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James Rennell Centre
for Ocean Circulation

INTERNAL DOCUMENT No. 14

Results from the analysis of an International Intercomparison Gas Standard

S M Boswell & D Smythe-Wright

1993

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Institute of
Oceanographic Sciences
Deacon Laboratory

Natural Environment Research Council

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ABSTRACT

There are now a number of laboratories in Europe and the USA that possess the capability to measure oceanic CFC concentrations. Variations in instrument design and methodology have necessitated intercomparison exercises in order to ensure consistent data quality amongst the various laboratories. The lack of suitable aqueous standards requires the use of gas phase standards for this purpose. Several different approaches were taken to constructing the calibration curves and these are discussed.

This report presents the results obtained by this laboratory as part of the WOCE CFC Standard Intercomparison. In it we describe the stages required to perform the analyses, together with a description of the data handling procedures used.

We performed two separate determinations, 6 days apart, of CFC-12 and CFC-11 in cylinder 8348. The first determination yielded concentrations in the range 274.4 to 275.3 pptv for CFC-11 and 499.8 to 501.2 pptv for CFC-12. The second determination yielded ranges of 273.4 to 274.0 pptv and 503.4 to 505.1 pptv respectively. All three approaches had precisions better than 1%.

Multiple analyses of aliquots of a standard of known composition were run as unknowns as a check on the validity of our approach. These analyses yielded accuracies and precisions of 0.5% and 0.8% for CFC-11 and 0.4% and 0.5% for CFC-12. These lie well within the requirements of WHP for CFC measurements.

CONTENTS

1. INTRODUCTION

There are now a number of laboratories in Europe and the USA that possess the capability to measure oceanic CFC (chlorofluorocarbon) concentrations. However, variations in instrument design and methodology, have led to a need for an intercomparison exercise in order to ensure consistent data quality amongst the various laboratories. The lack of suitable aqueous standards has necessitated the use of gas phase standards for this purpose. This report describes the results obtained by this laboratory as part of such an exercise, organised by J Bullister of PMEL (Pacific Marine Environmental Laboratory).

A number of cylinders were filled with ambient air and were analysed at PMEL for their concentrations of CFC-11 and CFC-12. These were then distributed to the participating laboratories. Each laboratory was required to analyse their cylinder of intercomparison gas for its CFC content, using their normal procedures. Sufficient gas was to be left in the cylinder that it could be reanalysed by PMEL so as to determine any drift in the concentration over the period of the exercise.

This report outlines the analyses undertaken here at the James Rennell Centre as part of this intercomparison. In it we describe the stages required to perform the analyses, together with a description of the data handling procedures. Results are presented from two independent calibrations of the PMEL standard, together with an assessment of the precision of the methods used.

2. CALIBRATION OF THE JRC CFC EQUIPMENT

The first step was to calibrate the CFC equipment using a compressed air standard, containing 320.0 pptv (parts per 10^{12} by volume) CFC-11 and 596.0 pptv CFC-12. This was supplied by R Weiss (Scripps Institution of Oceanography), having been prepared as per Bullister (1984), and is one of 3 such standards normally used by JRC for CFC analysis. Calibration was based on multiple injections of volumes of the standard. The JRC instrument has been fully described in Smythe-Wright (1990a and b) and has two sample loops, with volumes of 0.746276 ml (SSV) and 2.91762 ml (LSV). By using combinations of these a range of volumes of standard (0.746276-11.67048 ml) could be introduced into the instrument. For example, the sequence would typically be, in duplicate;

1LSV, 3SSV, 4LSV, 1SSV, 3LSV, 2SSV, 2LSV, 4SSV, LSV + SSV, 2(LSV + SSV), 3(LSV + SSV).

These standard injections were bracketed by system blanks and several LSVs, the latter being used to correct for instrument drift (see Section 2.2 below). All values were corrected for the system blank if one was present.

2.1 CALCULATING QUANTITY OF STANDARD INJECTED

There are two approaches to this, either by converting the volumes of standard to an absolute number of moles of gas present using

$$m = \frac{c.P.V}{R.T} \qquad \text{(Eqn. 1)}$$

or into an equivalent volume of gas at STP using

$$v_S = \frac{c.P.V.T_S}{T.P_S} \qquad \text{(Eqn. 2)}$$

where

m = number of moles

v_S = equivalent volume at STP

c = standard concentration (pptv)

P = measured pressure (mbar)

T = measured temperature (K)

T_S = standard temperature (273.15 K)

P_S = standard Pressure (1013.25 mbar)

V = volume of standard injected (ml)

R = Gas Constant (83144.1 is used here to give an answer in pmol).

