F. Menzia[2]
D. P. Wisegarver[1]

[1]Pacific Marine Environmental Laboratory
7600 Sand Point Way, N.E.
Seattle, WA 98115-0070

[2]Joint Institute for the Study of Atmosphere and Ocean
University of Washington
Seattle, WA 98195

July 1993

UNITED STATES
DEPARTMENT OF COMMERCE

Ronald H. Brown
Secretary

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

D. James Baker
Under Secretary for Oceans
and Atmosphere/Administrator

Environmental Research
Laboratories

Alan R. Thomas
Director

NOTICE

Contribution No. 1458 from NOAA/Pacific Marine Environmental Laboratory
Contribution No. 238 from Joint Institute for the Study of Atmosphere and Ocean

---

For sale by the National Technical Information Service, 5285 Port Royal Road
Springfield, VA 22161

Participating Laboratories:

NOAA-Pacific Marine Environmental Laboratory (NOAA-PMEL)
NOAA-Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL)
University of Miami (Miami)
Institut für Meereskunde Kiel (Kiel)
Universität Bremen (Bremen)
Scripps Institution of Oceanography (SIO)
Lamont-Doherty Earth Observatory (LDEO)
Brookhaven National Laboratory (BNL)
Rennell Centre for Ocean Circulation (Rennell)
Université P. et M. Curie (LODYC)

CONTENTS

WOCE 1991 Chlorofluorocarbon Standard Intercomparison Report

J.L. Bullister[1], F. Menzia[2], and D.P. Wisegarver[1]

ABSTRACT: A chlorofluorocarbon (CFC) standard intercomparison study was done among ten laboratories involved in measurements of dissolved and atmospheric CFCs as part of the World Ocean Circulation Experiment (WOCE) and other programs. The goal of this study was to compare CFC calibration scales and to allow CFC data sets collected by the participating groups to be merged together more easily. To prepare intercomparison gas samples, aliquots of dry air from a high pressure gas cylinder were transferred into a set of evacuated, high-purity gas cylinders and analyzed at PMEL for uniformity. One cylinder was distributed to each participating laboratory for analysis and return to PMEL. Within the precision of the analytical techniques used at PMEL, the CFC-11 and CFC-12 concentrations in the cylinders remained uniform throughout the intercomparison exercise. The CFC-113 and carbon tetrachloride content of the cylinders remained relatively uniform in all but one of the cylinders analyzed. The CFC-11 concentrations reported by participating laboratories ranged from 258.8 to 275.6 parts-per-trillion (PPT). The reported CFC-12 concentrations ranged from 487.4 to 503.5 PPT. Two laboratories reported values for CFC-113, and only one laboratory reported a value for carbon tetrachloride. Details of the calibration techniques used by the ten participating laboratories are given in the Appendices of this report.

I. BACKGROUND

A relatively large number of laboratories will make measurements of dissolved CFCs as part of the WOCE Hydrographic Programme (WHP). During the WHP one-time survey period, it is important to develop and maintain procedures that allow both new and experienced CFC groups to periodically evaluate the quality of their results. Regular intercomparisons made while the WHP program is underway may help identify analytical problems or discrepancies in calibration scales, and allow the data reported by various groups to be eventually merged more easily into a global CFC data set.

Proposed methods for CFC intercomparison have included:

1) Major intercomparison cruises involving all CFC groups planning to take part in the WHP.
2) Regional intercomparison cruises (e.g., among European groups) or intercomparisons between pairs of groups on hydrographic cruises.
3) Shore-based laboratory-to-laboratory CFC intercomparisons, perhaps involving seawater samples prepared in equilibrator chambers and gas standards.
4) Preparation and distribution of stable, dissolved CFC standards to all groups involved in WOCE.

---

[1] NOAA/Pacific Marine Environmental Laboratory, 7600 Sand Point Way, N.E., Seattle, WA 98115-0070
[2] Joint Institute for the Study of Atmosphere and Ocean, University of Washington, Seattle, WA 98195

5) Distribution of aliquots of CFC gas standard (in pressurized cylinders) on a regular basis to all groups involved in WOCE and to groups involved in atmospheric measurements of CFCs.

Each of the above methods has advantages and potential disadvantages.

In December 1989, nine CFC groups planning to make measurements as part of the WHP participated in a WOCE CFC Intercomparison Cruise on the R/V *New Horizon*. This cruise was co-ordinated by Dr. R.F. Weiss (SIO) and took place at a deep water station off the coast of southern California. A number of shallow and deep CTD/rosette casts were made during the cruise, and seawater samples with a wide range of dissolved CFC concentrations (including deep waters with near-zero CFC concentrations) were collected and analyzed. Air and gas standards and equilibrator samples were also measured by some groups during the intercomparison cruise. A discussion of the analytical systems used, water sampling methods and results has been prepared (Wallace, 1992). Such intercomparison cruises provide a very useful means for CFC groups to compare analytical techniques and results. Scheduling such large CFC intercomparison cruises on a regular basis in the future may prove difficult. The level of effort required by each CFC group to set up equipment and participate on an intercomparison cruise is similar to that required to prepare for a full-scale WHP expedition. With the WHP now underway, finding a time period which does not conflict with on-going field programs may also be difficult.

Items 2 and 3 above require considerable effort for the groups involved, but should prove easier to schedule. These methods can allow new groups some flexibility in arranging intercomparisons of their analytical techniques with more experienced groups. Item 4 above is attractive for a number of reasons, but reliable methods for preparing and distributing stable dissolved CFC standards are still in the developmental stage.

This report discusses the results of a program now underway to implement item 5 above. In July 1991, the CFC Tracer Group at NOAA-PMEL prepared a set of compressed CFC gas samples for distribution to CFC analytical groups planning to be involved in WOCE, and to groups involved in atmospheric trace gas monitoring programs. This shore-based method allows comparison of CFC gas standards, but does not reproduce all the steps required for sampling and analysis of dissolved CFCs in seawater, nor the difficulties which might be encountered at sea on an intercomparison or WHP cruise.

This method can help identify existing calibration differences among participating laboratories and provide a regular check for any long-term drift in CFC calibration scales. This relatively low cost technique allows each group a substantial period of time to analyze the sample, thereby reducing possible scheduling conflicts with ongoing programs. This intercomparison technique can be repeated at regular intervals and new CFC groups can be included in future gas standard intercomparisons. New CFC compounds can also be included in future intercomparisons as techniques are developed. At present, the PMEL Tracer group plans to continue this program at 2-year intervals for the duration the WHP one-time survey period.

II. METHODS OF PREPARING CFC INTERCOMPARISON STANDARDS

On 13 October 1990, four high-pressure Airco Spectra-Seal aluminum cylinders (type 3Al2015) were filled with compressed air to a pressure of ~180 atmospheres (atm) at a remote site (Cheeka Peak Mountain, 48°15′N, 124°45′W) on the Olympic Peninsula of Washington State, USA. A Bauer Purus E1 compressor was used to flush and fill the cylinders with air. Air entering the pump passed through a drying tube of Aquasorb desiccant (phosphorus pentoxide). The filtering system containing activated charcoal and molecular sieve was removed from the high pressure side of the Bauer pump during the filling of the cylinders. Each Spectra-Seal cylinder initially contained high purity nitrogen at pressure of ~3 atm. This nitrogen was vented to the atmosphere, and each cylinder was flushed 3 times with air from the compressor. This flushing procedure involved filling the cylinder to a pressure of 20 atm, then venting the contents to the atmosphere. Total flushing and filling time for each cylinder was about 3 hours.

These cylinders were returned to the laboratory at PMEL and analyzed for CFC-11 and CFC-12 by electron capture gas chromatography (EC-GC) using methods similar to those described in Bullister and Weiss (1988). Analytical methods and calibration scales used by the PMEL group are discussed in detail in Appendix A.

TABLE 1. Initial comparison of high pressure cylinders filled at Cheeka Peak on 13 October 1990 (Analyzed 31 December 1990–3 January 1991).

Cylinder Number	Press (atm)	CFC-12* (PPT)	CFC-11* (PPT)	Runs (n)	%StDev** CFC-12	%StDev** CFC-11
63855	176	496.99	272.93	4	0.3	0.1
88098	151	496.93	273.84	4	0.4	0.2
88110	163	495.55	272.27	4	0.3	0.2
88142	150	495.54	273.07	4	0.2	0.1

*All CFC concentrations are reported as mixing ratios (mole fraction CFC in dry air) in parts-per-trillion (PPT).

** The percent standard deviation (%StDev) for the number (n) of replicate runs.

Although the cylinders were filled in sequence over a period of about 12 hours, the measured CFC-11 and CFC-12 concentrations in the 4 cylinders were remarkably similar.

A specially designed metal manifold system was constructed in the laboratory at PMEL for preparing a batch of intercomparison samples. This gas transfer system allows a number of sample and standard cylinders to be attached to the manifold. Individual (or sets of) cylinders on the manifold can be vented to the atmosphere, evacuated or filled with pressurized gases. On 15 July 1991, ten type 3Al2015 aluminum cylinders (8 Scott Aculife and 2 Airco Specta-Seal) containing high purity nitrogen at low pressure (<10 atm) were connected to the manifold system. The ten cylinders were opened to the manifold, and the nitrogen was vented to the atmosphere. The manifold and cylinders were then evacuated to a pressure of less than 0.000150 atm. During the evacuation process, a liquid nitrogen trap was placed in line with the vacuum pump to prevent diffusion of oil or other contaminants into the manifold system and cylinders. A high pressure cylinder containing CFC-free nitrogen was attached to the manifold system. The high pressure cylinder and evacuated cylinders were then opened to the manifold and the evacuated cylinders were rapidly filled with nitrogen to a pressure of about 15 atm. The low-pressure cylinders were then removed from the manifold and analyzed to check for possible CFC contamination during the transfer processes. No measurable levels of CFC-11 or CFC-12 could be detected in the cylinders. The limit of detection for CFC-11 and CFC-12 using the PMEL EC-GC analytical system is estimated to be <1 PPT.

On 22 July 1991, the ten cylinders were re-attached to the manifold, along with cylinder 63855, which contained ~176 atm of compressed air collected at Cheeka Peak. The ten cylinders containing nitrogen were vented through the manifold, then re-evacuated and closed. Cylinder 63855 and one of the evacuated cylinders (8339) were then opened to the manifold, and air from 63855 allowed to rapidly expand into 8339. Both cylinder valves were closed while a slight flow of gas could still be heard flowing into 8339. Cylinder 63855, now containing air at approximately 92 atm, was then removed from the manifold for later use as a high pressure reference cylinder. The manifold was then re-evacuated, and then air contained in 8339 (at approximately 90 atm) allowed to expand into the 9 remaining evacuated cylinders. The cylinders were then removed from the manifold, and the ten low pressure cylinders (~8 atm) were analyzed for CFC-11 and CFC-12 relative to high pressure cylinder 63855. A summary of the intercomparisons made at PMEL between cylinder 63855 and the 9 low-pressure cylinders on 25 July 1991 is given in Table 2.

TABLE 2. Initial comparison of 63855 with low pressure cylinders (25 July 1991).

Cylinder Number	Press (atm)	Response-Factor CFC-12	Response-Factor CFC-11	Runs (n)	%StDev CFC-12	%StDev CFC-11
63855	92	1.0	1.0	4	0.50	0.34
8337	9	0.999	1.000	3	0.13	0.13
8338	9	1.001	1.002	4	0.05	0.07
8339	9	1.003	1.005	4	0.16	0.10
8340	9	1.000	1.001	4	0.39	0.58
8342	9	1.000	1.002	4	0.08	0.08
8344	9	0.999	1.001	3	0.06	0.07
8348	9	0.997	0.998	3	0.06	0.10
8352	9	1.004	1.003	4	0.61	0.12
63861	9	0.997	0.995	4	0.07	0.12
88126	9	1.004	1.000	4	0.05	0.02

During these comparisons, each series of replicate analyses of a low-pressure cylinder was bracketed by analyses of the high pressure cylinder 63855. Each set of low pressure standard runs and bracketing runs of 63855 typically required less than 1 hour. Small differences in the amount of gas injected for each analysis occurred due to variations in sample loop temperature and atmospheric pressure. All raw chromatographic peak areas have been multiplied by the factor:

$$Vs/V$$

where Vs = Volume of gas in the loop at 25 degrees C, 1 atm.
V = Volume of gas in the loop at the temperature and pressure during injection.

The Response Factor reported in Table 2 is the ratio of the average of the CFC peak areas of a low-pressure cylinder to the average of the CFC peak areas of the bracketing runs of cylinder 63855. In the last 3 columns, the number of replicate analyses (n) and the percent Standard Deviation (% StDev) of peak areas for sequential runs of each cylinder are given. At the start of the analyses on 25 July 1991, cylinder 63855 was analyzed 4 times to check for instrument stability, and the %StDev of these replicate analyses are also reported in Table 2.

To check for short-term drift in CFC-11 and CFC-12 concentrations, the cylinders were re-analyzed on 9 September 1991 (See Table 3). The backflush time on the chromatographic columns was delayed during these analyses to allow the CFC-113 peak to elute.

TABLE 3. Comparison of low pressure cylinders with 63855 (9 Sept 1991).

Cylinder Number	Press (atm)	Response-Factor CFC-12	CFC-11	CFC-113	Runs (n)	%StDev CFC-12	CFC-11	CFC-113
63855	92	1.0	1.0	1.0				
8338	9	0.9956	1.0026	0.9944	4	0.38	0.19	1.12
8339	9	1.0000	1.0049	1.0083	4	0.40	0.29	1.58
8340	9	1.0011	0.9934	1.0020	3	0.28	1.21	***
8342	9	0.9983	0.9992	1.0039	4	0.21	0.10	0.49
8344	9	0.9995	1.0021	1.0067	3	0.08	0.24	1.03
8348	9	0.9993	1.0038	0.9985	4	0.10	0.22	0.38
8352	9	0.9978	0.9958	0.9988	2	0.28	0.22	0.25
63861	9	1.0000	0.9964	1.0089	4	0.25	0.19	0.85
88126	9	0.9930	0.9919	1.0203	2	0.03	0.01	0.74

*** CFC-113 peak area measurements were obtained for only 1 analysis of 8340.

The low-pressure cylinders were then shipped to participating laboratories for analysis. Cylinders were air-freighted to the European laboratories and sent by surface freight to laboratories in the USA. In most cases, the cylinders were delivered to the participating laboratories within about 2 weeks of the shipment date.

The following groups received CFC intercomparison samples:

	Institution	Code	Contact
1)	NOAA-PMEL	NOAA-PMEL	J. Bullister
2)	NOAA-Climate Monitoring and Diagnostics Laboratory	NOAA-CMDL	J. Butler
3)	University of Miami	Miami	R. Fine
4)	Institut für Meereskunde Kiel	Kiel	M. Rhein
5)	Universität Bremen	Bremen	W. Roether
6)	Scripps Institution of Oceanography	SIO	R. Weiss
7)	Lamont-Doherty Earth Observatory	LDEO	W. Smethie
8)	Brookhaven National Laboratory	BNL	D. Wallace
9)	Rennell Centre	Rennell	D. Smythe-Wright
10)	Université P. et M. Curie	LOYDC	C. Andrié
11)	National Center for Atmospheric Research	NCAR	L. Heidt

Each participating group was asked to analyze the cylinder for CFC-11, CFC-12 and other gases, and to return the cylinder to PMEL with enough residual gas to allow re-analysis. Each group was asked to summarize their results for inclusion in this report (see Appendices).

Following return of all the cylinders to PMEL, the cylinders were re-analyzed. Table 4 shows the results of the these re-analyses.

TABLE 4. Comparison of returned low pressure cylinders with 63855 (8 April 1992).

Cylinder Number	Press (atm)	Response-Factor CFC-12	CFC-11	CFC-113	Runs (n)	%StDev CFC-12	CFC-11	CFC-113
63855	92.0	1.0	1.0	1.0				
8337	5.2	1.0053	1.0036	1.0006	5	0.20	0.18	0.84
8338	6.3	1.0068	1.0028	1.0055	5	0.13	0.21	1.02
8339	6.0	1.0062	0.9992	0.9887	5	0.21	0.27	0.81
8342	6.1	1.0003	1.0004	0.9814	5	0.42	0.35	0.61
8344	6.1	1.0075	1.0034	1.0445	5	0.17	0.35	1.08
8348	1.2	1.0040	0.9966	0.9830	6	0.18	0.28	0.87
8352	6.2	1.0061	0.9961	0.9882	5	0.36	0.38	1.16
63861	6.4	1.0068	0.9939	1.0434	5	0.16	0.27	1.40
88126	9.0	1.0055	0.9977	1.0002	5	0.14	0.17	0.50

All of the analyses shown in Tables 1–4 were performed on a system using Porasil C columns and pre-columns. To allow better chromatographic separation of CFC-113 and carbon tetrachloride (CFC-14) the cylinders were analyzed during the period 21–29 May 1992 using a chromatographic system with a DB-624 Megabore capillary column and precolumn.

TABLE 5. Comparison of low pressure cylinders with 63855, using DB-624 Megabore capillary column. (21–29 May 1992).

Cylinder Number	Press (atm)	Response-Factor CFC-113	CFC-14	Runs (n)	%StDev CFC-113	CFC-14
63855	92.0	1	1			
8337	5.2	0.994	1.003	1	-	-
8338	6.3	0.992	0.977	2	1.0	2.4
8339	6.0	1.013	1.003	2	3.1	1.2
8340	0	**	**			
8342	6.1	0.999	0.987	2	0.3	2.5
8344	6.1	1.057	1.007	4	1.5	1.1
8348	1.2	**	**			
8352	6.2	1.000	1.013	2	2.4	2.3
63861	6.4	1.122	1.045	2	4.8	1.1
88126	9.0	1.014	0.126	2	0.2	1.8

** Not analyzed due to low residual pressure in cylinder.

It should be noted from Tables 4 and 5 that 2 cylinders (8344 and 63861) showed somewhat elevated CFC-113 concentrations relative to 63855. The CFC-14 concentration in Spectra-Seal cylinder 88126 (Table 5) was much lower than in the other cylinders, perhaps indicative of removal of this compound inside the cylinder.

III. INTERCOMPARISON RESULTS

Table 6 summarizes the reported results from the laboratories participating in the intercomparison exercise. Appendices A–H include the discussion provided by each group on their analytical methods and results.

TABLE 6. CFC concentrations reported by participating groups.

Group	Cylinder Number	Press (atm)	CFC-11	CFC-12	CFC-113	CFC-14	CH_3Cl_3
NOAA-PMEL	63855	92.0	272.92	497.14			
NOAA-CMDL	8337	5.2	273.7	499.9	82.6	108.3	165.7
NCAR	8337	5.2	***	***			
Miami	8338	6.3	275.6	487.4			
Kiel	8339	6.0	270.4	503.5			
Bremen	8339	6.0	273.3	497.4			
SIO	8342	6.1	272.2	500.8			
LDEO	8340*	6.1	268.8	495.0	80.8		
BNL	8344	6.1	258.8	500.3			
Rennell	8348	1.2	273	502			
LODYC	8352	6.2	272.95	501.9			

*** Did not report results.

Note: Pressures (absolute) were measured upon the return of the cylinders to PMEL. Cylinders were shared by the following pairs: Kiel and Bremen, LDEO and BNL, NOAA-CMDL and NCAR. The cylinder originally shipped to LDEO (8340) was empty upon arrival, and returned un-analyzed to PMEL. LDEO then analyzed and reported values for the cylinder (8344) shipped to BNL.

