

Meta Data Report	
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Project/cruise:	Southern Ocean GasEx 2008
Dates:	29 February to 12 April, 2008
Ship:	Ronald H. Brown
Operation description:	Analysis of discrete samples for SF6. Samples collected from CTD casts, from underway scientific seawater line, and from submerged water pump
Sampling times and locations:	Sampled all CTD casts where Niskin bottles were tripped. One deep cast to 4600m, two mid-depth casts to 1500m, four shallow casts to 100m, and other casts usually to 500m. See CTD cast logs and bottle files for specific times, locations, and bottles for each cast. See event log for times and locations when sampled underway seawater line.
Overall sampling strategy:	Normally collected one sample from each depth that might contain the released SF6, plus three - six samples deeper. All available depths were sampled on the first four casts and on any later cast that was shallower than 500m. If multiple Niskins were tripped at a given depth, hydrography sampled only one of these. Duplicate samples were drawn from a Niskin, normally in the mixed layer, on nearly every cast. The first Niskin of a cast that was sampled was the deepest Helium sample, and the sampling continued in order to the surface Niskin. The deeper Niskins for SF6 sampling were done next, starting at the deepest.
Sampling technique:	The discrete samples were collected in 550 ml borosilicate glass bottles with ground glass stoppers. A sample bottle was shaken with 30-40 ml of water; then inverted and rinsed with 10-20 ml of water. The bottle was filled from the bottom with ~800 ml of bubble free water. The stopper was put in the bottle ensuring that no gas bubble was enclosed. After the sample was collected from a cast, a rubber band was slipped over the stopper. If the samples were not going to be analyzed within 10 hours, the glass bottles were stored in water.
Expected initial data products:	Preliminary SF6 concentrations are provided several times during cruise
Expected distributed data products, and time-frame for distribution:	Final SF6 concentrations will be available 2-3 weeks after the cruise
Analytical method	The samples were analyzed on an instrument patterned after Law et al. [1998] and built in 1998 at AOML. About 269 ml of sample water was sucked into an evacuated chamber through a showerhead. The SF6 that entered the headspace during filling and the SF6 that remained dissolved in the water were trapped by ultra high purity nitrogen onto a Carboxen 1000 trap held at -68 C. After a little more than 3 minutes of purging, the trap was isolated and heated to 150 C. The trapped gases were swept onto a 1.5 m x 0.3 cm OD molecular sieve 5A column. The SF6 was separated from oxygen and other gases and was measured with an electron capture detector (ECD). The detector was calibrated using six standards: <i>cyI#CA2071- 5.7 pptillion (V/V); cyI#CA2089- 55.1 ppt; cyI#CA3452- 112.3 ppt; cyI#CA2060- 166.6 ppt; cyI#CA2056- 345.0 ppt; and cyI#CA2093- 1109.0 ppt</i> . The custom software includes a chromatography package from Wilstein Software, which is used for acquisition of the ECD output and to reintegrate peaks. The SF6 peaks were reintegrated for all blank analyses, water analyses and the analyses of 5.5 ppt standard. The larger standards had very favorable signal to noise ratios.
	The pattern of analyses include initial and final groups of standards bracketing groups of water analyses. The water samples from each cast were typically split into two groups, each covering the entire water column. Within a group, the deepest water samples were analyzed before the more concentrated surface water samples. The Typical Analyses Sequence: 2-3 gas blanks; 15-20 gas standards spanning the entire range; gas blank; 1-2 stripper blanks; 7-9 water analyses; stripper blank; 1 analysis of 166.6 ppt standard; stripper blank; 7-9 water analyses; [repeat analyses of stripper blanks, 166.6 ppt std, and water samples two or three times]; stripper blank; gas blank; 5-15 standards; 2 gas blanks. The stripping chamber was evacuated and flushed with nitrogen before the first use. If the stripping chamber was not going to be used for more than 6 hours, it was rinsed with fresh water and then evacuated and flushed.
Instrument details	The ECD gas chromatograph is a Shimadzu Mini 2. The custom software was written with LabView 5.1 in 1998 and revised in 2002. The reference for a description of the instrument is Law, C.S, A.J. Watson, M.J. Liddicoat, and T. Stanton, Sulphur hexafluoride as a tracer of biogeochemical and physical processes in an open-ocean iron fertilization experiment. Deep Sea Research II, 45, 977-994, 1998.
Operation Log - during cruise	
Affected data: date	Comments
5 - 6 March, 2008	Attempts were made to use this discrete instrument to quantitate the amount of SF6 in water actively being bubbled in the dosing tank. All attempts resulted in peaks much larger than full scale for the ECD. The excessive amounts of SF6 were easily swept out of the instrument.
Station 3	one sample of a duplicate pair is stored for 23 hours before analyses - precision of duplicates was good
Station 5	one sample of a duplicate pair is stored for 24 hours before analyses, another sample of a different duplicate pair is stored for 32 hours. Precision of the 32-hour duplicates was poorer than normal.
Station 8	These samples were stored overnight before analyses as were some earlier stations and many later stations. This was the first station for which some outgassing bubbles in some samples was noticed. These tiny bubbles (<0.1 ml total volume) were not present when the bottle was sealed and did not seem to bias the SF6 results.
Station 10	The sampling order was more discontinuous than normal to accommodate noble gas sampling. For the collection of samples from the underway system after station 10, the outflow tube of the MicroTSG in the hydro lab sink was put in the bottom of a sample bottle and left to overflow the bottle for at least 2 minutes (flow at 1.3 l/min).
13 March, 2008	During analysis of sample bottles 15 (stn 9, N 22) the Labview program was in its 'pause and prompt' state longer than usual. The analytical system evacuates the stripping chamber and then presents a prompt screen until a "start" button is pushed by the analyst. The analyst has to draw some of the sample through the inlet tube and solenoid valve before pushing the "start" button. If the 'pause and prompt' state is long, the chance of outside air leaking into the chamber is greater (potential higher blank).
15 March, 2008	In an effort to have comparable results from the underway and discrete SF6 analytical systems, the single SF6 gaseous standard for the underway system (58.2 ppt) was run on the discrete system and three of the discrete standards (166.6, 55.1, and 5.7 ppt) were run on the underway system.