Both approaches were tried for the first analytical run, but the results were so close that only that based on Eqn. 1 are reported here.

2.2 Correction for Instrument Drift

The electron capture detector (ECD) is amongst the most sensitive of GC detectors, but it has the disadvantage that its response, as measured by peak area, is prone to drift with time. This was corrected for using the results of the 1LSV injections. These were measured periodically throughout each set of analyses and the instrument response used to calculate a Reciprocal Sensitivity factor (moles per unit area) for each of these large loops. A plot of this factor against run number (Figure 1) gave a measure of the degree of instrument drift over the series of analyses. The equation of a linear fit to this data was used to generate a run number dependant sensitivity factor which was applied to the measured area for all points on the calibration curve.

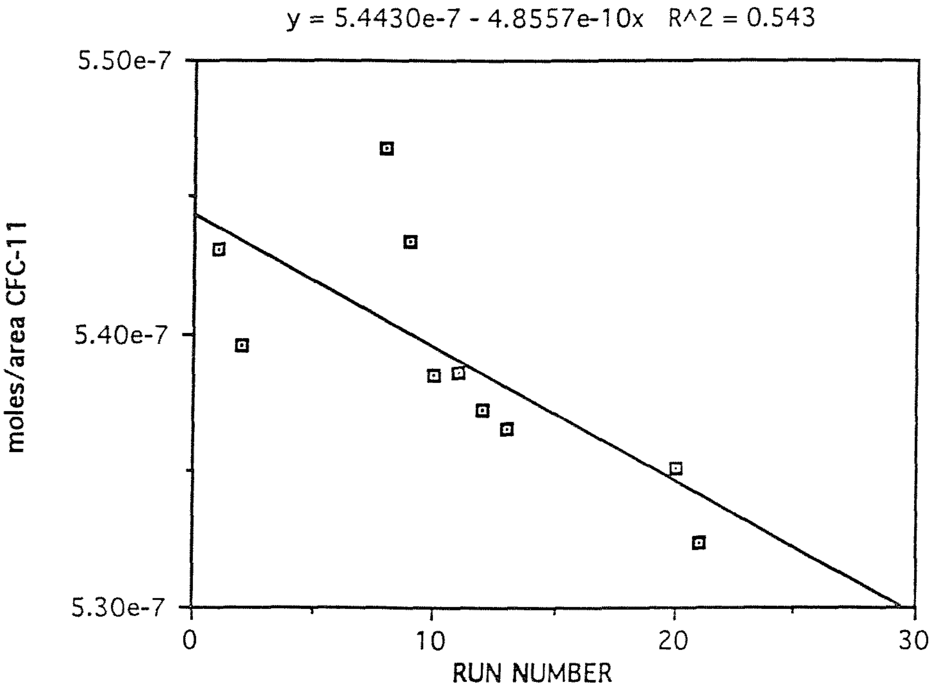

Figure 1 Plot of instrument response vs run number to assess instrument drift.

2.3 Curve Construction

The calibration curve was constructed by plotting this drift-corrected area (units = mol) against the quantity of CFC injected.

Since sensitivity drift was corrected for using large loops of standard, it was necessary to force the calibration curve through this value. To do this, the average of all the 1LSV analyses was taken and fifty of this value added to the data before the curve was constructed. Similarly, since blanks were corrected for independently of the curve fitting, it is normal practice to add fifty zero values to the data in order to force the curves through the origin (see Section 5 below). An example of a calibration curve is shown in Figure 2.