IV. DISCUSSION

CFC-11 and CFC-12 results:

Stability of CFC-11 and CFC-12 concentrations in cylinder 63855:

The CFC-11 and CFC-12 content of 63855 was calibrated versus primary standard CC36743 at PMEL on 31 December 1990 and 8 May 1992. (See discussion in Appendix A). Concentrations of 63855 versus Primary Standard CC36743 (values reported are on the SIO86 scale) were:

Cylinder Number	Date	Press (atm)	CFC-11 (PPT)	CFC-12 (PPT)	Runs (n)	%StDev CFC-11	%StDev CFC-12
63855	31-12-91	176	272.93	496.99	4	0.1	0.3
63855	08-05-92	92	272.90	497.28	9	0.4	0.7

Primary standard CC36743 was prepared at SIO in July 1985 using the methods described in Bullister (1984). This standard has been compared with other SIO primary standards (CC16436), and has been assigned a value of CFC-11 = 278.47 PPT, and CFC-12 = 473.85 PPT on the SIO 1986 calibration scale. The CFC-11 and CFC-12 content of this primary standard cylinder has remained essentially constant relative to other SIO primary standards, based on comparisons made in 1985 and 1989.

Based on comparisons with primary standard CC36743, it appears that any net drift in CFC-11 and CFC-12 concentrations in 63855 between December 1990 and May 1992 is within the precision of the analytical techniques.

Stability of CFC-11 and CFC-12 in low pressure cylinders:

The CFC-11 and CFC-12 response factors for the low pressure cylinders (relative to 63855) remained close to 1 throughout the experiment, even though the absolute pressures in the cylinders analyzed ranged from 1.2 to 90 atm. (see Tables 1–4).

The CFC content of the low pressure cylinders might be expected to show the greatest changes during the experiment if significant cylinder wall effects were present, or if the cylinder valves were a source of CFC contamination. Such effects are not apparent in Tables 1–4, and these data indicate that the CFC-11 and CFC-12 content remained nearly constant in the cylinders during the experiment. The cylinders used in these experiments will be archived and monitored on a long-term basis for possible drift in CFC concentration.

The PMEL group did note the presence of several small chromatographic peaks near the CFC-12 peak when the intercomparison cylinders (both low and high pressure) were analyzed. These peaks were more easily observed when the chromatographic peak data were stored digitally and re-displayed on an expanded scale. In some cases, the tail of the last small peak was observed to be fused with the leading edge of the CFC-12 peak on our chromatograms. These small peaks were observed on two different CFC analytical systems at PMEL (both systems used Porasil C columns and pre-columns), but were not observed in chromatograms of system blanks, the primary standard, or in other compressed air working standards in our laboratory. The size of these small peaks (relative to the CFC-12 peak) appeared to be greater for analysis made in 1992 than those made in 1991 (see Appendix A, Fig. 1). We are uncertain of the origin or identity of these peaks, and whether the apparent increases in size are due to the "grow-in" of an unknown compound, to changes in chromatographic separation, to changes in the response or sensitivity of the system, or to some artifact in our analytical system or technique.

Without good chromatographic separation and careful peak integration, the presence of such peaks may interfere with accurate CFC-12 peak integration on some systems and cause errors in reported CFC-12 concentrations. The presence of these peaks was not noted in the reports of the other groups participating in the intercomparison experiment. The PMEL CFC group has often observed the presence of a number of small, unidentified peaks in chromatograms generated from the analysis of seawater samples. The peaks are often larger and more numerous in analyses of near-surface seawater samples collected in areas of high biological productivity. We urge all groups involved in analysis of CFCs in air or water samples to routinely check for the possible presence of fused or co-eluting peaks in their chromatograms.

CFC-113 and Carbon tetrachloride

CFC-113 was measured in the cylinders at several points during the experiment using an analytical system with a Porasil C column and pre-column (Tables 3 and 4). The cylinders were also analyzed for CFC-113 and carbon tetrachloride on 21–29 May 1992 using a system with a DB-624 megabore capillary column and pre-column (see Table 5).

From Tables 3–5, it appears that the concentrations of CFC-113 in most of the low pressure cylinders remained within a few percent of that in 63855. When measured in May 1992 (with one exception—Spectra-Seal cylinder 88126), the carbon tetrachloride concentrations of the low pressure cylinders were within a few percent of that in 63855. The large apparent decrease of carbon tetrachloride concentration in cylinder 88126 is difficult to explain except by invoking a removal mechanism for this compound within the cylinder. It is interesting to note that this Specta-Seal cylinder was purchased at a different time from the other Spectra-Seal cylinders used in this experiment.

Only a few laboratories reported values for F-113 or carbon tetrachloride (see Table 6). We did not focus on the intercomparison of CFC-113 and carbon tetrachloride in this experiment, due to our lack of primary standards for these gases at PMEL, and our inexperience in storing and handling these gases in cylinders over extended periods of time.

Since the CFC-113 and carbon tetrachloride content of these cylinders were not calibrated with known, stable primary standards for these gases during the experiment, we cannot rule out the possibility that both high and low pressure cylinders drifted in CFC-113 and carbon tetrachloride concentration at similar rates during the experiment. We are also aware of the possibility of co-elution of the CFC-113 and carbon tetrachloride peaks with those from other compounds having similar retention times on the chromatographic columns used in these analyses.

Despite these possible problems, we are encouraged by the apparent overall uniformity of CFC-113 and carbon tetrachloride in most of the low pressure cylinders analyzed during this experiment. We hope to improve upon our techniques for working with these gases in time for the next WOCE CFC gas standard intercomparison experiment.

V. SUMMARY

The CFC-11 and CFC-12 concentrations in the intercomparison cylinders distributed to the participating laboratories in this study were uniform, within the analytical precision of the PMEL analytical techniques. No measurable change in CFC-11 and CFC-12 content could be detected in the cylinders following their return and re-analyses at PMEL. The range of CFC-11 and CFC-12 concentrations reported by the participating laboratories indicate some differences exist in their CFC calibration scales. When combining CFC seawater or air data sets reported by different groups, it may be useful in some cases to convert the reported concentrations to a common scale. These conversion factors for CFC-11 and CFC-12 can be obtained from the results shown in Table 6 of this intercomparison report. If revisions to a group's CFC calibration scale are made in the future, it should be possible to report these changes relative to the values reported in Table 6.

VI. REFERENCES

Bullister, J.L. (1984): Atmospheric chlorofluoromethanes as tracers of ocean circulation and mixing: Measurement and calibration techniques and studies in the Greenland and Norwegian Seas. Ph.D Thesis, University of California, San Diego, 172 pp.

Bullister, J.L., and R.F. Weiss (1988): Determination of $CC1_3F$ and $CC1_2F_2$ in seawater and air. *Deep-Sea Res., 35*, 839–853.

Weiss, R.F., J.L. Bullister, R.H. Gammon, and M.J. Warner (1985): Atmosphere chlorofluoromethanes in the deep equatorial Atlantic. *Nature, 314*, 608–610.

Wallace, D.W.R., (1992): WOCE Chlorofluorocarbon Intercomparison Report, WHPO Publication 92-1, unpublished manuscript.

APPENDICES: DISCUSSION OF ANALYSIS PROCEDURES

The following Appendices (A–J) were provided by the participating laboratories. Each laboratory was requested to provide the following information:
Items:

1) ID number of the intercomparison cylinder analyzed.
2) Analysis date(s).
3) Initial and final pressure of the cylinder.
4) Concentration of CFC-11, CFC-12.
5) Concentration of CFC-113, carbon tetrachloride and other gases measured.
6) Number of replicate analyses, analytical precision for each compound.
7) Calibration scale used for reporting concentrations.
8) Estimate and discussion of overall accuracy of reported values of each compound.
9) CFC concentrations in the reference standards, balance gas (air, nitrogen, etc), cylinder type, manufacturer, and cylinder ID number.
10) Source or method of preparing standards (or reference to published report of technique).
11) Sample chromatograms, general discussion of results, precision, accuracy, analytical problems encountered, additional comments, etc.

Appendix A: NOAA-PMEL
Appendix B: NOAA-CMDL
Appendix C: Miami
Appendix D: Kiel
Appendix E: Bremen
Appendix F: SIO
Appendix G: LDEO
Appendix H: BNL
Appendix I: Rennell
Appendix J: LODYC

APPENDIX A

1991 WOCE CFC Standard Intercomparison Results—NOAA-PMEL

John Bullister, Fred Menzia, and David Wisegarver
NOAA/PMEL
7600 Sand Point Way, NE
Seattle, WA 98115 USA
Telephone 206-526-6741
FAX 206-526-6744
OMNET: J.Bullister
Internet bullister@noaapmel.gov

The PMEL CFC Tracer group prepared and distributed the gas standard cylinders used in the 1991 WOCE CFC Standard Intercomparison. Although the PMEL group analyzed all ten of the intercomparison cylinders prepared for this study, we chose one cylinder (Airco Specta-Seal cylinder number 63855) as our primary intercomparison cylinder in this study.

In contrast to the other CFC groups participating in the intercomparison study, which had their intercomparison cylinder available for a few months at most, the PMEL cylinder (63855) has remained at PMEL since its filling in October 1990. The PMEL group had the opportunity to analyze cylinder 63855 for CFC-11 and CFC-12 content at several times during the following 18 months.

The procedures used for filling cylinder 63855 with air at Cheeka Peak, Washington on 13 October 1990 are discussed in the Methods section in the above report. Air in cylinder 63855 was first analyzed for CFC-11 and CFC-12 (versus "primary" standard CC36743) on 31 December 1990 (see Table 1 below). On 22 July 1991, approximately ½ of the air initially stored in cylinder 63855 was transferred into ten cylinders for use in the intercalibration study. Within the precision of the analytical techniques, no significant differences could be detected in the CFC-11 and CFC-12 concentrations of the air held in 63855 and the ten other intercomparison cylinders following this transfer. A detailed discussion of these procedures and comparisons is given above in Methods section above.

Cylinder 63855 was re-analyzed versus "primary" standard CC36743 on 8 May 1992.

The results of the analyses of 63855 are shown in Table 1 below. Since cylinder 63855 was analyzed at two widely separated times, the concentrations reported for this cylinder in Table 6 of the report are the averages of the December 1990 and May 1992 analyses.

TABLE 1. Comparison of 63855 with primary standard CC36743.

Cylinder Number	Press (atm)	Analysis Dates	CFC-12* (PPT)	CFC-11* (PPT)	Runs (n)	%StDev CFC-12	%StDev CFC-11
63855	176	31-12-90	496.99	272.93	4	0.3	0.1
63855	92	08-05-92	497.28	272.90	9**	0.7	0.4

Average of the December 1990 and May 1992 analyses: CFC-12 = 497.14
CFC-11 = 272.92

* All values are reported as mixing ratios (mole fraction CFC in dry air) in parts-per-trillion (PPT).

** The May 1992 analyses were done over a 2-day period. The results of the first day (5 analyses) were combined with those on the second day (4 analyses) to calculate the averages and %StDev shown in Table 1.

DISCUSSION

Analytical Methods:

All analyses were done by electron capture-gas chromatography, using methods described in Bullister and Weiss (1988). Calibration curves for CFC-11 and CFC-12 were generated from analyses of various volumes of "primary standard" gas held in cylinder CC36743. The quantities of CFC-11 and CFC-12 used to generate the calibration curves spanned the range of CFC-11 and CFC-12 injected during analyses of 68355. Techniques used for fitting detector response (chromatographic peak area) to amount of CFC standard analyzed, and for estimating the concentration of CFC-11 and CFC-12 in "unknowns" are discussed in Bullister and Weiss (1988).

Sample Chromatograms:

Typical chromatograms generated from the analyses of approximately 3 cc samples of air from 63855 on 9 Sept 1991 and 14 April 1992 are shown in Fig. 1a and 1b, respectively. Fig. 1c show the analysis of a 3 cc sample of blank (purge) gas. These chromatograms were stored in digital format, and can be reviewed and enlarged on a PC monitor using ChromPerfect chromatographic software. When the chromatograms obtained from the analyses of cylinder 63855 were reviewed on an expanded scale as shown in Fig. 1, several small peaks before the F12 peak (at about 3 minutes retention time) could be observed. The relative size of these small peaks seemed to be greater for the analyses made on 14 April 1992 (see discussion in Section IV above) and their retention times seemed to differ between the two sets of analyses. These peaks were not observed on chromatograms generated by analysis of blank gas (see Fig. 1c). We are uncertain as to the origin or identity of these peaks, which were also observed in the other intercomparison cylinders.

By careful re-integration of the chromatograms using ChromPerfect software, we feel that these small peaks make only a small contribution (less than 1%) to the calculated CFC-12 peak areas. We hope that future work will allow us to determine the origin and identity of these peaks.

Standards:

Compressed gas held in cylinder CC36743 was used to calibrate cylinder 63855 in this study. Cylinder CC6743 is an Airco Specta-Seal DOT type AL2015 aluminum cylinder. It contains a mixture of CFC-11, CFC-12 and N20 in nitrogen. This "primary standard" was prepared at SIO in July 1985, and has been assigned values of CFC-11 = 278.47 PPT, CFC-12 = 473.85 PPT on the SIO86 scale. All concentrations reported are "mixing ratios," expressed as mole fractions of CFC in dry gas. The pressure of "primary standard" CC36743 during the analyses in December 1990 and May 1992 was approximately 20 atm. It is an interesting coincidence that the concentrations of CFC-11 and CFC-12 in "primary standard" CC36743, prepared in the laboratory at SIO in 1985, are within about 5% of the CFC-11 and CFC-12 concentrations of the compressed air samples collected at the Cheeka Peak, WA site in late 1990.

The methods of preparing and calibrating SIO primary standards are discussed in Bullister (1984). The estimated accuracy of this scale is about 1.5% for CFC-11 and 0.3% for CFC-12 (Weiss *et al.* 1985).

To check for the long term stability of the CFC-11 and CFC-12 content of "primary standard" C36743, this cylinder was initially compared to another SIO primary standard (CC16436) in July 1985, and during the WOCE CFC Intercomparison Cruise in December 1989. Within the precision of the CFC analytical techniques, the concentrations of CFC-11 and CFC-12 in CC36743, measured relative to CC16436, did not show measurable changes over this 4-year period.

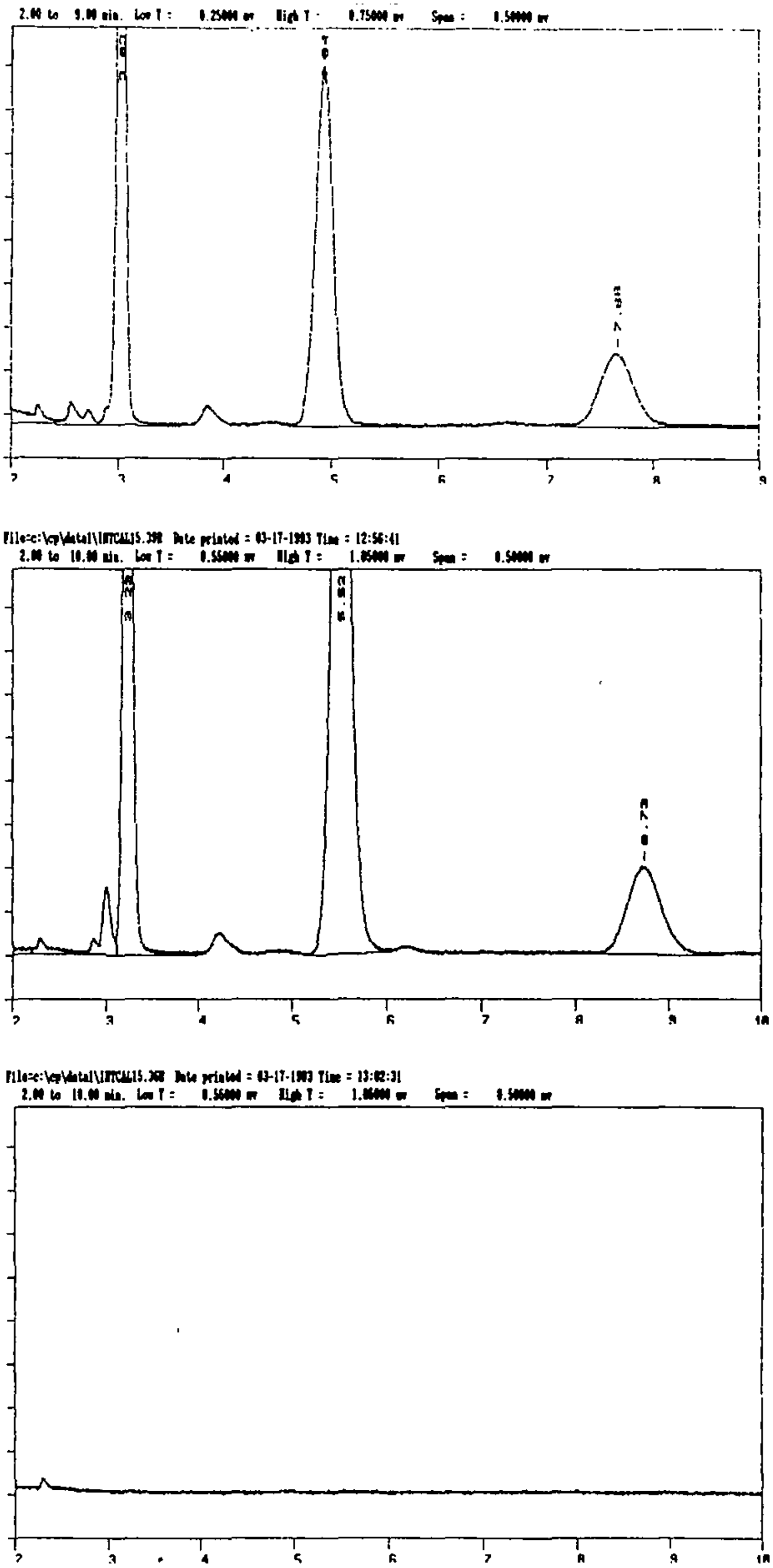


Figure 1. Sample chromatograms of a 3.070 ml injection of:
- a. Air from cylinder #63855 (analysed on 9 September 1991).
- b. Air from cylinder #63855 (analysed on 14 April 1992).
- c. Blank gas (analysed on 14 April 1992).

APPENDIX A: Fig.