18 March, 2008	Both system and stripper blanks are significantly higher. The second dosing tank is being bubbled on the afterdeck, and the lab air was enriched in SF6. No leaky fittings could be found on the analytical system despite a day of searching. After ~48 hrs the blanks decreased, but remained higher than at the start of the last night was the first station (16) on the starboard patch. I took a sample from the underway system to quickly check the strength of ECD signal. When the sample was run, the peak went offscale. The ECD was set for 2nAmp standing current through station 14. I decreased the setting to 1 nAmp. To span the largest peak from the water analyses of station 16, I had to trap 6 regular gas loops (1.606 ml) of the most concentrated standard (1109 ppt). I am concerned about peak shape changes while trapping that many loops sequentially, so I put the second gas sample loop valve back on the system. [It was taken off during a previous experiment.]
25 March, 2008	I made a large loop (~7 ml) and created new analytical methods to adequately flush the loop while and after using it with standard blank gas. I will have to determine the exact volume of the new gas loop. Try again to locate the source of the elevated blanks, especially the stripper blanks. Still, could not find any fitting that leaked. At the end of a day of analyses, the chamber is rinsed with fresh water to reduce the corrosion on the solenoid valves attached to the drain and vacuum connectors. I stripped a sample of the fresh water on the ship and discovered that it was as concentrated as the surface 'in-patch' water (>200 fmole/liter). The chamber will continue to be rinsed with fresh water, but it will go through a couple evacuation-purge cycles before being left for the night (no reduction in the blanks developed, but the procedure was program was in its 'pause and prompt' state longer than usual).
25 March, 2008	During analyses of sample bottles 202 (stn 25, N 3), 206 (stn 25, N 9) and 10 (stn 26, N 18) the Labview program was in its 'pause and prompt' state longer than usual.
26 March, 2008	During analysis of sample bottles 203 (stn 27, N 8) the Labview program was in its 'pause and prompt' state longer than usual.
28 March, 2008	During analysis of sample bottles 2 (stn 32, submerged pump) the Labview program was in its 'pause and prompt' state longer than usual.
29 March, 2008	During analyses of sample bottles 2 (stn 35, N 7) and 17 (stn 35, underway system) the Labview program was in its 'pause and prompt' state longer than usual.
30 March, 2008	During analysis of sample bottles 202 (stn 37, N 6) the Labview program was in its 'pause and prompt' state longer than usual. During analysis of sample bottles 206 (stn 37, N 10) there seemed to be air in the inlet line and the water level in the stripping chamber seemed lower than usual. Maybe the inlet tube was not submerged as low as it should have been [but how would the Pt wire water sensors stop the water flow automatically - splashes with gas going in?]
31 March, 2008	During sampling, the stopper on bottle 203 (stn 41, N 3) was removed ~3 minutes after sampling so some more a little more water from the niskin was gently added to the very top of the bottle and the stopper
3 April, 2008	During the chromatograms of bottle 11 (stn 47, N 17) and bottle 12 (stn 47, N 18) the baseline got significantly noisier. This behavior has been seen on past expeditions associated with locally strong RF transmissions (e.g. keying and/or talking on hand held radio). No cause was located.
Data Processing Log - post cruise	
	The first step in the data processing is subtracting the appropriate analytical blank from the raw peak areas: gas blank for standard and air analyses, stripper blank for the water analyses. The gas and stripper blanks were plotted and appeared to cluster around different values over separate time periods. This pattern was to be expected since there was only one analytical blank who typically ran the samples from two casts together. The analytical system was used for ~1/2 a day and then sat unused for ~1/2 a day. Nineteen ranges of time were used for blank correction, due primarily to the variability of the stripper blanks. The same gas blank value was applied in sequentially ranges often. The applied blank values and a summary of the analytical blank results are provided below.
	The analytical blanks showed no systematic trends for all but one range, so a single blank value was used for the entire range. Within one time period, the stripper blank clearly increased and then decreased. Rather than use one value, the applied blank for the water analyses was a time-weighted linear interpolation between bracketing analytical stripper blanks. For most of the water and gas analyses, the applied blank was significantly less than 1% of the sample signal.
	The blank-corrected peak areas for the standard analyses were plotted versus time. The response of the ECD was fairly stable within the setting used for a patch (i.e. 2 nA standing current for patch#1; 1 nA standing current for patch#2). Three time periods were chosen for each setting. Within each time period, a least-squared regression of the standards produced a 4th degree polynomial equation relating peak area and femtomole SF6. The peak areas for the seawater analyses were not larger than for the standards; however, there were some atypical analyses (e.g. tap water after 26 March) that had peaks larger than the standards in that time period. Since the detector response was similar in the adjoining time periods, the data for a couple standard runs were copied to adjoining time periods to extend the standard curves for some atypical analyses.
	The 4th degree polynomial equations were used to convert the blank-corrected peak areas for the water analyses to aqueous concentrations (femtomole/liter). The results of the water analyses were examined within the context of the surrounding SF6 analyses, of the titrated oxygen samples, and of the general hydrography. A quality control flag similar to the WOCE protocol were assigned to each water analysis. There were four analyses that were deemed 'bad', two of which had observations during analysis to explain the bad result. There were fifteen analyses that were deemed 'questionable', seven of which had observations to explain the poor result. The remaining 650 seawater analyses were deemed 'good', though nine analyses had observations that could have explained poor results. The assignment of a 'bad' quality control flag was conservative so that expected results would not be excluded from examination by others.
	For the duplicate water samples drawn from niskin bottles, the relative precision was 3.3% for all 38 duplicate pairs and 1.4% for the 31 duplicate pairs definitely above background SF6 concentrations (i.e. >8 fmole SF6/liter). For the nineteen sets of multiple samples collected from the underway sea water line the average precision was 5.3%, which reflects analytical variability as well as changes in the water being sampled. A restrip of a concentrated water sample was done on nearly every day. All 27 restrips of a water sample contained 2% or less of the total SF6 extracted from a water sample, so no correction for stripping efficiency was done.