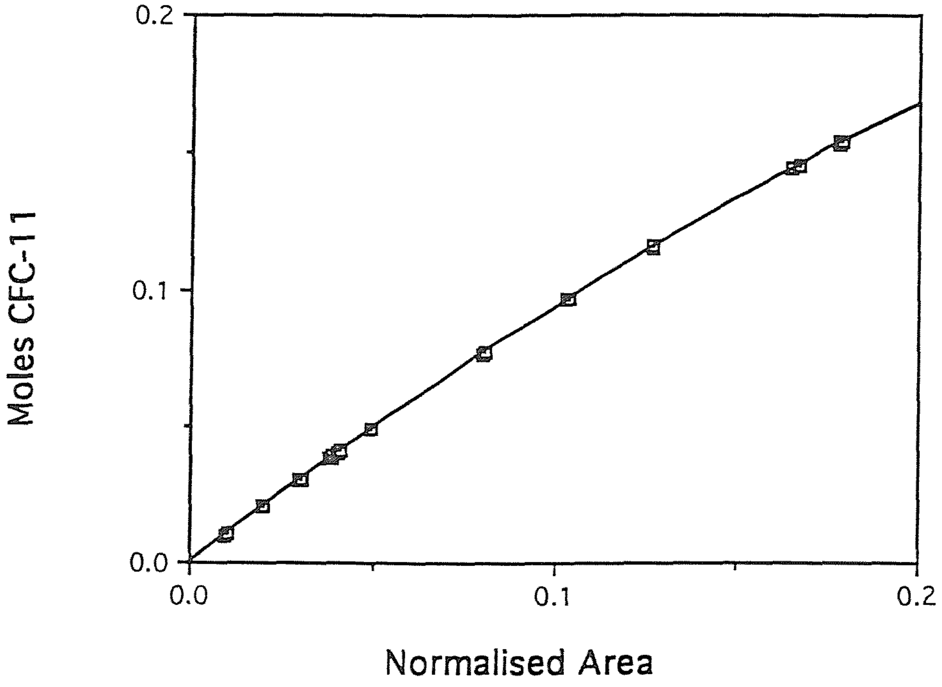

Figure 2 Normalised area calibration curve for CFC-11.

In constructing the calibration curves, four types of weighting were tried in order to assess the effects this had on the calculated concentrations.

- the conventional method: weighting with 50 1LSV and 50 zero values (WZ).
- 50 1LSV, but no zero weighting (W).
- as WZ plus weighting based on 50 of the averaged 1SSV values (WZS).
- unweighted data (U).

The reason for trying these approaches was that the conventional method did not appear to fit the SSV data very well (see Section 5 below).

A polynomial fit to this data was then used to convert the drift corrected measured peak areas of unknowns into moles of CFC. This was finally converted back to a concentration in air, using the inverse of Eqn. 1.

3. ANALYSIS OF INTERCOMPARISON STANDARD

Two independent determinations of the intercomparison standard, cylinder number 8348, were made, six days apart. The procedure used was to construct a calibration curve as above and then analyse replicate large loops of the intercomparison standard bracketed by analyses of the Weiss standard. The first measurements of the intercomparison standard were based on a full calibration curve, followed by 7 Weiss standards, 8 intercomparison standards and then 6 more Weiss standards.

The second determination used only a partial calibration curve, with measurements of 6 Weiss standards, 4 intercomparison standards and finally 2 Weiss standards. The use of replicate analyses permit an assessment of the precision of the measurements, the bracketing Weiss standards also providing a check on the accuracy of the curve construction. By the time of this determination the instrument was showing signs of needing to be baked out (cleaned). Therefore we are less certain of the data quality from these measurements.

4. RESULTS

The results from both determinations of the intercomparison standard are given in Table 1, together with the associated data from the 1LSV replicates of the Weiss standard. A full listing of the analytical data is given in Appendices A and B. The column headings refer to the construction methods described above. There is good agreement between the results from the two determinations and from the different weighting methods used. The only exception was the results obtained using unweighted data from the first determination which differ markedly from the other results.

4.1 Results from Intercomparison Standard

The results from the weighted analyses of the data covered a range of 499.8 to 501.2 pptv for CFC-12 and 274.4 to 275.3 pptv for CFC-11 from the first determination. The second determination produced values between 503.4 and 505.1 pptv for CFC-12 and between 273.2 and 274.0 pptv for CFC-11. Both sets of results agree internally to well within the precision of the actual analyses. The same is true when comparing the CFC-11 results from the two separate determinations. However, the CFC-12 values obtained from the first determination do appear significantly lower than those from the second. However, even in taking the most extreme case this difference is small, only 5.3 pptv, or 1.1%. One standard deviation of each result would bring both into agreement.

4.2 Results from Weiss Standard

As a check on our approach, it is useful to look at the 1LSV measurements of the Weiss standard, comparing the results from the curve fitting with the known absolute values (596.0 pptv for CFC-12 and 320.0 pptv for CFC-11) for this gas. The variations between the true and calculated values for these 1LSV analyses are small, the maximum differences being 2.4 pptv for CFC-12 and 1.8 for CFC-11. These are respectively only 0.4 and 0.3% from the true values.