APPENDIX B

1991 WOCE CFC Standard Intercomparison Results—NOAA-CMDL

James H. Butler, James W. Elkins, Richard C. Myers, and Scott O. Cummings
NOAA Climate Monitoring and Diagnostics Laboratory/
Nitrous Oxide and Halocarbons Division
R/E/CG1 325 Broadway
Boulder, CO 80303 USA

Methods:

All calibrations were conducted on electron-capture gas chromatographs. CFC-12 was separated on a Porasil column, all other halocarbons were separated on an SP-2100 column. The GC's were configured for backflushing. Responses for these gases in cylinder RR-10833 were ratioed to those for the gases in one of our secondary standards (AAL-15904). Cylinder AAL-15904 is a Scott, Aculife-treated aluminum cylinder, which was filled to 2000 psi with NWR air on 10/25/89, and subsequently calibrated with a series of gravimetrically prepared, primary standards which were made up in our laboratory. Best-fit curves of the ratios of primary standards to AAL-15904, from measurements made over 3–6 months, constitute the scale for subsequent calibrations by ratio to AAL-15904.

All of our values are reported as dry mole fractions and therefore represent true mixing ratios. They are NOT measures by volume (i.e., pptv), as our primaries are prepared by gravimetric techniques and hence are based upon mass determinations rather than volumetric preparations. This may seem like a small, perhaps at times insignificant, distinction, but it is an important one. Therefore, we like our numbers to be expressed as ppt or ppb; this way, we make no assumptions about Van der Waal forces, etc.

The mixing ratios (ppt) of the various gases in our secondary standard (AAL-15904) are as follows:

CFC-12	467.7	(3.2)
CFC-11	252.5	(3.4)
CFC-113	73.8	(2.0)
CH_3CCl_3	146.1	(2.7)
CCl_4	103.0	(1.8)

where the numbers in parentheses are standard deviations for a single measurement.

Cylinder RR-10833 was ratioed to AAL-15904 on 5 separate days over a 3-week period in October 1991. On each day, RR-10833 was run six times, with each analysis bracketed by analyses of the secondary standard, for a total of 13 runs on the GC. In calculating our statistics, the mean ratio for each daily run is treated as a single data point. This is because differences in measurements on different days are often sufficiently large as to void the assumption of normality in the entire data set. This is a conservative way to report our results; although the standard deviation, which represents differences among daily means, can be smaller, the smaller value for n (5 vs 30) and larger value for t, generally make for wider confidence limits. At least five runs are required to obtain a reasonably constant measure of the standard deviation and to reduce Student's-t to a reasonable value.

Results:

The results for our calibrations of Cylinder RR-10833, expressed as dry mole fractions, are as follows:

CFC-12	499.9	(1.7)
CFC-11	273.7	(0.4)
CFC-113	82.6	(0.5)
CH_3CCl_3	165.7	(0.3)
CCl_4	108.3	(0.3)

where the number in parentheses is the standard deviation for a single measurement. Confidence limits on our estimates would be computed as follows (e.g., 95% CL for CFC-12).

$$95\%\,C.L. = \pm\frac{ts}{\sqrt{n}} = \pm\frac{(2.776)(1.7)}{\sqrt{5}} = \pm\ 2.1$$

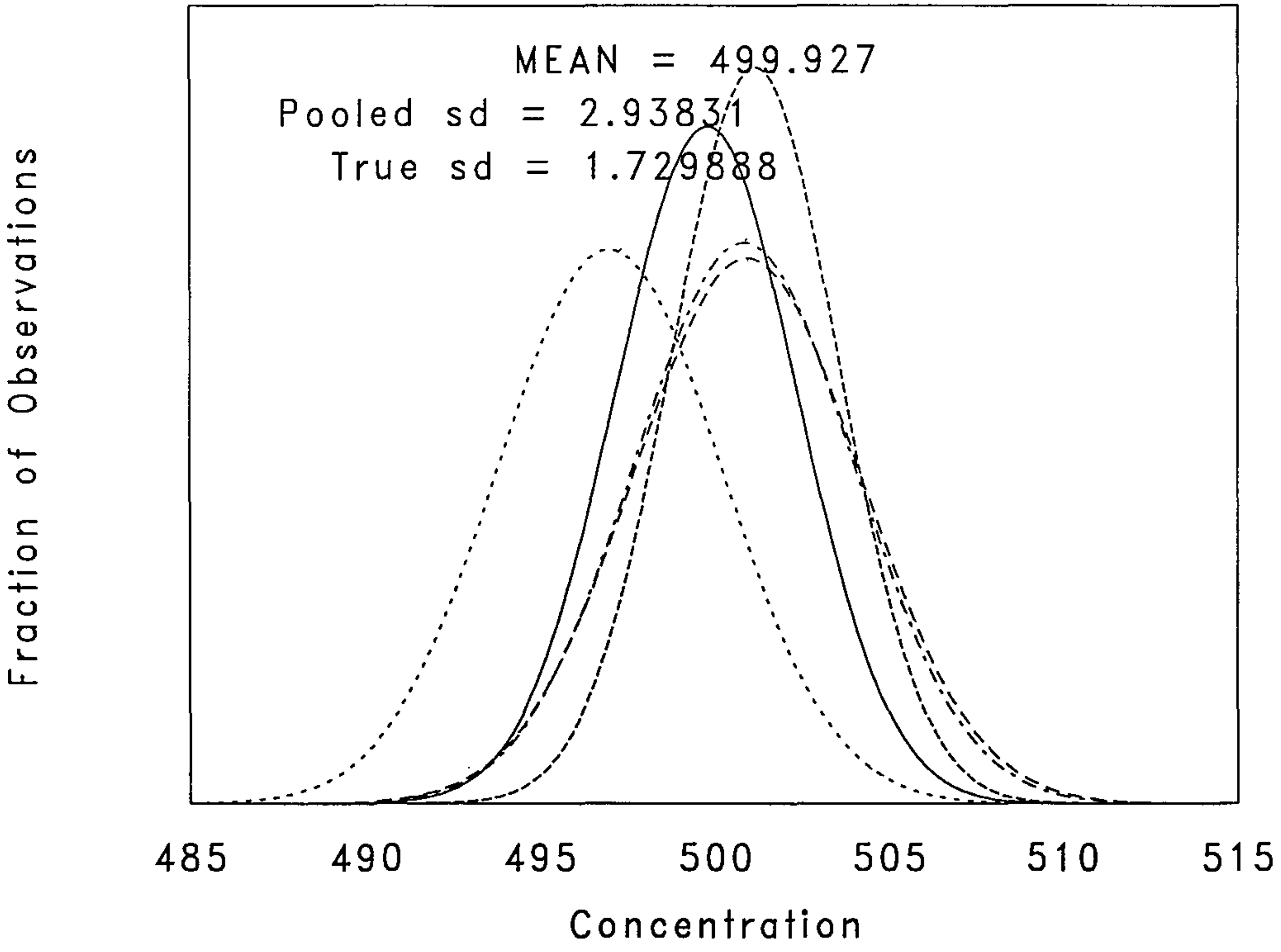
Accuracy:

We express absolute accuracy as the residual standard deviation of a fit through a series of prepared standards. Granted, one could argue that such a measure is not absolute, and we agree. However, in the absence of any absolute "standard" to go by, this is as close an estimate as is possible. As NOAA/CMDL uses gravimetric standards, each cylinder is prepared with considerable accuracy in weighing. By fitting the data for a number of standards over a range of concentrations, we are able to estimate our ability to prepare the standards, including errors in transfer, contamination, etc. One thing that might not show up is purity of original gases; however, we compensate in part for that by preparing standards from liquid and gas sources.

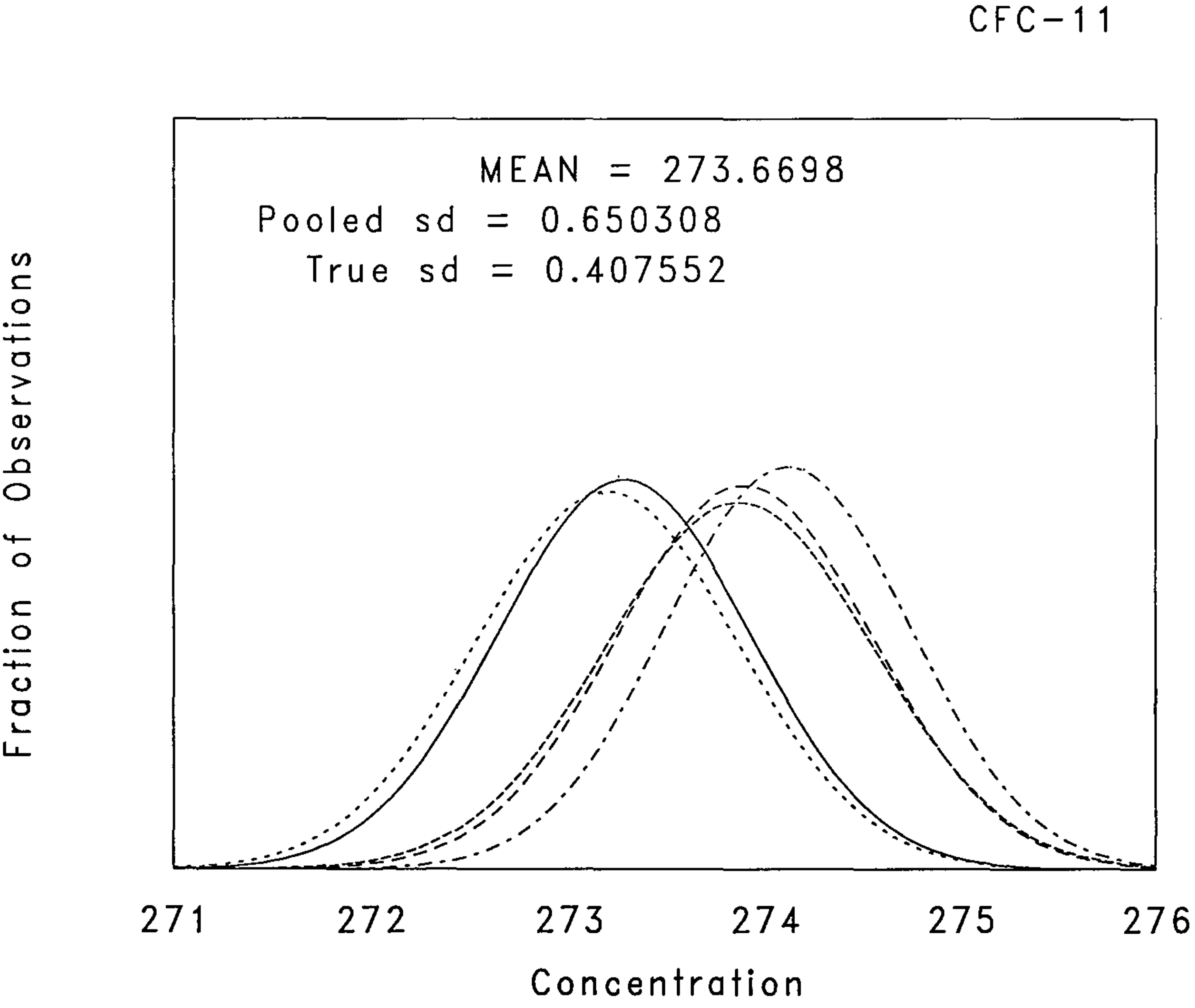
You can see from the attached plots that the residual standard deviation of the curves for CFC's 11 and 12 is on the order of 1%. As with our estimates of precision, we feel this is a conservative approach. For example, if we treat our data by looking at the logs of ratios (i.e., Weiss's approach) the variation appears to be about half of the residual standard deviation (figures also attached).

Also attached are some figures showing the presumed normal distributions of the daily runs for each of the gases. On these figures, the "pooled" standard deviation is computed from the geometric, weighted means of the variances for all runs. The "true" (poor choice of words?) standard deviation is simply the standard deviation of the five daily means.