Blanks for SO GasEx 2008 Cruise

note: when the same blank value is used in sequential ranges, the average is done over all the sequential ranges

2nA setting on ECD, patch 1

decimal year-day		applied blanks		gas blanks-measured			stripper blanks-measured		
start interval	stop interval	gas blk	strip blk	average	stdev	count	average	stdev	count
66.5	67.1	0	1200				1422	521	8
69.4	69.8	0	4000				10329	8081	3
70.4	71.0	0	1500				2041	1316	8
71.4	73.3	0	1900				2388	1153	18
73.5	76.1	0	600	68	186	40	910	595	14
78.2	79.0	800	1100	648	385	5	1291	338	8
79.3	79.6	1800	0	2243	1723	8	0	0	0
79.7	81.0	2500	4000	2522	1488	15	4652	2518	4

1nA setting on ECD, patch 2

decimal year-day		applied blanks		gas blanks-measured			stripper blanks-measured		
start interval	stop interval	gas blk	strip blk	average	stdev	count	average	stdev	count
82.0	83.5	1500	3000	1832	2201	12	3573	2180	17
83.5	85.0	500	2500	88	280	10	2861	1427	15
85.0	87.0	2500	7000	2657	858	9	7580	5737	23
87.0	88.1	1800	5000	1948	662	5	5595	2239	10
88.1	89.1	1200	3500				3588	2215	7
89.1	91.2	1200	2400	934	769	23			
91.2	93.2	800	2400				2861	1437	42
93.2	94.2	800	1500				1989	1634	7
94.2	95.2	800	3200				3764	1688	9
95.2	95.8	800	interpolate				9046	2655	11
95.8	97.0	800	6000	709	644	35	5781	1452	11

Calibration Curves for SO GasEx 2008 Cruise

2nA setting on ECD, patch 1

decimal year-day		coefficients for 4th degree polynomial equation				
start interval	stop interval	count - stds	x4	x3	x2	x
66.5	73.3	133	-4.429E-24	3.173E-17	-7.613E-11	1.308E-04
73.5	76.1	86	-4.203E-24	2.948E-17	-6.884E-11	1.231E-04
78.2	81.0	72	-3.381E-24	2.457E-17	-6.007E-11	1.175E-04

1nA setting on ECD, patch 2

decimal year-day		coefficients for 4th degree polynomial equation				
start interval	stop interval	count - stds	x4	x3	x2	x
82.0	87.0	211	2.095E-25	5.549E-18	-2.759E-11	1.871E-04
87.0	94.2	227	-7.676E-24	4.599E-17	-8.527E-11	2.045E-04
94.2	97.0	107	-5.137E-24	3.385E-17	-7.074E-11	2.035E-04