5. DISCUSSION

The different approaches to calibration curve construction produce very similar results for both the intercomparison standard and the Weiss standard. The offset in the results from the unweighted data might be expected: since all the data are drift corrected by normalising to 1LSV, the calibration curve should pass through this value. If it is not constrained to do so by weighting, the other data may bias the curve fitting routine away from the 1LSV value. This is probably the cause of the discrepancies in the unweighted results from the first determination, where the Weiss standard concentrations measured low and the intercomparison standard results are lower than those produced by the other approaches. The unweighted data will not be further discussed, except to point out that even these results are correct to within WHP standards (see Section 5.1 below).

5.1 Comparison with WHP Requirements

It is important to look at these results in relation to the requirements of the WOCE Hydrographic Programme. This calls for an accuracy of 1-2% with precisions of 1%. Multiple analyses of 1LSV of the Weiss standard, yielded precisions well within this requirement for both determinations and all curve fitting approaches. The maximum errors for CFC-12 and CFC-11, based on all three curve constructions, were 1.6 and 1.0% respectively for the first determination, and 1.2 and 1.5% for the second.

5.2 Assessment of Curve Validity

The calculated 1LSV values would be expected to be close to the true values as the curves are weighted to pass through this point. It is therefore a good idea to look at the rest of the curve to get a proper assessment of its validity. Table 2 shows the differences from the true values of the calculated concentrations of all the Weiss standard analyses in the first determination. These data show that at volumes above 1LSV all three construction approaches produce concentrations close to the true values. However, the results from the multiple SSV injections fit less well. The conventional curve construction (1LSV and zero weighting) fared worst in this comparison with differences of up to 3.2% for CFC-12 and 5% for CFC-11, both from 1SSV analyses. The other two approaches were similar, with maximum errors of 2.3 and 3.4% for that with no zero weighting and 2.2 and 3.2% for that including 1SSV weighting.

There is an associated problem concerned with the intercept of these curves with the y-axis. This represents an offset to the calculated number of moles which, since blanks have already been corrected for, should be zero. The conventional method, since it is zero weighted, has a small intercept, equivalent to an offset of less than 0.3 pptv for both compounds. The other two approaches however fare worse, with offsets of between 6 and 8 pptv.

There appear to be two possible causes for these discrepancies at the low end of the calibration curves. One is that the small sample loop may not be correctly calibrated. A slightly larger small loop volume would have the effect of pulling the calibration curve up as a whole and especially the SSVs, reducing both the above errors. However, to totally account for these errors a 3% increase in loop volume would be required, which seems unreasonable from its calibration data. Therefore it seems likely that at least some of the errors are due to unseen blank problems with the small loop. This could arise from contamination of the valve or its connecting pipework, or from a slight leak round the valve rotor, although the purge housings should minimise the latter.

6. CONCLUSIONS

1) As part of the WOCE CFC Standard Intercomparison, the James Rennell Centre performed two separate analyses for CFC-12 and CFC-11 of cylinder 8348. The first was carried out over two days, 20th-21st January 1992, the second on the 27th January. There was good agreement between results from both determinations.

2) Several data processing approaches were tried, applying different weightings to the construction of the calibration curve. The first determination of the intercomparison standard yielded concentrations in the range 274.4 to 275.3 pptv for CFC-11 and 499.8 to 501.2 pptv for CFC-12. The second determination yielded ranges of 273.4 to 274.0 pptv and 503.4 to 505.1 pptv respectively. All three approaches had precisions better than 1%.

Calibration curves constructed without weighted data produced results noticeably different from the three weighted approaches. We therefore feel that such an approach is not suitable for high precision measurements.

3) The instrument was calibrated against a standard of known composition. Multiple analyses of aliquots of this standard were run as unknowns as a check on the validity of our approach. These analyses yielded accuracies and precisions of 0.5% and 0.8% for CFC-11 and 0.4% and 0.5% for CFC-12. These lie well within the requirements of WHP for CFC measurements.

4) Analysis of our calibration curves indicates that there may have been a slight blank problem associated with our small standard loop. This would result in slightly overestimated concentrations at the lower end of the calibration curve. This effect is quite small, not more than 1% at the concentration of the intercomparison standard, but we might expect out results to be slightly higher than the true values. It is important that this problem be addressed, as it is at low concentrations where blanks pose the most serious threat to data quality.

5) Despite zero weighting all the curves displayed a small though significant intercept value. It is unclear from our work to date how this should be handled in calculating concentrations.