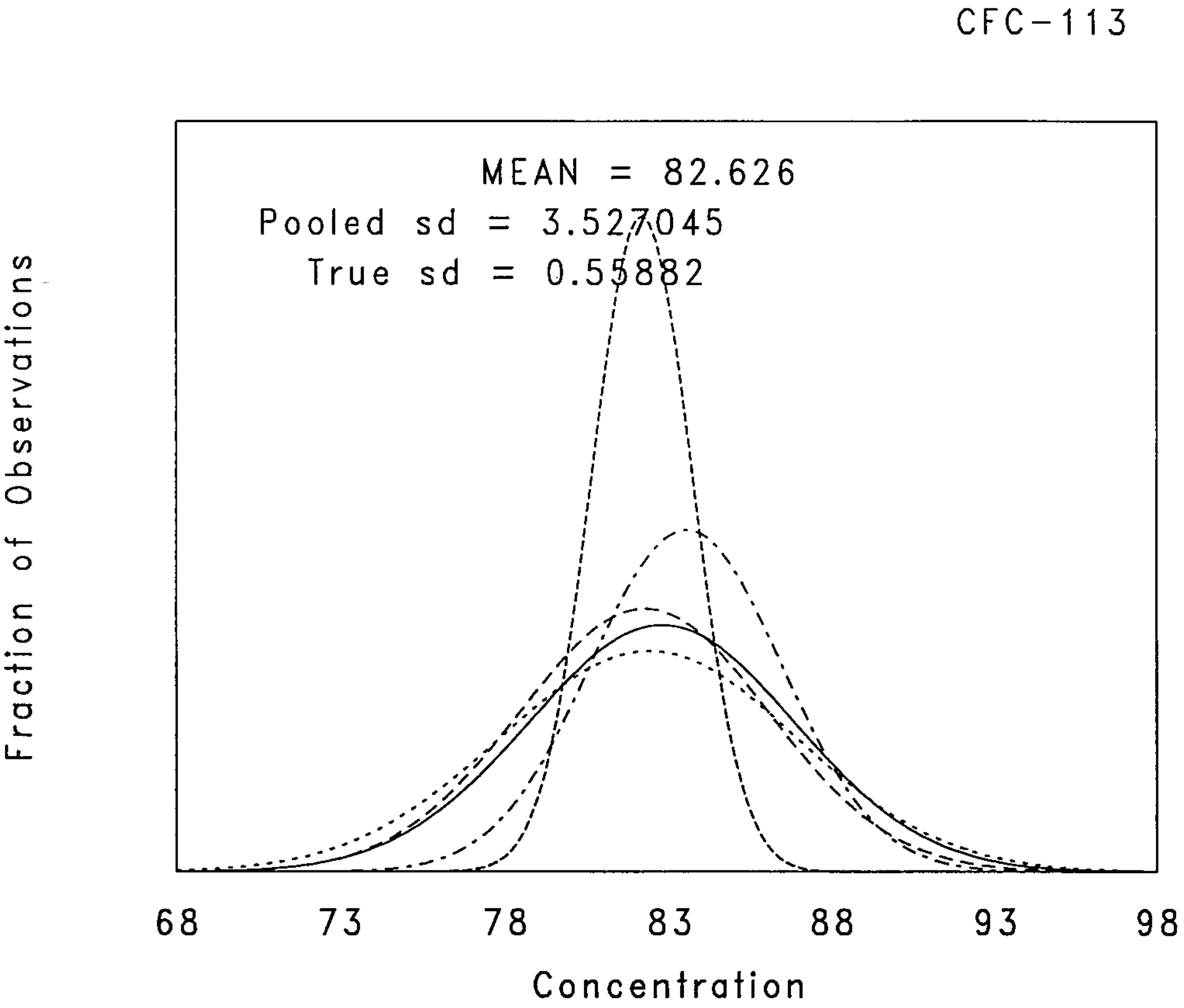
CFC-12



APPENDIX B: Fig. 1

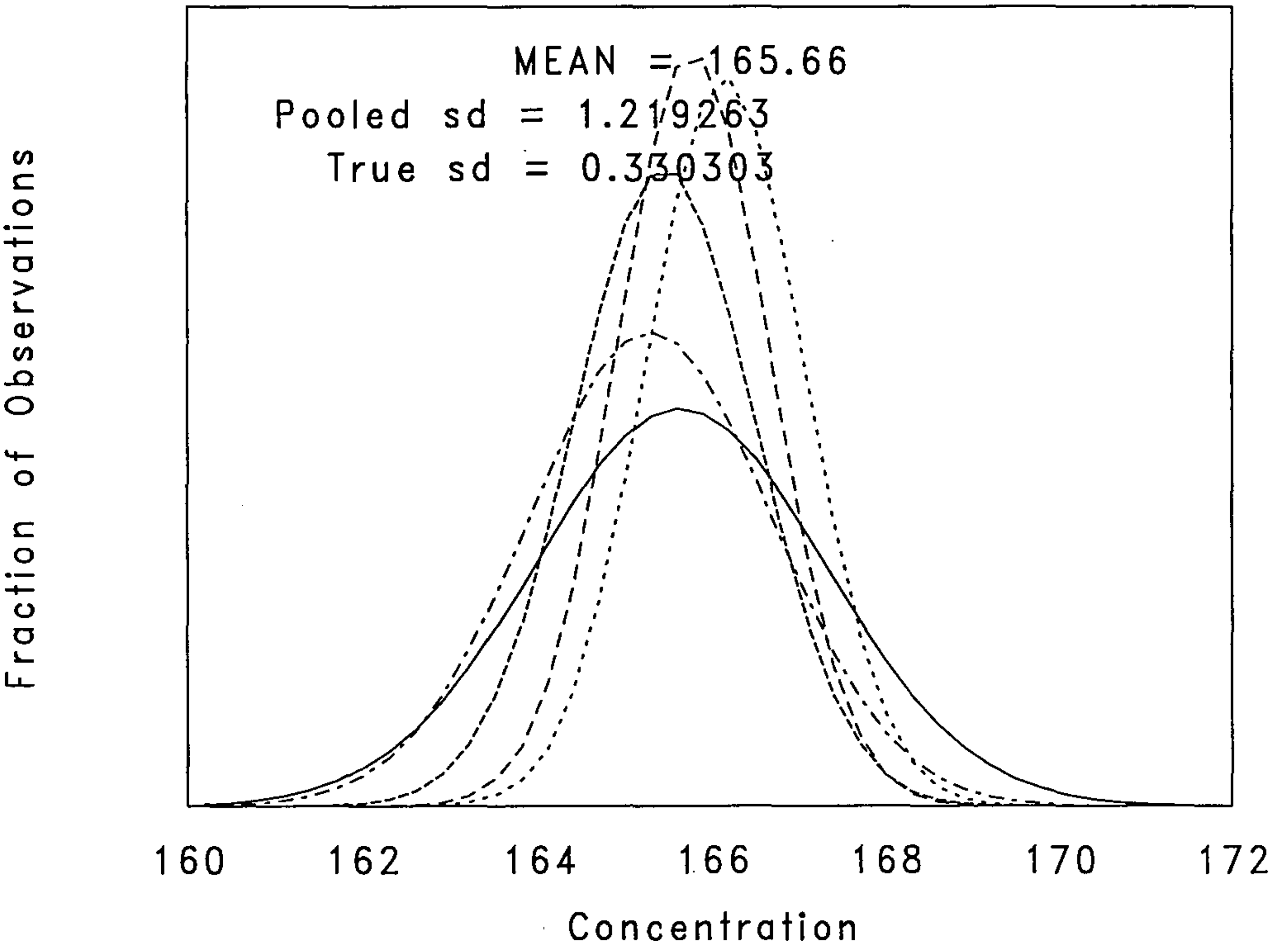


APPENDIX B: Fig. 2

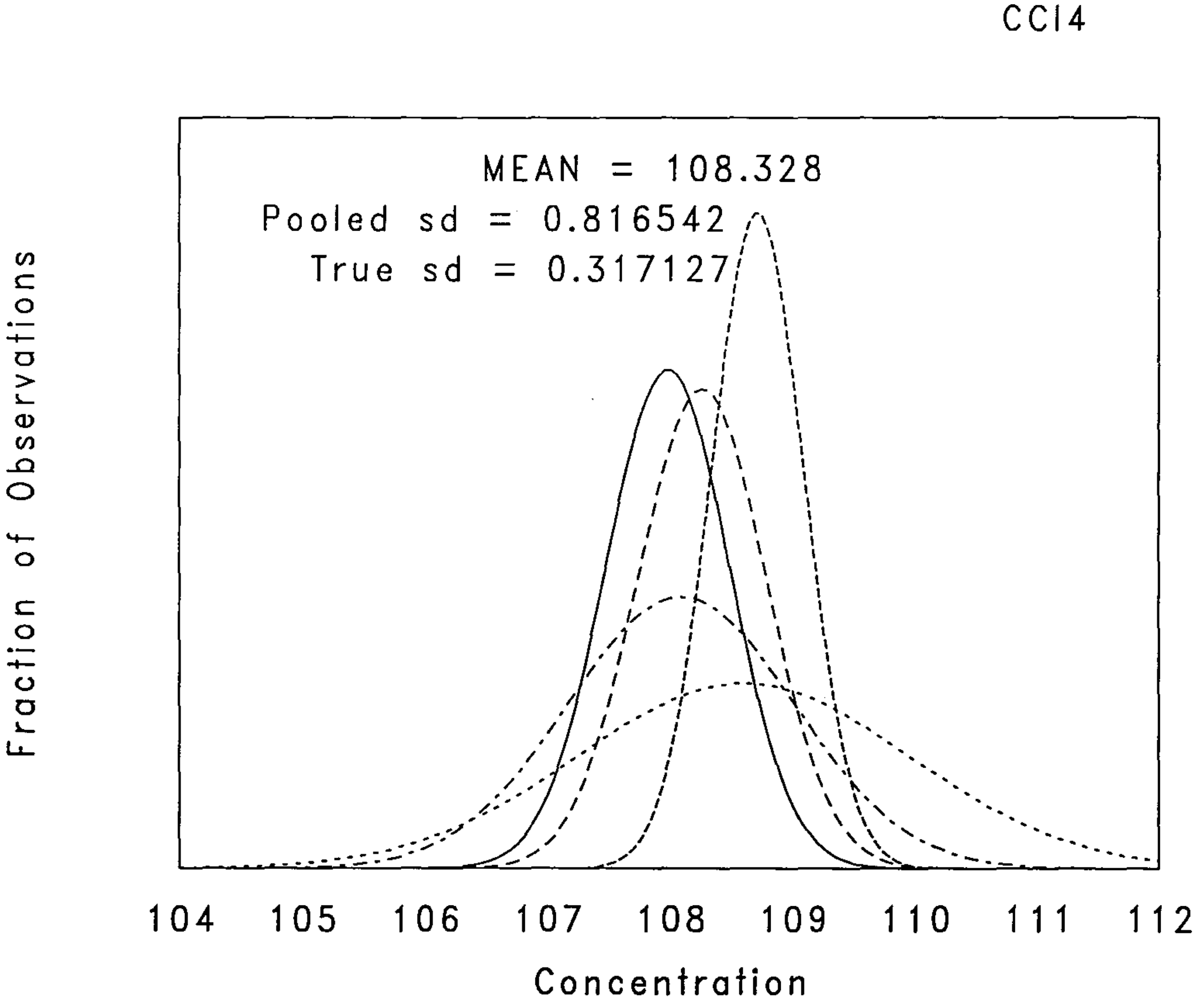


APPENDIX B: Fig. 3

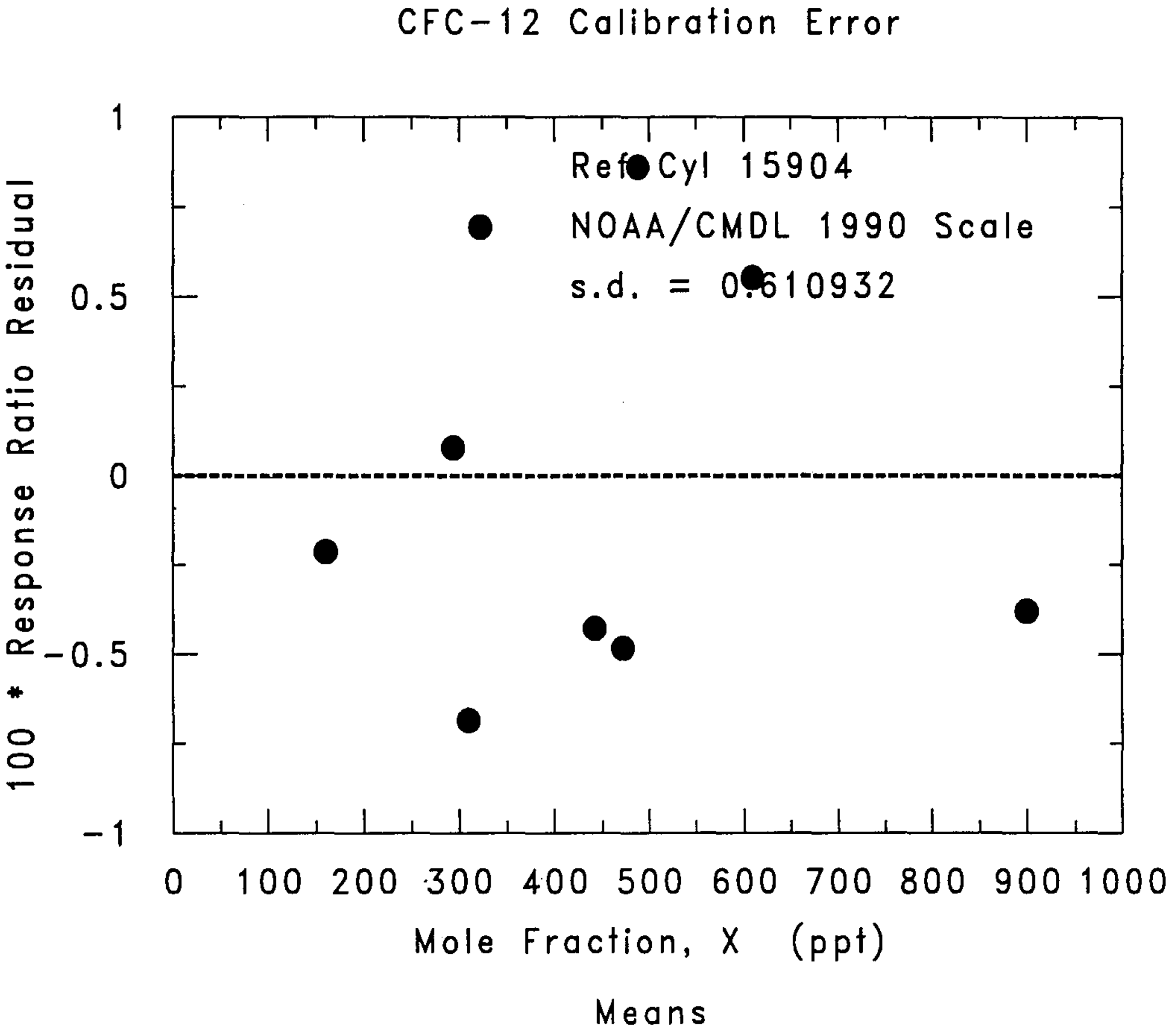
CH3CCl3



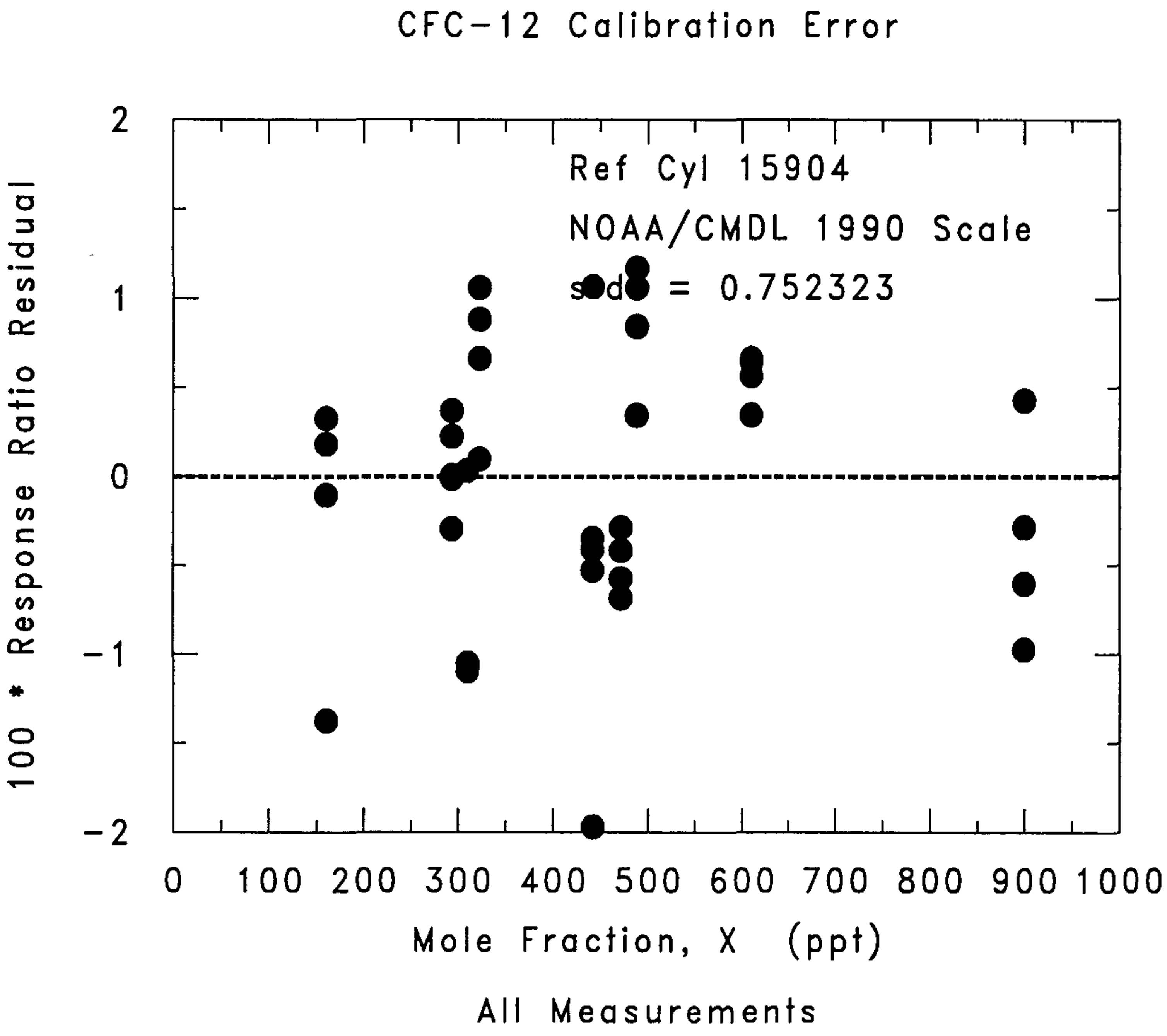
APPENDIX B: Fig. 4



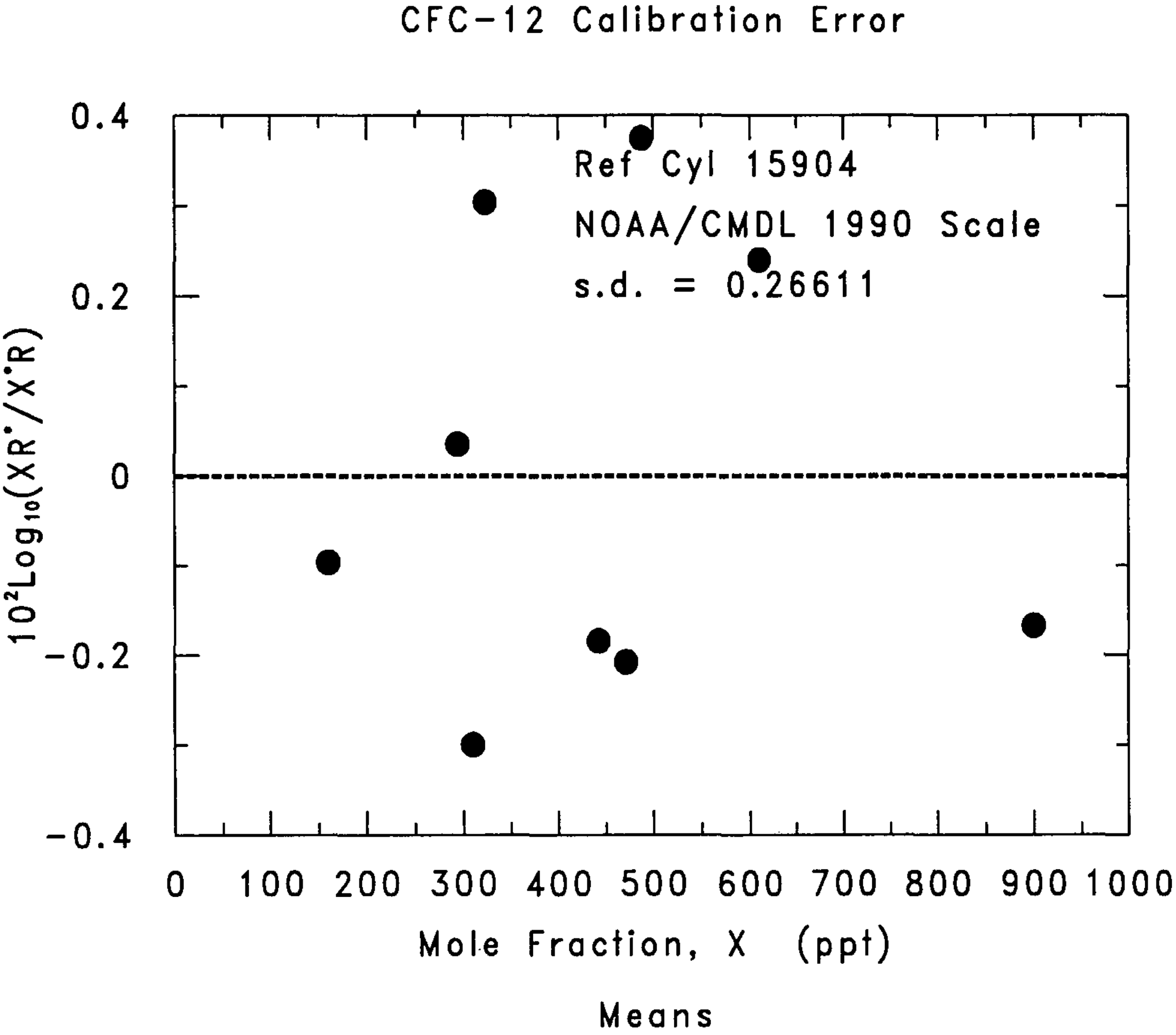
APPENDIX B: Fig. 5



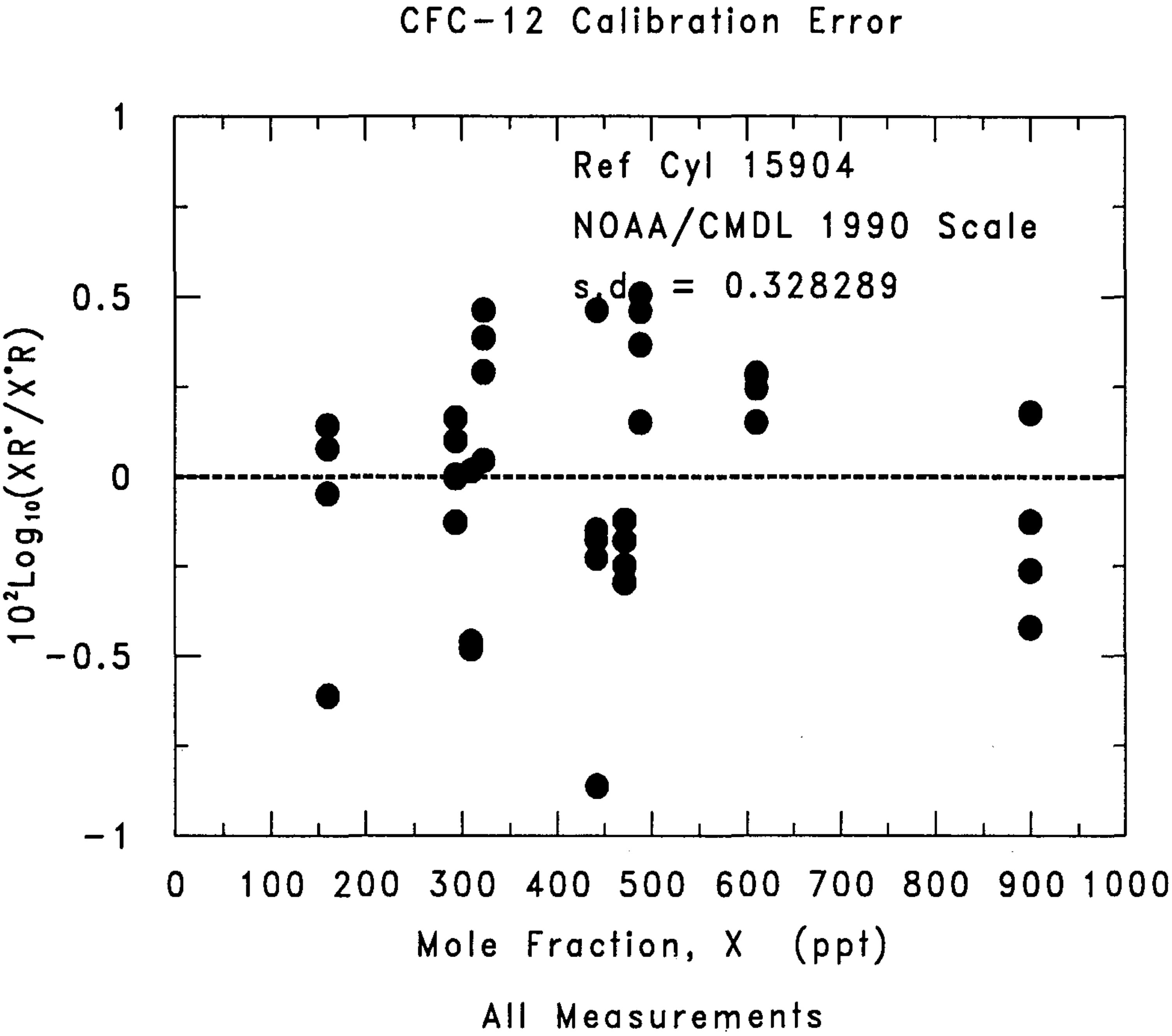
APPENDIX B: Fig. 6



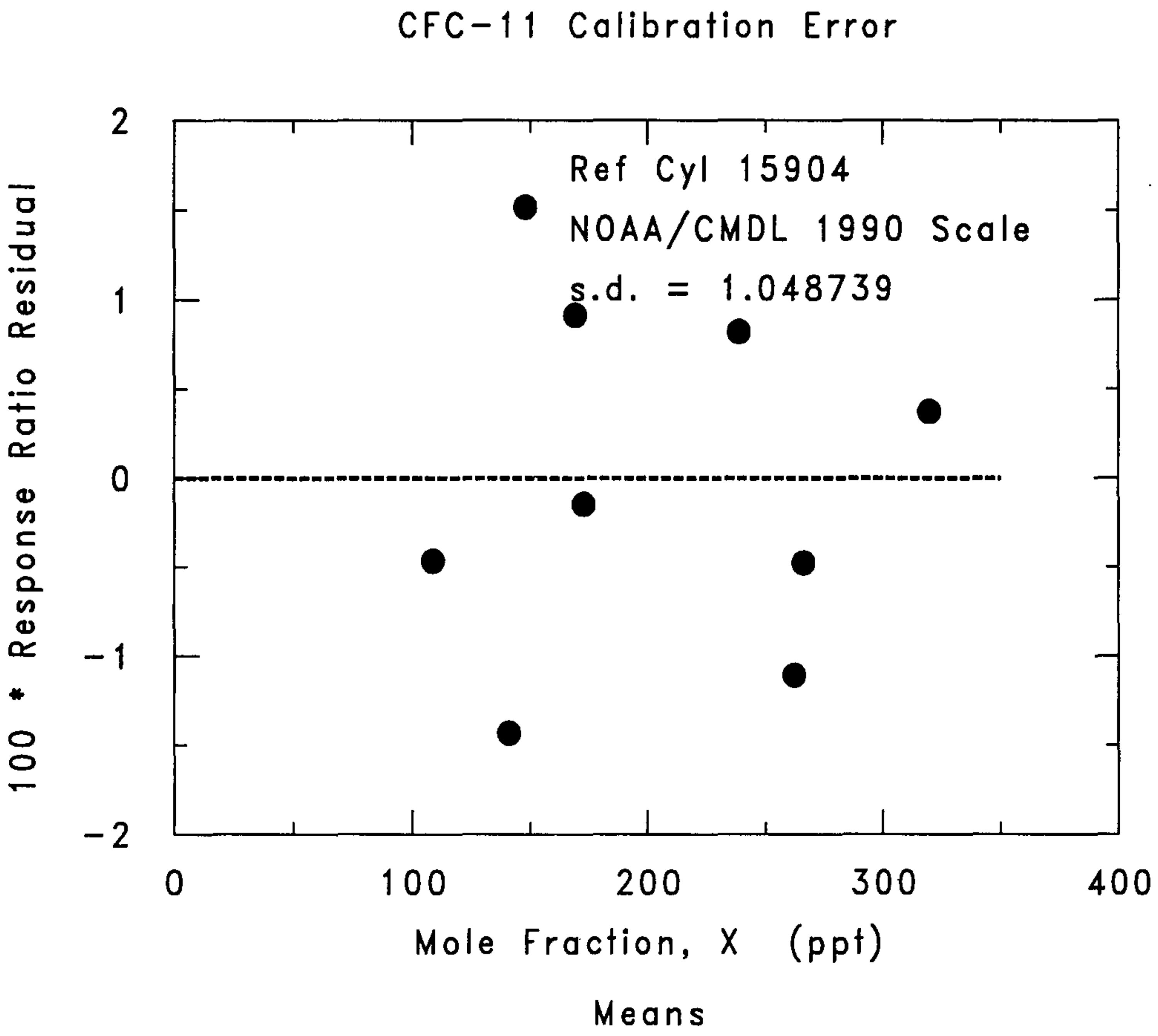
APPENDIX B: Fig. 7



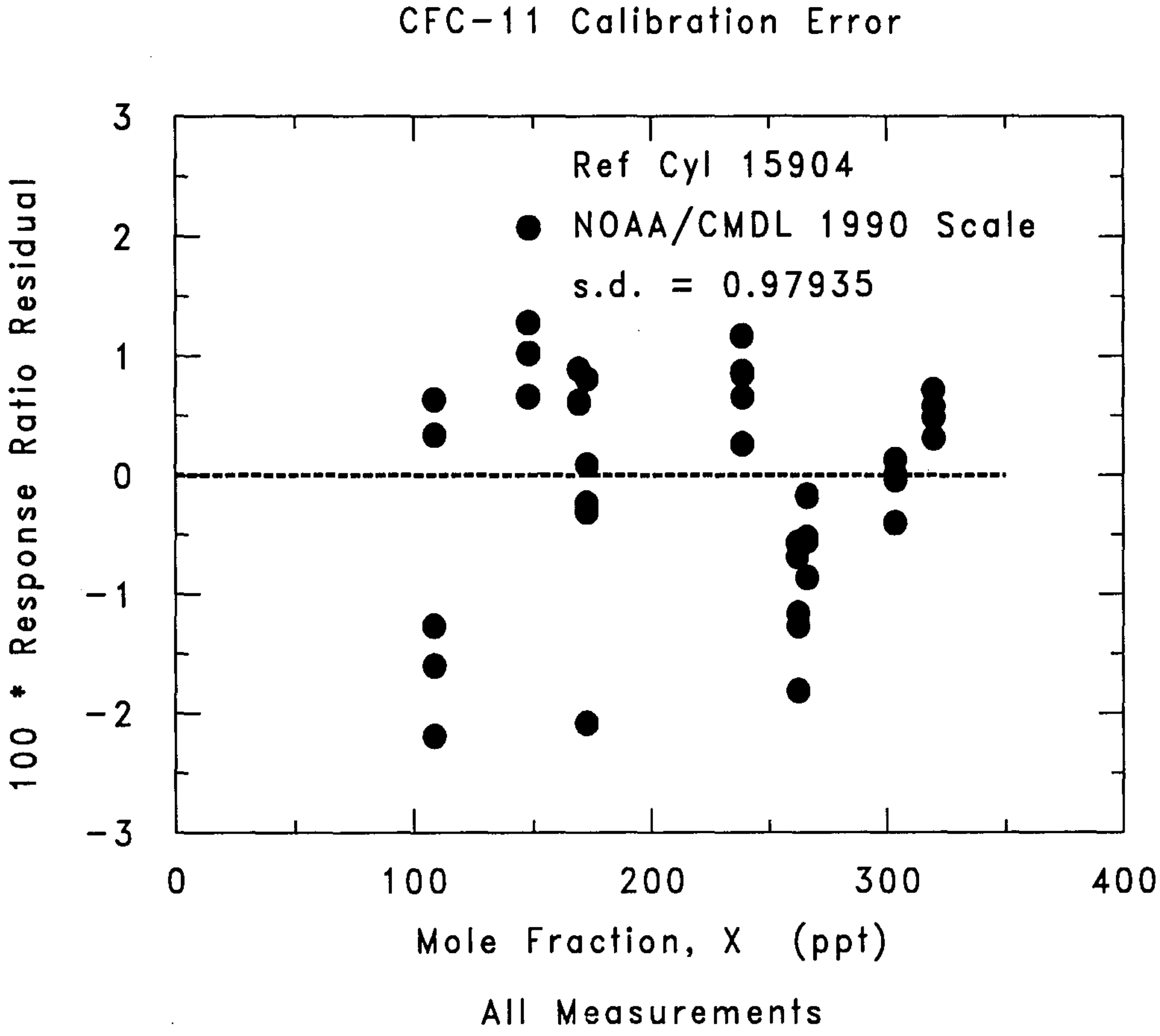
APPENDIX B: Fig. 8



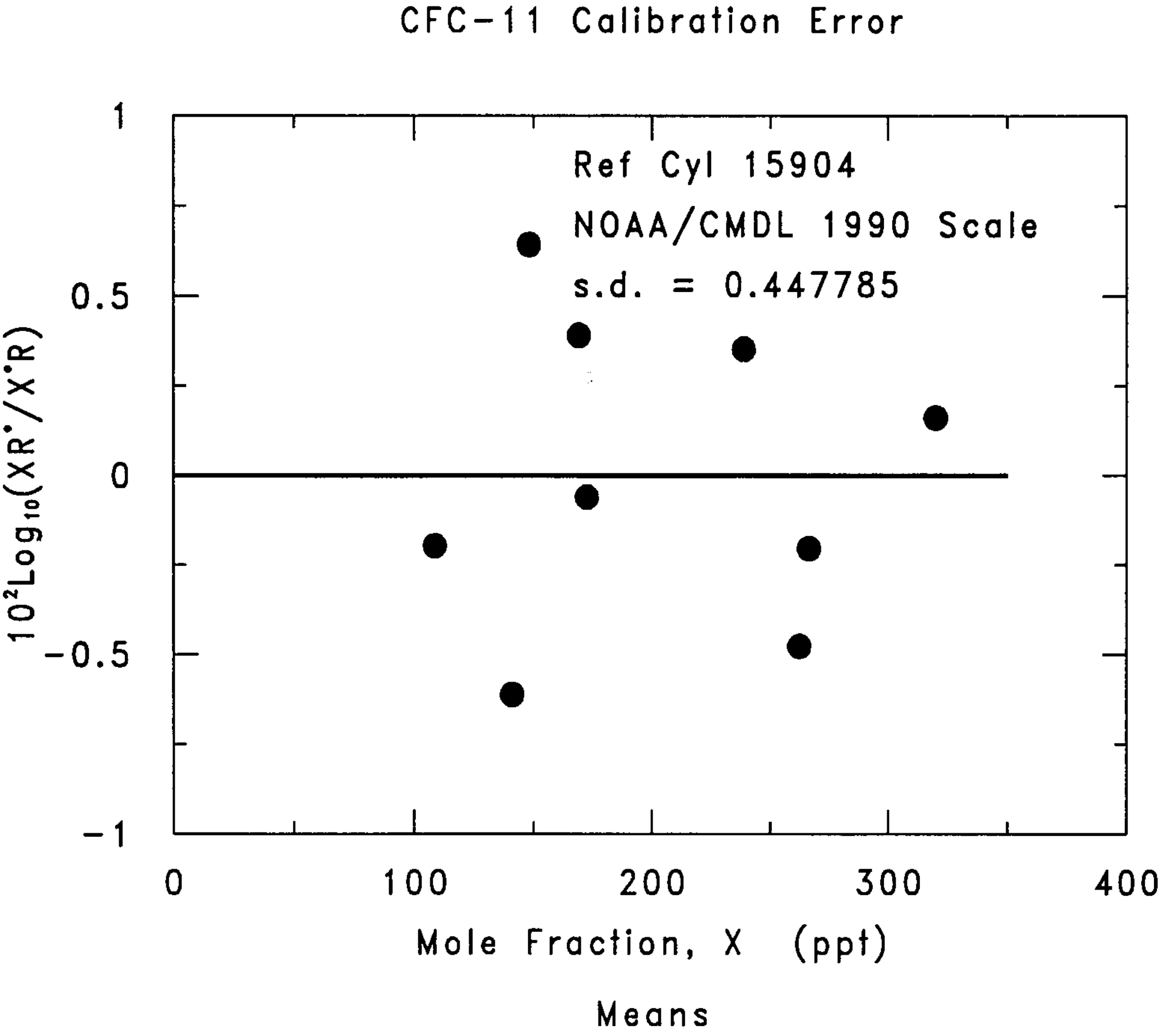
APPENDIX B: Fig. 9



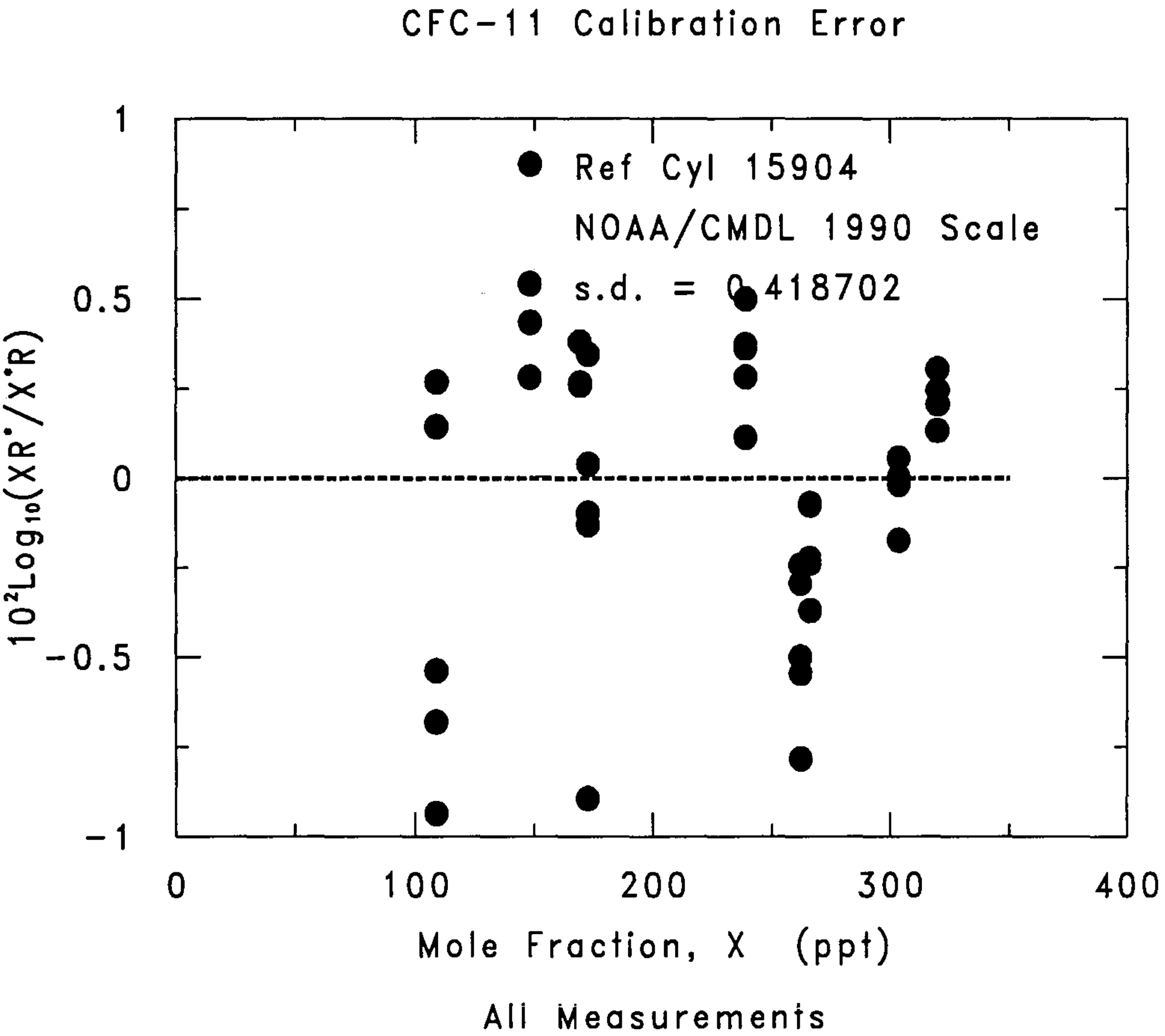
APPENDIX B: Fig. 10



APPENDIX B: Fig. 11



APPENDIX B: Fig. 12



APPENDIX B: Fig. 13

APPENDIX C

1991 WOCE CFC Standard Intercomparison Results—Miami

Kevin Sullivan and Rana Fine
Rosensteil School of Marine and Atmospheric Science
University of Miami
4600 Rickenbacker Causeway
Miami, FL 33149 USA
Telephone: 305-361-472
OMNET: R.Fine
Internet: fine@RCF.rsmas.miami.edu

Items:

1) ID number of the intercomparison cylinder analyzed: 008338.
2) Analyses of the cylinder were done on 19 and 20 Dec 1991, but only those on the 20th were used in the averages.
3) The initial and final pressures of the cylinder were close to the lower limit on the regulator.
4–6) CFC-11 and CFC-12 were the only gases analyzed. The results reported are based on nine analyses: 275.6 (±1.7) pptr 11, 487.4 (±1.5) pptr 12.
7–11) as discussion:

The intercalibration cylinder was compared to our working standard that was closest in concentration (163.7 pptr 11, 293.4 pptr 12). This working standard in turn had been compared to our primary standard which had been calibrated on the SIO 1986 scale (109.5 pptr 11, 129.2 pptr 12). Our standards are prepared by filling a short length of stainless steel tubing with gases obtained from Union Carbide, which are approximately 1000 ppm in either CFC-11 or CFC-12. The tube is then flushed into an aluminum cylinder with zero air. The aluminum cylinder is pressurized with a series of zero air cylinders of higher pressure. The resulting standards rarely exceed 2000 psi.

The target concentrations of the standards were chosen so that the largest convenient analysis of the standard gas (3 sequential 0.5 and 3 ml aliquots) contains approximately as much CFC as a 3 ml aliquot of clean marine air. These lower-than-atmospheric concentrations allow the calibration curves to extend further towards the lowest aqueous concentrations quantitated. Unfortunately, the longer the aliquots of CFC's remain on the cold trap, the broader the peaks will be in the chromatogram. For the best intercomparison of gases, the concentrations should be close so that the same volume of gas could be collected on the cold trap. For this intercalibration, analyses of different volumes of the unknown gas resulted in concentrations that were approximately 1% different for CFC-11.

The precision within triplicate analyses of the same volume was better than 0.1% relative standard deviation for both CFC; however, inclusion of all nine analyses of either 3 ml or 6 ml increased the relative standard deviations to 0.6% for CFC-11 and 0.3% for CFC-12. Three sequential analyses of 3 ml aliquots resulted in concentrations of 277.80 (±0.06) pptr 11 and 487.88 (±0.32) pptr 12. Three sequential analyses of 6 ml aliquots resulted in 274.42 (±0.06) pptr 11 and 488.46 (±0.32) pptr 12. The differences in the concentrations of CFC-11 are statistically significant, but it is not obvious which value is more accurate. Inclusion of three earlier analyses with both of these triplicates results in the reported concentrations: 275.61 (±1.72) pptr 11 and 487.42 (±1.49) pptr 12, rounded to four significant figures.

The dependence of the calculated concentration upon the volume of gas analyzed is believed at least partially to be due to the changes in the peak shape while the analytes reside in the cold bath. The cold trap has two components, Porasil C and Porapak T. The Porapak T has a high affinity for CFC-12, and so CFC-12 does not migrate much along the adsorbent bed during the trapping period. The Porasil C does not retain CFC-11 as well, and so CFC-11 will migrate and diffuse more while on the cold trap. Also sequential aliquots of CFC in a single analysis will migrate and diffuse to slightly different extents. Therefore, a careful comparison of the chromatograms for a single aliquot of one gas and for an analysis containing two or more aliquots of another gas, which is less concentrated in CFC's, would likely show slightly different CFC-11 peak shapes even if the total number of moles trapped is the same. The change in the peak shape would be very slight, but could contribute to the difference in the calculated concentrations of CFC-11 in the intercalibration cylinder.