7 REFERENCES

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TABLE 1

Results from the analysis of the PMEL Intercomparison Standard.

1st Determination of Intercomparison Standard.

	WZ12	WZ11	W12	W11	WZS12	WZS11	U12	U11
Intercomparison standard	501.2	275.3	500.7	274.8	499.8	274.4	496.6	272.0
standard deviation	3.4	2.1	3.5	2.2	3.5	2.1	3.5	2.2
% s.d.	0.7	0.8	0.7	0.8	0.7	0.8	0.7	0.8
1lsv weiss standard	594.6	319.5	594.9	319.7	593.6	318.8	590.5	316.6
standard deviation	3.3	1.7	3.4	1.7	3.4	1.7	3.4	1.7
% s.d.	0.6	0.5	0.6	0.5	0.6	0.5	0.6	0.5

2nd Determination of Intercomparison Standard.

intercomparison standard	505.1	274.0	503.4	273.4			503.4	273.2
standard deviation	2.7	2.4	2.7	2.4			2.7	2.4
% s.d.	0.5	0.9	0.5	0.9			0.5	0.9
1lsv weiss standard	595.4	319.6	595.6	319.6			595.5	319.5
standard deviation	4.2	1.6	4.3	1.7			4.3	1.7
% s.d.	0.7	0.5	0.7	0.5			0.7	0.5

TABLE 2

Concentration differences for 1st calibration curve.

Sample	WZ12	WZ11	W12	W11	U12	U11	WZS12	WZS11
1SSV	18.5	12.8	-8.4	-9.4	-5.5	-9.3	10.7	7.7
1SSV	19.2	12.0	-7.7	-10.2	-4.8	-10.1	11.3	7.0
1SSV	17.8	16.0	-9.1	-6.0	-6.1	-6.0	10.0	11.0
2SSV	14.0	11.1	7.6	5.3	3.4	2.2	10.2	8.9
2SSV	11.7	10.9	5.3	5.1	1.0	2.1	7.8	8.7
2SSV	17.1	12.1	10.8	6.4	6.5	3.3	13.2	9.9
3SSV	10.5	9.8	9.3	8.6	4.3	5.2	8.4	8.6
3SSV	9.1	7.8	7.9	6.5	2.9	3.2	7.1	6.6
3SSV	14.9	10.5	13.8	9.3	8.8	5.9	12.9	9.3
1LSV	0.4	-0.8	0.7	-0.6	-3.8	-3.7	-0.7	-1.5
1LSV	-3.2	-4.5	-2.9	-4.4	-7.4	-7.4	-4.2	-5.2
1LSV	-1.8	1.1	-1.5	1.3	-5.9	-1.7	-2.8	0.4
1LSV	1.4	-0.3	1.8	-0.1	-2.7	-3.2	0.4	-1.0
1LSV	-4.8	-1.1	-4.5	-0.9	-9.0	-4.0	-5.8	-1.8
1LSV	-4.8	0.1	-4.5	0.3	-9.0	-2.7	-5.8	-0.6
1LSV	-2.8	1.2	-2.5	1.4	-7.0	-1.7	-3.8	0.5
1LSV	3.5	0.5	3.8	0.7	-0.6	-2.4	2.5	-0.2
1LSV	3.9	0.9	4.2	1.2	-0.3	-1.9	2.9	0.2
1LSV	-2.2	1.1	-1.9	1.3	-6.4	-1.8	-3.3	0.4
1LSV	-3.1	0.2	-2.8	0.4	-7.3	-2.7	-4.2	-0.5
1LSV	-5.0	1.3	-4.8	1.5	-9.2	-1.6	-6.1	0.6
1LSV	-1.9	-3.2	-1.6	-3.0	-6.1	-6.1	-3.0	-3.9
1LSV	-3.8	-3.6	-3.5	-3.4	-8.0	-6.5	-4.9	-4.3
1LSV	2.4	-1.6	2.8	-1.4	-1.7	-4.4	1.4	-2.3
1LSV	2.8	-1.5	3.2	-1.4	-1.3	-4.4	1.8	-2.2
1LSV	-1.8	-0.2	-1.5	0.0	-5.9	-3.1	-2.8	-0.9
1LSV	-5.0	-1.9	-4.7	-1.7	-9.2	-4.8	-6.0	-2.6
4SSV	11.1	7.7	11.6	8.1	7.1	5.0	10.2	7.1
4SSV	7.7	7.8	8.1	8.2	3.7	5.2	6.8	7.2
4SSV	10.3	9.4	10.8	9.8	6.4	6.7	9.4	8.8
1LSV+1SSV	0.8	1.8	1.6	2.7	-2.0	0.1	0.6	1.5
1LSV+1SSV	-0.1	0.7	0.7	1.6	-2.9	-1.1	-0.4	0.4
2LSV	5.7	-1.5	5.9	-0.8	4.8	-1.9	6.7	-1.1