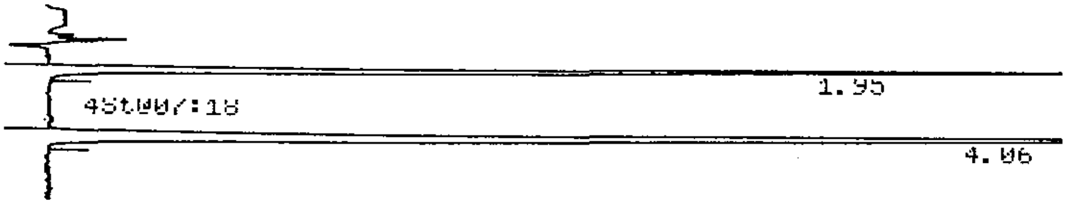
Another factor that could be partially responsible for the CFC-11 results is the shape of the calibration curve. A plot of the sensitivity (area counts per mole CFC) versus the moles analyzed, which is the first derivative of the calibration curve, shows a relative maximum for CFC-11 but not for CFC-12. This relative maximum is representative of the detector response, but is likely enhanced by the changes in peak shape with larger volumes analyzed. Different equations fit to the data could yield comparable regression results, and yet appear quite different. The results are influenced by the selection of the calibration curve and the location of the analyses on the calibration curve. In this case if equation #6 is chosen, the 3 and 6 ml analyses would give 277.80 and 274.42 pptr 11, but if equation #4 is chosen the results would be 274.40 and 276.42 pptr 11, respectively. If a calibration equation split the difference between these two equations, the results for the 3 and 6 ml analyses would agree better. The equation with the best fit was chosen.

```
          4.04      39916        770327        01

Approximate Concentration (PPTrillion) in  6.2663    milliliters
F12=  468.5961        F11=  220.43743
F12/F11=  2.1257556
```

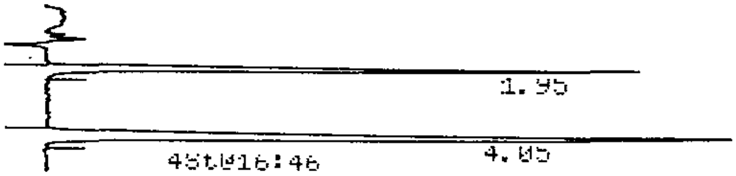
STANDARD CYLINDER

010
1730
24

```
CHANNEL A      INJECT  12/20/91 15:04:34
```



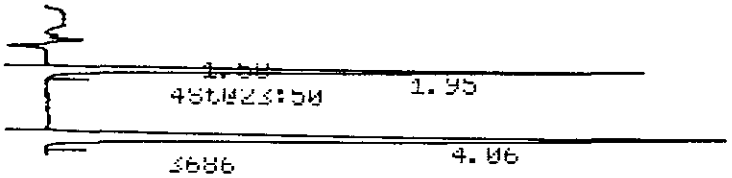
```
 Peak     Ret. Time   Height       Area      BL Code

   1         1.95     21305       407989      01
   2         4.06     38579       759814      01
Approximate Concentration (PPTrillion) in  6.2663    milliliters
F12=  469.5083        F11=  217.83389
F12/F11=  2.1553502

I1=0
I2=1
IF="  I7 IV= 0

CHANNEL A      INJECT  12/20/91 15:12:18
```



```
 Peak     Ret. Time   Height       Area      BL Code

   1         1.95     10909       205601      01
   2         4.05     19017       374503      01

Approximate Concentration (PPTrillion) in  2.9719    milliliters
F12=  450.39849       F11=  241.80759
F12/F11=  1.8626317
```

010
2405
1050

```
1[illegible]:20:41
CHANNEL A      INJECT  12/20/91 15:21:27
```



```
 Peak     Ret. Time   Height       Area      BL Code

   1         1.95     11003       204445      01
   2         4.06     18818       373210      01

Approximate Concentration (PPTrillion) in  2.9719    milliliters
F12=  447.59074       F11=  241.02431
F12/F11=  1.8570357
```

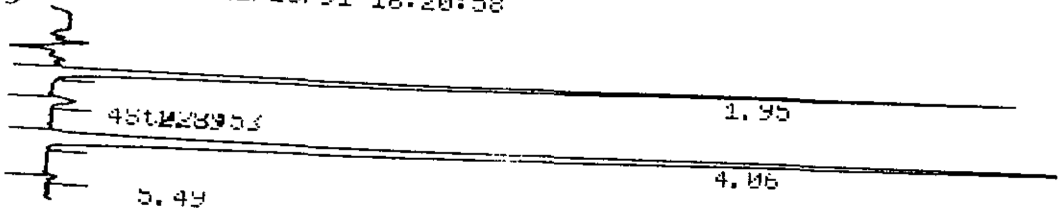
126

APPENDIX C: Fig. 1

INTERCALIBRATION CYLINDER

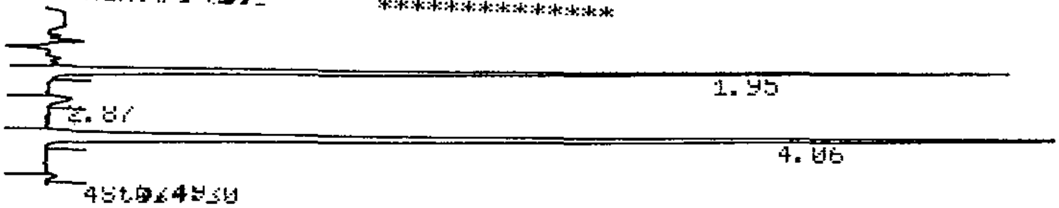
1020.0
24.05

```
CHANNEL A     INJECT  12/20/91 16:20:58
```

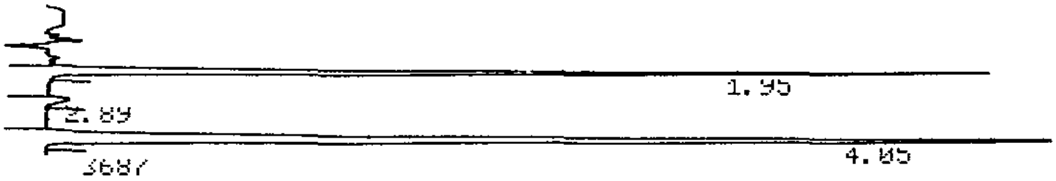


```
Peak     Ret. Time   Height        Area      BL Code
  1         1.95      17763       328622       01
  2         2.89        466        12383       01
  3         4.06      31410       616757       01
  4         5.49        258         6374       01
Approximate Concentration (PPTrillion) in  2.9719    milliliters
F12=  767.3296          F11=  382.42353
F12/F11=  2.0064916

Parameters for Run # [illegible]          ***************
```

61.0
1029.9
24.1

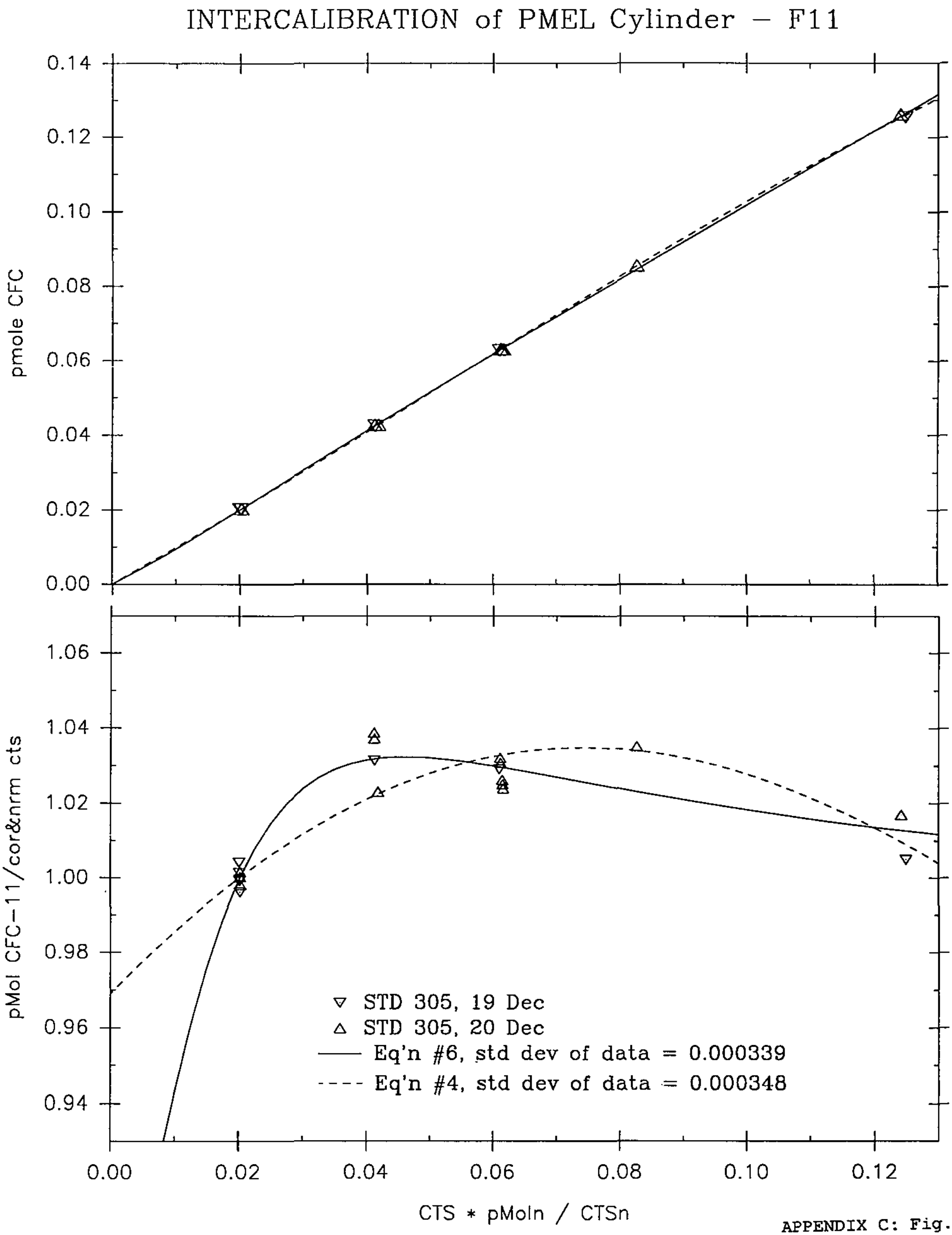


```
Peak     Ret. Time   Height        Area      BL Code

  1         1.95      17692       328552       01
  2         2.87        446        12423       01
  3         4.06      31442       616970       01
  4         5.49        264         6348       01

Approximate Concentration (PPTrillion) in  2.9719    milliliters
F12=  767.08479         F11=  382.51435
F12/F11=  2.0053752

PLOT OFF
PLOT "A" AUTO
 16:38:09Parameters for Run #  82.        ************ **
    Sample Type ? 3
       Pressure ? 1025.9
    Temperature ? 24.1
  # Large Loops ? 0
 # Medium Loops ? 1
  # Small Loops ? 0
Syringe I.D. (Note: A=1, B=2, C=3...)? 0

CHANNEL A     INJECT  12/20/91 16:39:12
```

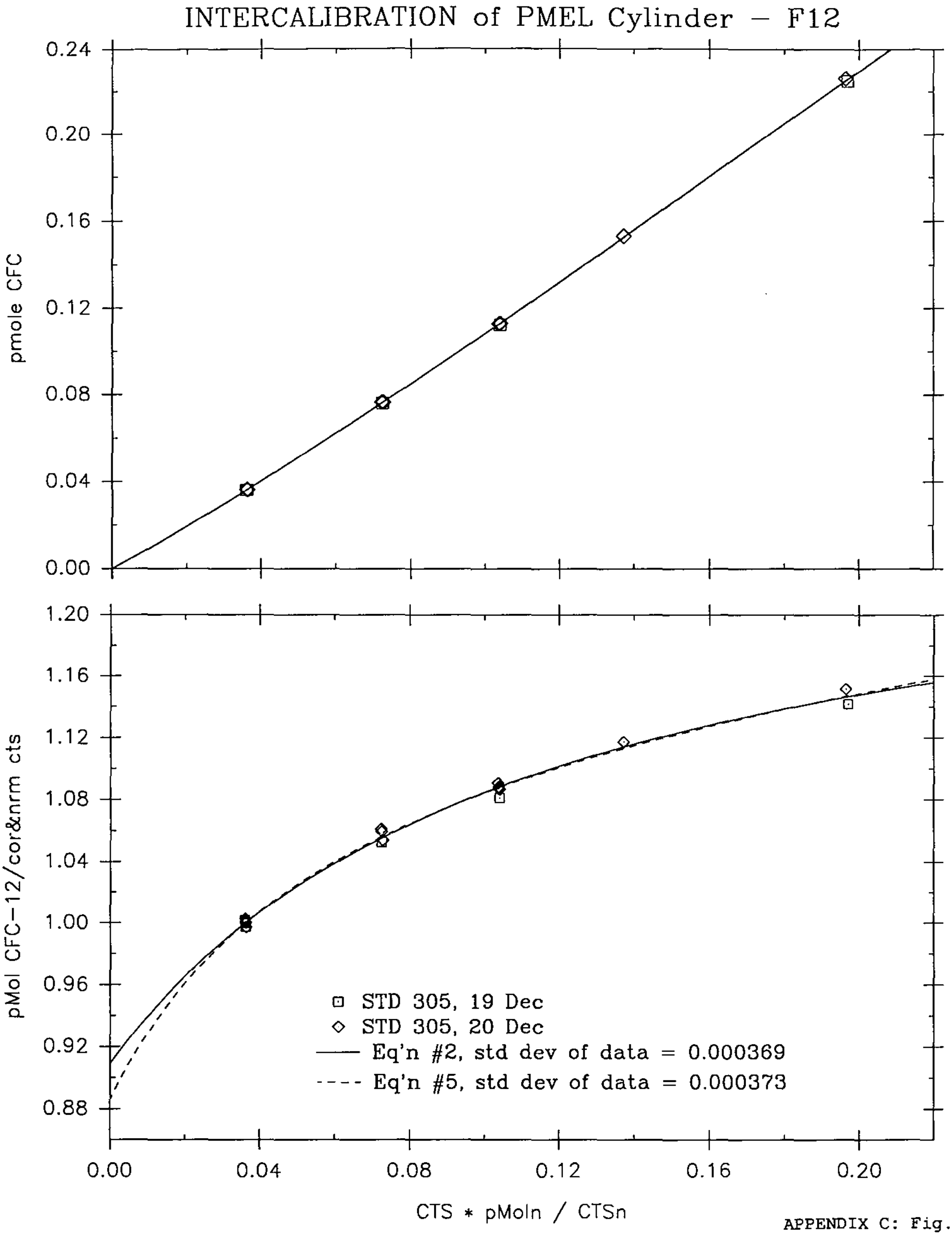


```
Peak     Ret. Time   Height        Area      BL Code

  1         1.95      17453       328988       01
  2         2.89        427        11942       01
  3         4.05      31405   61704[illegible]   01
```

APPENDIX C: Fig. 2



APPENDIX C: Fig. 3



APPENDIX C: Fig. 4

APPENDIX D

1991 WOCE CFC Standard Intercomparison Results—Kiel

Monika Rhein
Institut für Meereskunde Kiel
Dusternbrooker Weg 20
D 2300 Kiel
Germany
OMNET: IFM.KIEL

Items:

1) ID of cylinder analyzed: 008332.
2) Date Analyzed: Oct 25, 1991.
3) Initial and final pressures of cylinder: not checked.
4) a) CFC-11 [ppt]: 270.4 ± 4.1 (±1.5%).
   b) CFC-12 [ppt]: 503.5 ± 6.4 (±1.3%).
5) No values.
6) a) CFC-11: 12 replicates, 4 different sample volumes, 1.5%.
   b) CFC-12: 12 replicates, 4 different sample volumes, 1.3%.
7) SIO-scale.
8) The standard deviations of the 12 replicates are for CFC-11: 1.5%, for CFC-12: 1.3%, the standard deviations reported by the Scripps lab for the reference standard are for CFC-11: 0.47%, for CFC-12: 0.23%, and the CFC-12 blank during the day of measurement was 0.3 ± 0.015 mVs (6.2 ± 0.3 ppt). The CFC-12 concentration has been corrected by this blank. Concentrations of the intercomparison cylinder have been determined on four different sample volumes (0.5 ml, 1 ml, 2 ml and 2.5 ml) and a reference standard calibration curve was done before (No. 1) and after (No. 2) the measurements of the inter-comparison cylinder. The results differ slightly for each volume, and the reported mean and standard deviation are averages of all measurements for calibration curve 1 and thus should include errors resulting from the calibration procedure. The uncertainty by application of the second calibration curve increases the uncertainty by 1% for CFC-12 and 1.5% for CFC-11. The accuracy is estimated to be ±2% for both, CFC-11 and CFC-12.
9) Reference standard is SIO tank, No. 83979, provided by Ray Weiss CFC-11 [ppt]: 288.1 ± 0.23%; CFC-12 [ppt]: 553.8 ± 0.47%, manufacturer of the cylinder: SpectraSeal, material: aluminum.
10) Standard was prepared by Ray Weiss, Scripps Institution of Oceanography.
11) Chromatograms:

Fig. 1: Tank 008332, sample: 3.04 mg, atten: = 1.
Fig. 2: Blank, atten: = 1, CFC-11: –, CFC-12: 0.3 mVs.
Fig. 3: Tank 83979, sample: 3.04 mg, atten: = 1.
Fig. 1, Fig. 2, the top of the CFC-12 peak is cut off.
Discussions: See 8.