2LSV	3.7	-0.7	3.9	-0.1	2.8	-1.1	4.7	-0.4
2LSV	-4.2	-0.3	-4.0	0.3	-5.1	-0.7	-3.2	0.0
2LSV+2SSV	4.3	1.1	4.0	1.1	4.0	1.0	5.5	1.7
2LSV+2SSV	-4.9	-0.8	-5.1	-0.8	-5.2	-1.0	-3.7	-0.3
3LSV	2.0	0.2	1.5	-0.3	2.0	0.1	3.0	0.7
3LSV	-1.6	1.0	-2.2	0.5	-1.7	0.9	-0.6	1.5
3LSV	2.7	0.6	2.1	0.1	2.6	0.5	3.7	1.1
3LSV+3SSV	-1.6	1.6	-1.8	1.4	-1.6	1.6	-1.6	1.7
3LSV+3SSV	-2.7	-1.4	-2.9	-1.6	-2.7	-1.4	-2.7	-1.4
4LSV	-0.9	-0.3	-0.7	-0.1	-0.8	-0.3	-1.3	-0.5
4LSV	1.0	0.4	1.2	0.6	1.0	0.4	0.5	0.2
4LSV	2.1	-0.6	2.4	-0.4	2.2	-0.5	1.6	-0.8

(+) numbers are overestimates (-) umbers are underestimates

Appendix A. Data from 1st determination

Run Number	Sample	Loop Volume (ml)	Temp (oC)	Press (mbar)	Area CFC-12	Area CFC-11	WZ12 (pptv)	WZ11 (pptv)	W12 (pptv)	W11 (pptv)	U12 (pptv)	U11 (pptv)	WZS12 (pptv)	WZS11 (pptv)
1	1LSV	2.917620	24.2	1019.10	40071	68687	596.4	319.2	596.7	319.4	592.2	316.3	595.3	318.5
2	1LSV	2.917620	24.3	1018.95	39828	67843	592.8	315.5	593.1	315.6	588.6	312.6	591.8	314.8
3	3SSV	2.238828	24.9	1019.25	31609	53921	606.5	329.8	605.3	328.6	600.3	325.2	604.4	328.6
4	4LSV	11.670480	25.0	1019.20	144617	318266	595.1	319.7	595.3	319.9	595.2	319.7	594.7	319.5
5	1LSV+1SSV	3.663896	25.0	1019.15	49553	87776	596.8	321.8	597.6	322.7	594.0	320.1	596.6	321.5
6	1SSV	0.746276	25.0	1019.10	11064	17806	614.5	332.8	587.6	310.6	590.5	310.7	606.7	327.7
7	3LSV	8.752860	25.1	1019.05	111152	226272	598.0	320.2	597.5	319.7	598.0	320.1	599.0	320.7
8	2SSV	1.492552	24.9	1019.00	21549	35763	610.0	331.1	603.6	325.3	599.4	322.2	606.2	328.9
9	2LSV	5.835240	24.8	1019.05	76985	143075	601.7	318.5	601.9	319.2	600.8	318.1	602.7	318.9
10	4SSV	2.985104	24.8	1019.05	41562	72296	607.1	327.7	607.6	328.1	603.1	325.0	606.2	327.1
11	2LSV+2SSV	7.327792	24.7	1019.15	94812	185923	600.3	321.1	600.0	321.1	600.0	321.0	601.5	321.7
12	3LSV+3SSV	10.991688	24.7	1019.15	136698	298807	594.4	321.6	594.2	321.4	594.4	321.6	594.4	321.7
13	1LSV	2.917620	24.7	1019.25	39881	69209	594.2	321.1	594.5	321.3	590.1	318.3	593.2	320.4
14	3SSV	2.238828	24.8	1019.25	31555	53741	605.1	327.8	603.9	326.5	598.9	323.2	603.1	326.6
15	4LSV	11.670480	24.9	1019.50	145134	320196	597.0	320.4	597.2	320.6	597.0	320.4	596.5	320.2
16	1SSV	0.746276	24.8	1019.55	11088	17825	615.2	332.0	588.3	309.8	591.2	309.9	607.3	327.0
17	3LSV	8.752860	24.7	1019.60	110715	227946	594.4	321.0	593.8	320.5	594.3	320.9	595.4	321.5
18	2SSV	1.492552	24.8	1019.60	21489	35858	607.7	330.9	601.3	325.1	597.0	322.1	603.8	328.7
19	2LSV	5.835240	24.7	1019.55	76808	143907	599.7	319.3	599.9	319.9	598.8	318.9	600.7	319.6
20	4SSV	2.985104	24.7	1019.60	41375	72565	603.7	327.8	604.1	328.2	599.7	325.2	602.8	327.2
21	1LSV+1SSV	3.663896	24.6	1019.60	49564	87933	595.9	320.7	596.7	321.6	593.1	318.9	595.6	320.4
22	2LSV+2SSV	7.327792	24.6	1019.90	93576	185354	591.1	319.2	590.9	319.2	590.8	319.0	592.3	319.7
23	3LSV+3SSV	10.991688	24.8	1020.25	136563	296391	593.3	318.6	593.1	318.4	593.3	318.6	593.3	318.6
28	1LSV	2.917620	25.3	1023.95	40183	69306	597.4	319.7	597.8	319.9	593.3	316.8	596.4	319.0
30	1LSV	2.917620	25.5	1023.85	39760	69113	591.2	318.9	591.5	319.1	587.0	316.0	590.2	318.2
31	3SSV	2.238828	25.5	1023.80	31907	54525	610.9	330.5	609.8	329.3	604.8	325.9	608.9	329.3
32	4LSV	11.670480	25.5	1023.75	145696	321123	598.1	319.4	598.4	319.6	598.2	319.5	597.6	319.2
33	1SSV	0.746276	25.4	1023.60	11085	18148	613.8	336.0	586.9	314.0	589.9	314.0	606.0	331.0
34	3LSV	8.752860	25.4	1023.45	111615	228907	598.7	320.6	598.1	320.1	598.6	320.5	599.7	321.1
35	2SSV	1.492552	25.5	1023.30	21701	36181	613.1	332.1	606.8	326.4	602.5	323.3	609.2	329.9
36	2LSV	5.835240	25.4	1023.05	75956	144854	591.8	319.7	592.0	320.3	590.9	319.3	592.8	320.0
37	4SSV	2.985104	25.5	1022.75	41566	73240	606.3	329.4	606.8	329.8	602.4	326.7	605.4	328.8