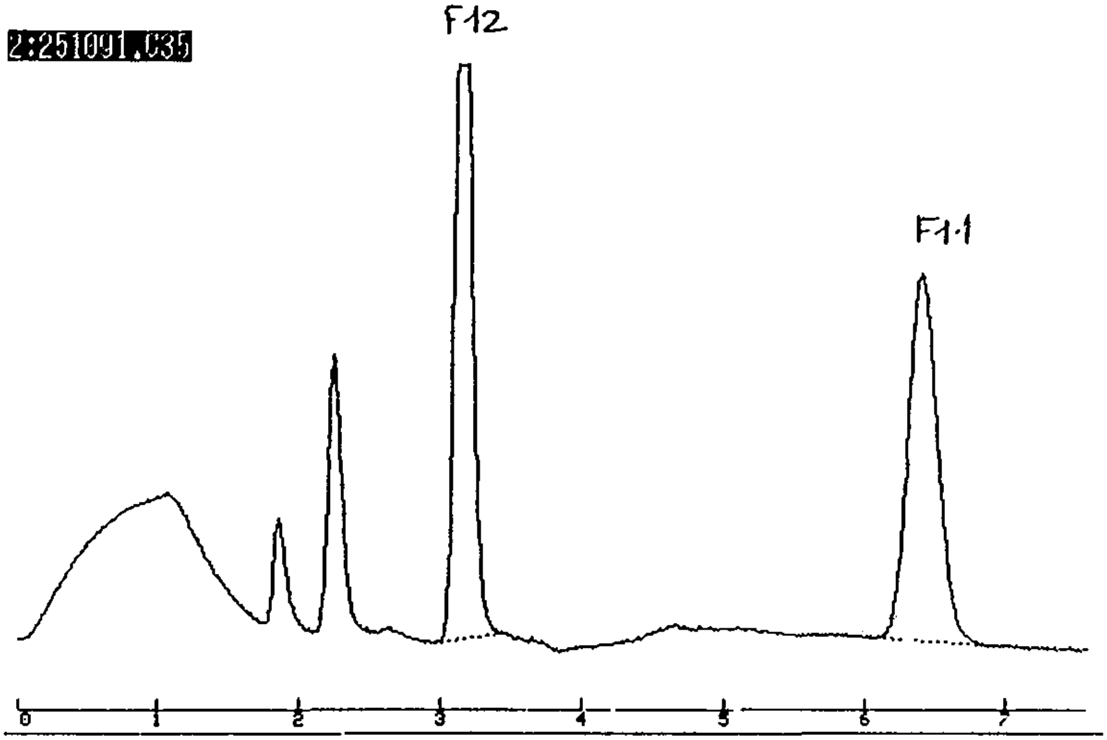
Individual CFC measurements of the CFC intercomparison cylinder, referenced to standard calibration curve No. 1:

CFC-12 [ppt]	502.1	502.1	498.9	(0.5 ml sample volume)
	515.6	509.9	508.2	(1.0 ml)
	493.9	494.9	498.5	(2.0 ml)
	507.7	504.6	505.4	(2.5 ml)

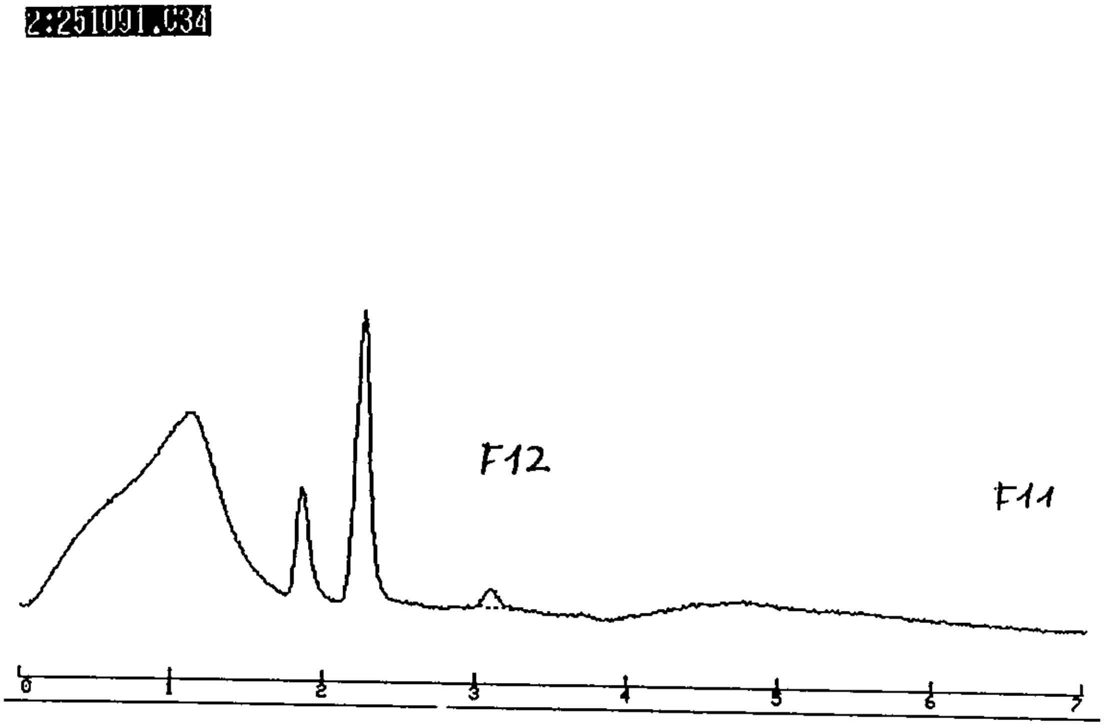
mean: 503.5 ± 6.4 (±1.3%)

CFC-11 [ppt]	269.6	270.8	270.2	(0.5 ml sample volume)
	273.3	279.7	271.0	(1.0 ml)
	267.1	265.9	268.7	(2.0 ml)
	274.7	268.0	265.0	(2.5 ml)

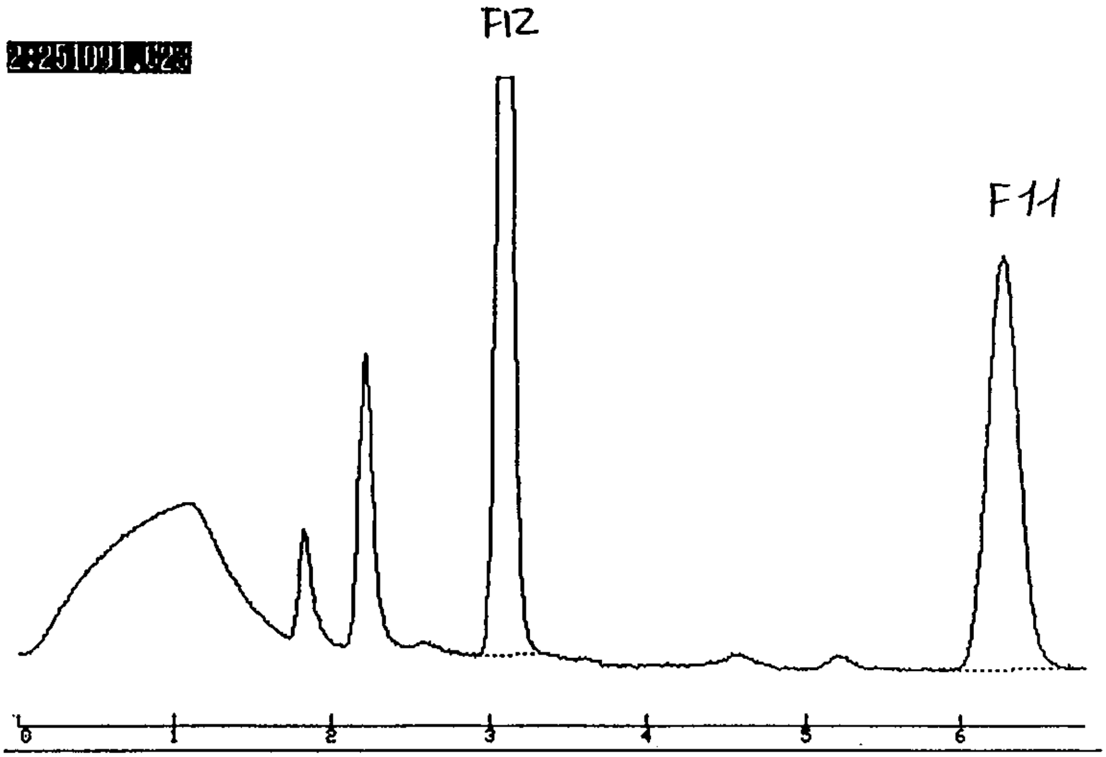
mean: 270.4 ± 4.1 (±1.5%)



APPENDIX D: Fig. 1



APPENDIX D: Fig. 2



APPENDIX D: Fig. 3

APPENDIX E

1991 WOCE CFC Standard Intercomparison Results—Bremen

Dr. Wolfgang Roether
Universität Bremen
Fachberich 1
P.O. Box 330 440
D-2800 Bremen 33
Germany
OMNET: W.Roether

Items:

1) Cylinder analyzed: 8339.
2) Analysis date: 19 Nov 1991.
4) Measured values are F-12: 497.4, F-11: 273.3 pptv (+).
6) 6 replicas each, standard reproducibility for individual measurement ±0.15% for both; allowing additionally for standard drift and calibration curve error, the over-all precision of reported values is estimated at ±0.4 % for both.
7) Values are on SIO scale (+).
8) The values for the standard that we use (see 9) have reported standard errors on the SIO scale of ±0.24% in F-12 and ±0.37% in F-11. These uncertainties have to be added to the precision given under 6), so that the expected accuracy is ±0.5% for F-12 and ±0.55% for F-11 (+).
9) We use standards provided by R. Weiss. The cylinder used as our standard has the no. 83976, and the gas was calibrated on 11 July 1990. The values were 546.6 pptv for F-12 and 286.1 for F-11. We own a second cylinder same type (No. 83973, calibrated 10 July) and measured this gas the same day when your gas was run. This measurement exceeded R. Weiss' reported values for this cylinder by 0.3 ± 0.5% (standard error, estimated as under 8)) for both F-11 and F-12.
10) Standards provided by R. Weiss.
11) Measurement by (modified) classical Bullister and Weiss technique; the instrument went very smoothly that day. I believe it would be of interest in future intercomparisons to have a somewhat standardized way to calculate and report errors (see items 6) and 8) above).

APPENDIX F

1991 WOCE CFC Standard Intercomparison Results—SIO

R.F. Weiss, F.A. Van Woy, P. Salameh
Scripps Institution of Oceanography
University of California, San Diego
A-020
La Jolla, CA 92093 USA
OMNET: R.Weiss
Internet: rfw@siorfw.ucsd.edu

Items:

1) ID number of the intercomparison cylinder analyzed: 8342.
2) Analysis date(s): 22 Sep and 15 Oct 1991.
3) Initial and final pressures of the cylinder: Insufficient to register on the high-pressure inlet gauge of our regulator, but probably <20 psig.
4) Concentrations of CFC-11, CFC-12:

22 September 1991 Results:

	CFC-12 [ppt]	CFC-11 [ppt]
	501.8	271.8
	499.2	271.4
	499.5	270.9
	504.3*	272.2
	499.1	272.4
	499.7	273.6
	498.6	272.4
	497.9	273.0
	500.5	272.2
x	499.5	272.2
s	1.2	0.8
n	8	9

* datum rejected >2s from mean

15 October 1991 Results:

	CFC-12 [ppt]	CFC-11 [ppt]
	506.4*	272.2
	503.3	272.1
	503.7	270.7
	503.8	271.4
	501.3	272.7
	501.0	272.9
	501.7	273.2
	501.0	272.4
x	502.3	272.2
s	1.2	0.8
n	7	8

* datum rejected, regulator insufficiently flushed

Combined Results:

	CFC-12 [ppt]	CFC-11 [ppt]
x	500.8	272.2
s	1.9	0.8
n	15	17

5) Concentrations of CFC-113, carbon tetrachloride and other gases measured: Not measured.

6) Number of replicate analyses, analytical precision for each compound: See Item 4 above.

7) Calibration scale used for reporting concentrations: SIO 1986.

8) Estimate and discussion of overall accuracy of reported values of each compound: the estimated accuracy of the SIO 1986 calibration scale is 0.5% for CFC-12 and 1.3% for CFC-11 (Bullister and Weiss, *Deep-Sea Res.*, *35*, 839–853, 1988).

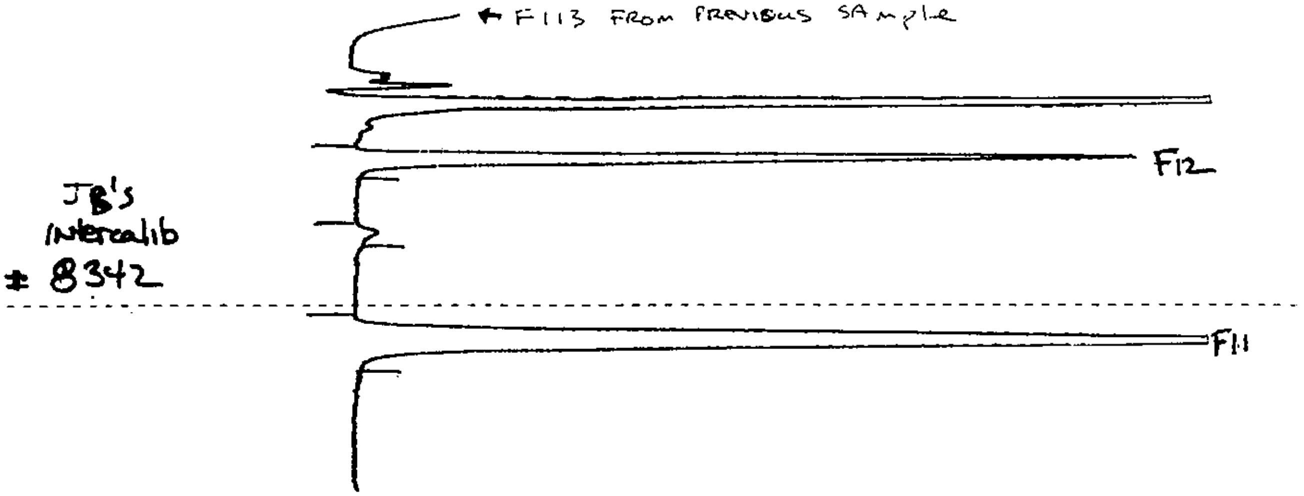
9) CFC concentrations in the reference standards, balance gas (air, nitrogen, etc), cylinder type, manufacturer, and cylinder ID number: our reference standard contains 367.07 ppt

CFC-12 and 216.56 ppt CFC-11. The balance gas is "ultra-zero" artificial air. The cylinder is aluminum, manufactured by Luxfer, with Spectra Seal internal coating. Its ID number is 16438.

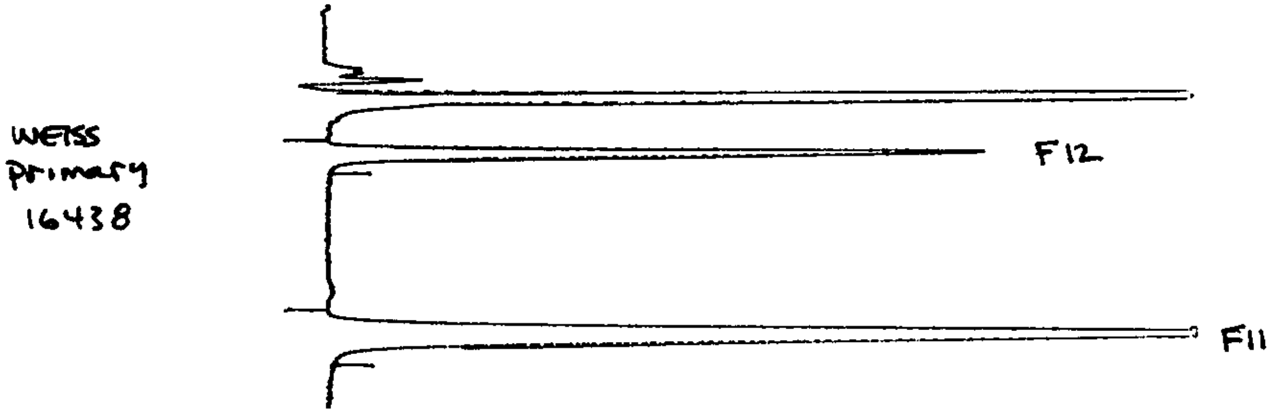
10) Source or method of preparing standards (or reference to published report of technique): The calibration is by static dilution using a "bootstrap" technique based on nitrous oxide. See: J.L. Bullister, Ph.D. Thesis, University of California, San Diego, 172 pp., 1984.

11) Sample chromatograms, general discussion of results, precision, accuracy, analytical problems encountered, additional comments, etc: please see Item 4 above. Some of the runs were high in both CFCs, which probably was due to inadequate flushing of the regulator, since we were trying to use as little of the gas as possible. These first runs are not included in the tabulations. The cylinder valve was kept closed whenever possible to prevent contamination of the tank. In most of the analyses the sample stream to the cylinder valve was evacuated to reduce the potential of contamination.

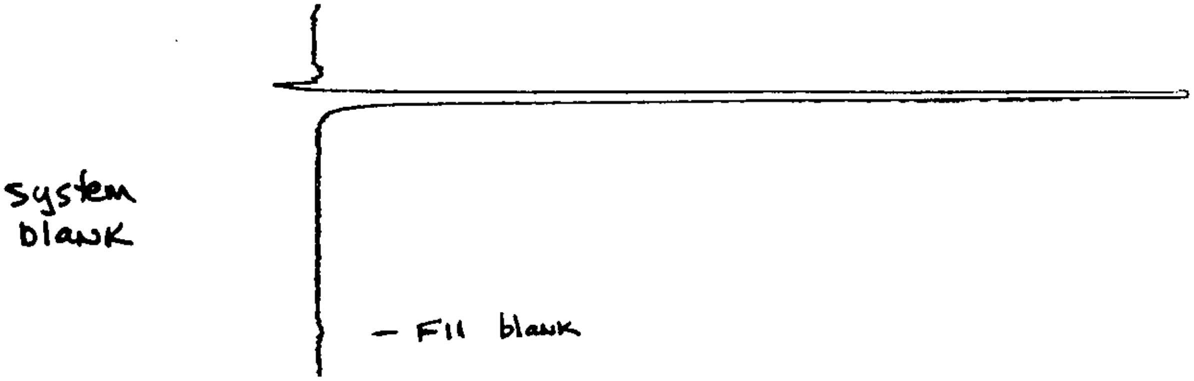
The following figure is three chromatograms of ~3 ml injections of intercomparison tank 8342, Weiss primary tank 16438 and blank gas.



```
RUN#= 1046283    SMP TYP= 6          1306:23 7/  230991
PRES= 1012.      TEMP= 25.5           RT      AREA          PK HT
#LASV= 1         #SASV=              138     156683          7478
                                     208       3726           164
                                     307     419939         17746

APPROX VALUES--PPT                F12= 0.             F11= 0.
```



```
RUN#= 1046284    SMP TYP= 4          1338:25 7/  230991
PRES= 1011.7     TEMP= 25.5           RT      AREA          PK HT
#LASV= 1         #SASV=              138     125505          5982
                                     307     344840         14473

APPROX VALUES--PPT                F12= 0.             F11= 0.

1/SEN--PMOL/CTS                   F12=0.2302↑-06    F11=0.1449↑-06
```



APPENDIX F: Fig. 1.

APPENDIX G

1991 WOCE CFC Standard Intercomparison Results—LDEO

William M. Smethie, Jr., Chris Toles
Lamont-Doherty Earth Observatory
Palisades, NY 10964
Telephone: 914-365-8566
Fax: 914-365-3183
Omnet: LDGOCHEM
Internet: bsmeth@ldgo.columbia.edu

Cylinder 8340 was received by Lamont in September 1991. In December when we tried to perform the analysis, we discovered that the cylinder was at atmosphere pressure. It was returned to NOAA-PMEL. We then made arrangements to analyze the cylinder that had been sent to Brookhaven National Laboratory, which was cylinder 8344.

Results:

Date of analysis: 18 Dec 91
No. of replicates: 5
F-11 (ppt): 268.8 ± 1.0%
F-12 (ppt): 495.0 ± 0.6%
F-113 (ppt): 80.8 ± 1.9%
Calibration scales: F-11 and F-12 SIO 1986
F-113 NOAA-CMDL

Standards:

LDEO standard 1173 was used for F-11 and F-12. It was prepared in 1983 by spiking clean marine air with F-11 and F-12 and is contained in an ARCO Spectra Seal aluminum cylinder. It has been analyzed by the SIO lab three times between 1983 and 1990 and no drift has been observed. The last analysis was on 11 Jan 90; the F-11 concentration was 158.1 ± 0.6 ppt and the F-12 concentration was 422.9 ± 1.1 ppt.

LDEO standard 8335 was used for F-113. It was prepared in 1991 by Doug Wallace at BNL by diluting a high concentration standard with clean nitrogen and is contained in Scott Acculife aluminum cylinder fitted with a stainless steel tank valve that was specially cleaned to avoid F-113. The regulator used on this tank was a Scott high purity regulator that was also specially cleaned to avoid F-113. The F-113 concentration in this cylinder was analyzed against a standard prepared from Niwot Ridge air by Jim Butler of the NOAA Climate Monitoring and

Diagnostics Laboratory. This standard was collected from Niwot Ridge in November 1990 and analyzed at the NOAA CMDL in January 1992. It is contained in a Scott Acculife aluminum cylinder (#CLM002415). The analysis of LDEO standard 8335 against CLM002415 was carried out in December 1992, 1 year after the intercomparison sample was analyzed.

Methods:

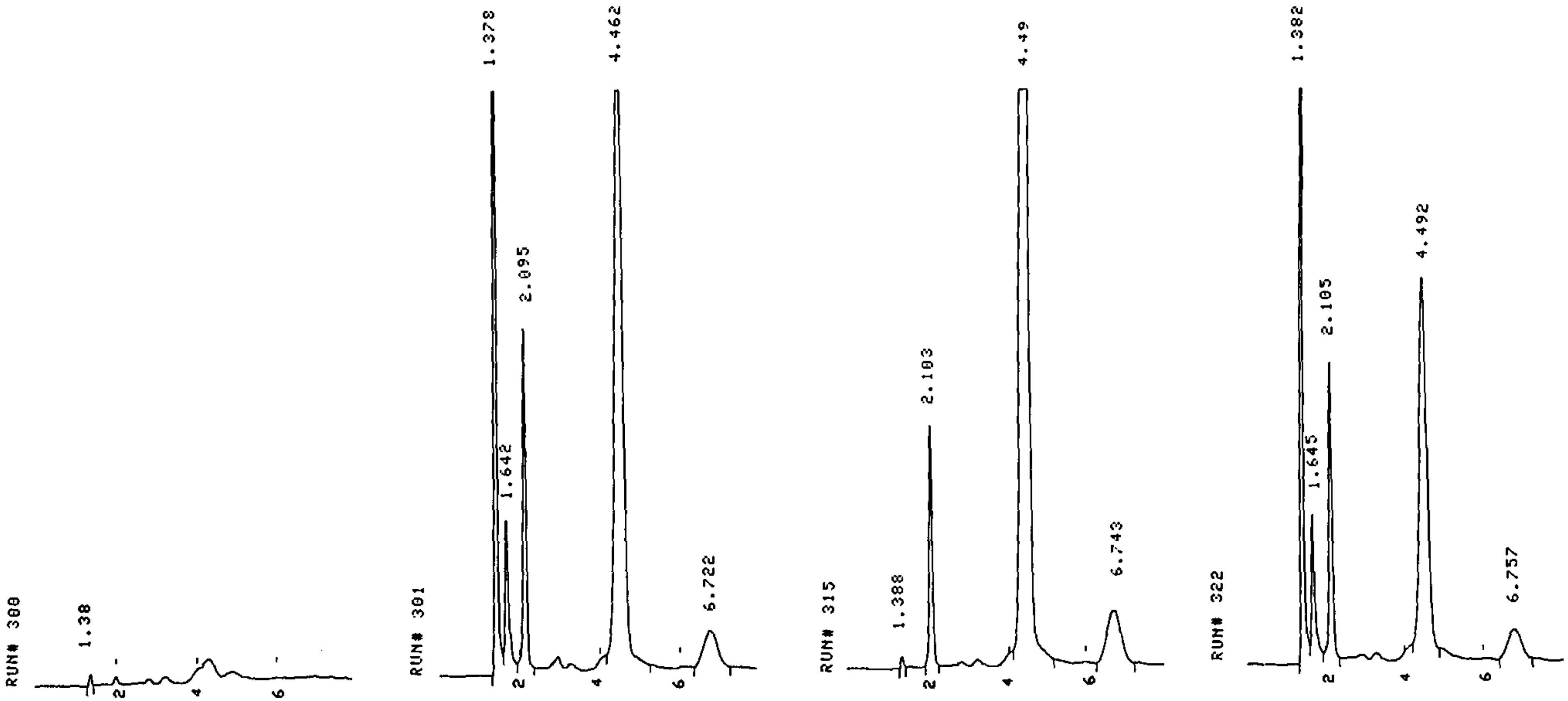
The intercomparison sample was analyzed using a Shimadzu 8A gas chromatograph with an electron capture detector. Aliquots of the sample and standards were measured into calibrated loops and the contents of the loop flushed to a trap of unibeads 2s cooled to –65°C. The trap was heated to 100°C and the flushed into the gas chromatograph. Calibration curves were run by injecting different size loops. The raw data was reduced by the method described in Bullister and Weiss (1988). Operating parameters are given below.

Precolumn: 22 inches × 1/8 inch stainless steel with 100 mesh porasil B
Main column: 23 feet × 1/8 inch stainless steel with 20% SP2100 on 100 mesh supelcoport
Column temperature: 63°C
Detector temperature: 240°C
Carrier gas: nitrogen
Flow rate: 50 cc/min
Sample size: 4 cc

Sample chromatograms for a system blank, the NOAA intercomparison sample, LDEO standard 8335, and LDEO standard 1173 are presented in Fig. 1. The retention times in minutes are 2.1 for F-12, 4.5 for F-11 and 6.7 for F-113. The two peaks preceding F-12 are thought to be oxygen and nitrous oxide.

Reference:

Bullister, J.L., and R.F. Weiss (1988): Determination of CCl_3F and CCl_2F_2 in seawater and air. *Deep-Sea Res. 35*, 839–853.



System Blank

Intercomparison
Cylinder 8344

LDEO Std 8335

LDEO Std 1173

APPENDIX G: Fig. 1

APPENDIX H

1991 WOCE CFC Standard Intercomparison Results—BNL

Dr. Doug Wallace
Brookhaven National Laboratory
Building # 318
Upton, NY 11973 USA
OMNET: D.Wallace
Internet: wallace@bnlux0.bnl.gov

Items:

1) Cylinder analyzed: PMEL Cylinder ID#: 8344.
2) Analysis dates: 3/26/92; 3/27/92.
3) Initial and final pressure: not recorded.
4) Concentration of CFC-11: 258.8.
5) Concentration of CFC-12: 500.3.
6) Number of analyses: 6.

Analytical precisions (1 standard deviation):

F12: 0.5%
F11: 0.4%
F113: 1.0%
CCl_4: 1.0%

7) Calibration scale: SIO 1986.
8) Estimate of accuracy relative to our standard ~0.8% for F12 and F11.
9) Our standard used for comparison: BNL Std. #S6; CC76512.

Analyzed by Ray Weiss (SIO), January 12, 1990

F12 = 318.1 q 0.24% on SIO 1986 scale
F11 = 542.8 q 0.37% on SIO 1986 scale

10) Prepared January 1990 from pure compounds via 2-stage gravimetric process; diluted with nitrogen. (Nominal concentrations based on gravimetry: F12 = 325; F11 = 569).
11) Our technique uses a wide-bore capillary column and uses trapping at ambient temperatures. While we measured F113 and CCl_4 in the PMEL intercalibration standard, we do not report the values here as we have no reliable primary standard for these

compounds to date. Our seawater data are currently being calculated on the current ALE-GAGE scale based on clean air measurements taken at sea. We took the opportunity to intercompare the PMEL intercalibration sample with a working standard containing the latter compounds which we recently prepared for Bill Smethie (LDEO). We also took the opportunity to obtain calibration factors between the PMEL sample, the LDEO standard prepared by us, and working standards belonging to the Bedford Institute of Oceanography (BIO). The calibration factors for these intercomparisons have been tabulated and have been sent to LDEO and BIO; they are available on request.

APPENDIX I

1991 WOCE CFC Standard Intercomparison Results—Rennell

Denise Smythe-Wright and Stephen Boswell
James Rennell Centre for Ocean Circulation
Gamma House
Chilworth Research Centre
Southampton, SO1 7NS, UK
Tel. 0703 766184
Fax 0703 767507
OMNET: rennell.centre
Internet: dsw@uk.ac.nso.ub

As part of the CFC Standard Intercomparison the James Rennell Centre carried out two separate analyses of cylinder 8348. The first was carried out over 2 days, 20th–21st Jan, the second on the 27th Jan 1992.

Only CFC-12 and CFC-11 were determined in these analyses.

Analysis Method:

The instrument used for these analyses was based on that of Bullister and Weiss (1988) with modifications according to Smythe-Wright (1991). Calibration was based on an SIO compressed air standard (Spectra-Seal aluminum cylinder No. 70340), prepared as per Bullister (1984), with concentrations of 596.0 pptv for CFC-12 and 320.0 pptv for CFC-11. Combinations of two sample loops, volumes 0.746276 and 2.91762 ml, gave a range of injection volumes up to 11.67 ml and allowed the construction of a calibration curve based on 12 points. All injections were corrected for loop temperature and pressure.

For the analysis of 20/21 Jan, the calibration curve was constructed using duplicate runs of all injection volumes. Eight analyses of large loops of the intercomparison standard were then performed, bracketed by the SIO standard. The calibration curve for the second determination was constructed from only single analyses at each point and on only four replicates of the intercomparison standard.

Results:

The results of the two determinations are given in Tables 1 and 2. Data are presented for both the intercomparison standard and for the bracketing SIO standard analyses. The latter were not used in constructing the curves and thus provide a check on the accuracy and precision of our method.

TABLE 1. Results of 1st Determination (20–21 Jan).

	No of Analyses	CFC-12 pptv	%SD	CFC-11 pptv	%SD
INTERCOMP STND	8	500.7	0.7	274.8	0.8
SIO STND	13	594.9	0.6	319.7	0.5

TABLE 2. Results of 2nd Determination (27 Jan).

	No of Analyses	CFC-12 pptv	%SD pptv	CFC-11	%SD
INTERCOMP STND	4	503.4	0.5	273.4	0.9
SIO STND	8	596.0	0.8	320.0	0.5

For the first determination the SIO standards yielded results that were <0.2% low for both compounds: precisions were much better than 1% in both cases. The precisions of the intercomparison standard analyses were slightly worse than these but still better than 1%.

The second determination produced both CFC-12 and CFC-11 concentrations spot on the notional SIO values with precisions of 0.8 and 0.5% respectively. For the intercomparison standard the CFC-12 precision was 0.5% whilst that for CFC-11 was 0.9%, with the concentrations being respectively slightly higher and slightly lower than those observed in the first determination.

Discussion:

The results of our analyses show good agreement between the two determinations. The use of the bracketing SIO standards to assess the accuracy of our method gave results very close to the notional value for that standard with good precisions. The precisions on our analyses of the intercomparison standard were also good and the two determinations agreed to within 0.6% for both CFC-12 and CFC-11 concentrations.

However, analysis of our calibration curves indicates that there may be a slight blank problem associated with our small standard loop. This results in slightly overestimated concentrations at the lower end of the calibration curve. This effect is quite small, not more than 1%, but we would expect our results to be slightly higher than the true values.

At the time of the second determination our instrument was showing signs of needing a bakeout. This, together with the restricted calibration curve and fewer analyses might be expected to produce worse results. This, however, is not obvious from our data, there being only a slight deterioration in the CFC-12 precisions of the SIO analyses in the second determination.

APPENDIX J

1991 WOCE CFC Standard Intercomparison Results—LODYC, Paris

Chantal Andrié
LODYC/ORSTOM
Université P. et M. Curie
4 Place Jussieu, Tour 14 (2°et)
75252-PARIS Cedex 05
Telephone (1) 44 27 70 77
FAX (1) 44 27 38 05
Internet: andrie@lodyc.jussieu.fr

Results:

TABLE 1.

Cylinder Number	Analysis Dates	CFC-12 (PPT)	CFC-11 (PPT)	Runs (n)	%StDev CFC-12	%StDev CFC-11
8352	03-10-91	501.9	272.95	9	0.5	0.8

Discussion:

Analytical methods:

All analyses were done by electron capture gas-chromatography, using methods described by Bullister and Weiss (1988).

Because we have only one CGC-580 fitting, the measurements were done in the following way:

1) On 1 October 1991, control of the calibration of our secondary standard (French fitting) against our primary SIO 1990 standard, cylinder #87130 (US fitting).
2) On 3 October 1991, intercalibration measurements of #8352 (US fitting) against our secondary standard (French fitting).

This procedure allowed alternate measurements of each cylinder instead to make separated measurement series for each cylinder and to change and purge again the single regulator equipped with a CGC-580 fitting. But the resulting overall accuracy is somewhat greater (0.5% for

CFC-12 and 0.8% for CFC-11) than the standard deviation on the nine intercalibration measurements (see Table 1).

Due to the very similar ranges of CFC-12 and CFC-11 concentrations in each cylinder, calculations of the "unknown" CFC contents of the cylinder #8352 have not been done through calibration curves but by direct ratios against the secondary standard contents.

Sample Chromatograms:

Typical chromatograms generated from the analyses of a 3,387 cc sample of air from cylinder #8352, our secondary standard, and a blank gas are shown in Fig. 1; retention times for CFC-12 and CFC-11 are, respectively, 106" and 175". There are no significant differences between chromatograms of #8352 or LODYC standard; there are no small peaks before CFC-12 peak. Some CFC-11 is detected in the blank gas; this value (around 1% of the total CFC-11 signal) has been considered in the calculations.

Standards:

Our "primary standard," #87130, is an Airco Spectra-Seal Aluminum cylinder. This standard was prepared at SIO in July 1990 and has been assigned values of CFC-11 = 315.2 ppt (±0.17%), CFC-12 = 592.4 ppt (±0.21%) on the SIO scale. All concentrations reported are mixing ratios, expressed as mole fractions of CFC in dry air.

Marine compressed air into an aluminum tank has been used as secondary standard to calibrate cylinder #8352 in this study.

The pressures of each standard tank was around 80 atm during these measurements.

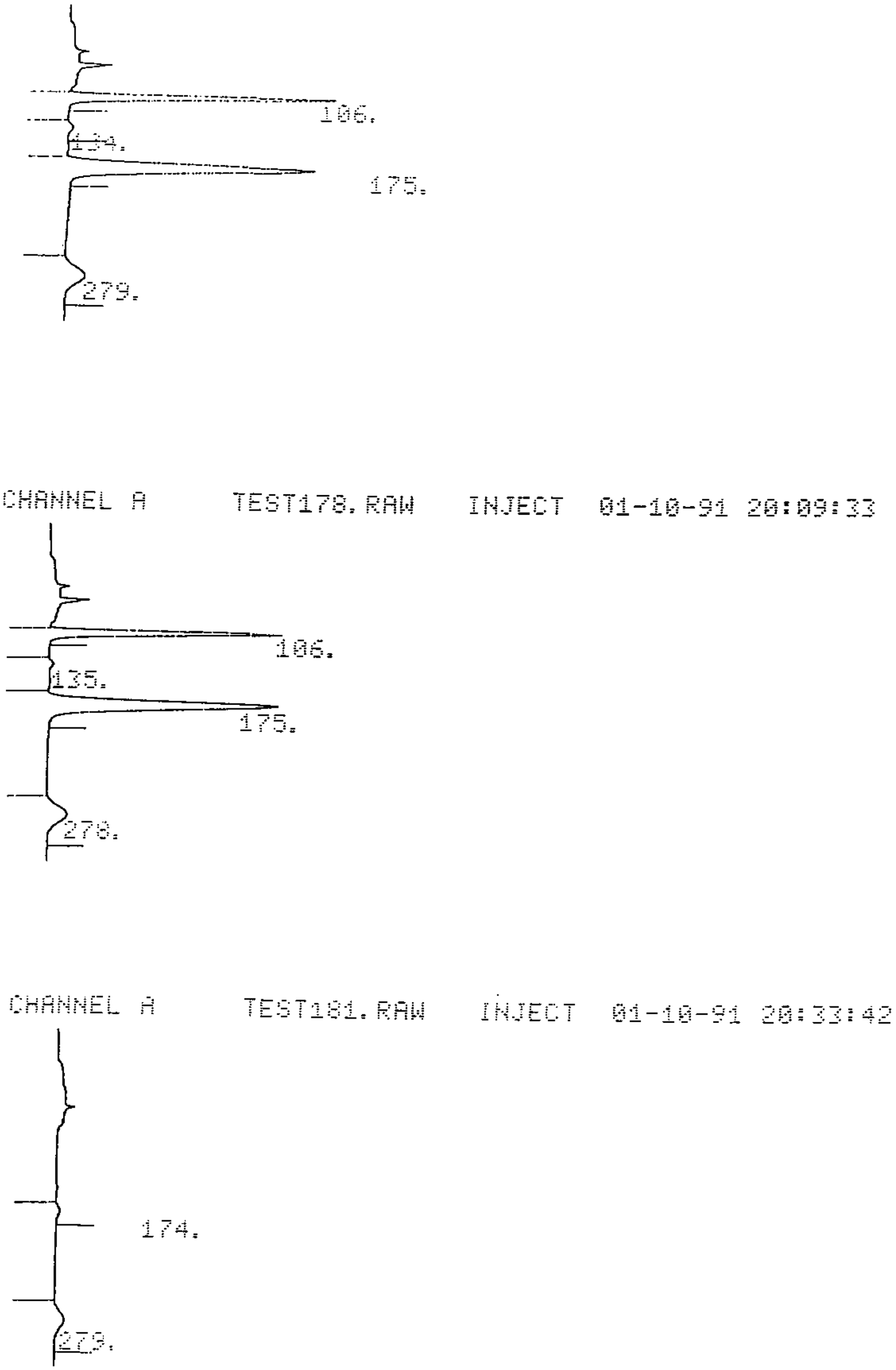


Figure 1 : Sample chromatograms (analysed on 1 october 1991) of a 3,387 ml injection of :
a : Air from cylinder #8352.
b : Air from LODYC secondary standard.
c : Blank gas.

APPENDIX J: Fig. 1

*U.S. GOVERNMENT PRINTING OFFICE: 1993-774-025/89035