Appendix A. Data from 1st determination

Run Number	Sample	Loop Volume (ml)	Temp (oC)	Press (mbar)	Area CFC-12	Area CFC-11	WZ12 (pptv)	WZ11 (pptv)	W12 (pptv)	W11 (pptv)	U12 (pptv)	U11 (pptv)	WZS12 (pptv)	WZS11 (pptv)
38	1LSV	2.917620	25.4	1022.65	39731	69460	591.2	320.1	591.5	320.3	587.0	317.3	590.2	319.4
39	1LSV	2.917620	25.5	1022.45	39837	69677	593.2	321.2	593.5	321.4	589.0	318.3	592.2	320.5
40	1LSV	2.917620	25.5	1022.35	40232	69526	599.5	320.5	599.8	320.7	595.4	317.6	598.5	319.8
41	1LSV	2.917620	25.6	1022.15	40237	69605	599.9	320.9	600.2	321.2	595.7	318.1	598.9	320.2
42	1LSV	2.917620	25.6	1022.20	39850	69660	593.8	321.1	594.1	321.3	589.6	318.2	592.7	320.4
43	1LSV	2.917620	25.6	1022.25	39797	69484	592.9	320.2	593.2	320.4	588.7	317.3	591.8	319.5
44	1LSV	2.917620	25.6	1022.20	39672	69738	591.0	321.3	591.2	321.5	586.8	318.4	589.9	320.6
45	PMEL	2.917620	25.6	1022.30	33779	59208	498.6	274.3	498.1	273.8	494.0	271.0	497.2	273.4
46	PMEL	2.917620	25.5	1022.25	34127	59383	503.9	275.0	503.4	274.4	499.3	271.6	502.5	274.1
47	PMEL	2.917620	25.6	1022.25	34322	59270	507.1	274.5	506.6	273.9	502.5	271.1	505.7	273.6
48	PMEL	2.917620	25.5	1022.30	33979	58868	501.6	272.5	501.0	271.9	497.0	269.2	500.1	271.6
49	PMEL	2.917620	25.5	1022.40	34053	59806	502.7	276.6	502.2	276.1	498.1	273.3	501.2	275.8
50	PMEL	2.917620	25.6	1022.50	33736	59233	497.8	274.1	497.3	273.5	493.2	270.7	496.4	273.2
51	PMEL	2.917620	25.6	1022.70	33664	59639	496.6	275.8	496.1	275.2	492.0	272.4	495.2	274.9
52	PMEL	2.917620	25.4	1022.70	34001	60563	501.5	279.6	501.0	279.2	496.9	276.4	500.1	278.8
53	PMEL	2.917620	25.6	1022.45	37287	61159	553.3	282.5	553.3	282.1	548.9	279.2	552.1	281.7
54	1LSV	2.917620	25.0	1022.55	39959	69052	594.1	316.8	594.4	317.0	589.9	313.9	593.0	316.1
55	1LSV	2.917620	24.6	1022.55	39891	69084	592.2	316.4	592.5	316.6	588.0	313.5	591.1	315.7
56	1LSV	2.917620	24.3	1022.55	40327	69625	598.4	318.4	598.8	318.6	594.3	315.6	597.4	317.7
57	1LSV	2.917620	24.1	1022.60	40380	69697	598.8	318.5	599.2	318.6	594.7	315.6	597.8	317.8
58	1LSV	2.917620	23.9	1022.85	40119	70081	594.2	319.8	594.5	320.0	590.1	316.9	593.2	319.1
59	1LSV	2.917620	23.7	1022.90	39942	69767	591.0	318.1	591.3	318.3	586.8	315.2	590.0	317.4

Appendix B. Data from 2nd determination

Run Number	Sample	Loop Volume (ml)	Temp (oC)	Press (mbar)	Area CFC-12	Area CFC-11	WZ12 (pptv)	WZ11 (pptv)	W12 (pptv)	W11 (pptv)	U12 (pptv)	U11 (pptv)
1	1LSV	2.917620	25.3	1034.35	43282	71667	591.4	320.3	591.5	320.4	591.5	320.2
2	1LSV	2.917620	25.3	1034.40	44082	72133	602.9	322.1	603.3	322.2	603.3	322.0
3	1SSV	0.746276	25.7	1034.15	12898	18707	661.0	333.2	592.9	314.1	593.0	314.1
4	4LSV	11.670480	25.2	1034.05	151936	338452	595.5	319.9	596.0	320.0	596.0	320.0
5	2LSV	5.835240	25.1	1033.85	82794	148850	595.9	319.8	595.9	320.3	595.9	320.3
6	2SSV	1.492552	25.7	1033.80	23674	37529	616.5	331.4	599.6	326.3	599.6	326.1
7	3LSV	8.752860	25.3	1033.65	118918	235541	597.7	320.4	596.0	320.0	596.1	320.0
8	1LSV	2.917620	25.3	1033.50	43315	71113	592.4	316.3	592.6	316.3	592.6	316.1
9	1LSV	2.917620	25.4	1033.05	43433	71514	594.6	318.0	594.8	318.0	594.8	317.8
10	1LSV	2.917620	25.4	1032.95	43849	72146	600.7	320.4	601.0	320.5	601.0	320.3
11	1LSV	2.917620	25.3	1032.90	43707	72157	598.5	320.1	598.8	320.2	598.7	320.0
12	1LSV	2.917620	25.2	1032.75	43446	72355	594.6	320.6	594.8	320.7	594.8	320.5
13	1LSV	2.917620	25.2	1032.50	42934	72430	587.3	320.8	587.4	320.8	587.4	320.7
16	PMEL	2.917620	25.3	1032.05	37219	60983	505.6	270.8	503.9	270.1	503.9	270.0
17	PMEL	2.917620	25.1	1032.00	37431	61736	508.3	273.6	506.7	273.0	506.7	272.9
18	PMEL	2.917620	25.0	1031.90	37182	62462	504.7	276.5	503.0	275.9	502.9	275.8
19	PMEL	2.917620	25.1	1031.65	36964	62125	501.9	274.9	500.1	274.4	500.0	274.2
20	1LSV	2.917620	25.3	1031.45	43644	72525	598.5	319.6	598.8	319.7	598.8	319.5
21	1LSV	2.917620	25.2	1031.40	43488	72917	596.1	320.9	596.4	321.0	596.3	320.8

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