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STANDARD OPERATING PROCEDURES
SAMPLING AND ANALYSIS OF FORMALDEHYDE EMISSIONS

MONITORING AND LABORATORY DIVISION
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California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure Approval

Title: Sampling and Analysis of Formaldehyde Emissions from Composite Wood Products

SOP: NLB SOP SAS20, Revision 1

Section: Special Analysis Section

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Division: Monitoring and Laboratory Division

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1.0 SCOPE

This method specifies procedures for measuring formaldehyde emissions from composite wood products (CWPs). CWP samples are loaded into a small testing chamber using procedures based on ASTM D6007-02: *"Standard test method for determining formaldehyde concentrations in air from wood products using a small-scale chamber".* The chamber air is sampled using 2,4-dinitrophenylhydrazine (DNPH) silica gel cartridges to capture the formaldehyde. Cartridges are eluted with acetonitrile and the DNPH-derivative sample is measured using high performance liquid chromatography with ultraviolet detection (HPLC-UV). The procedure is based on ASTM D5197-03: *"Standard test method for determination of formaldehyde and other carbonyl compounds in air (active sampler methodology)"*.

This analytical method may achieve a detection limit of 0.6 ppb and an estimated quantitation limit (EQL) of 3 ppb for formaldehyde.

2.0 SUMMARY OF METHOD

A section of composite wood sized to meet the air flow and surface area requirements as defined in the ASTM D6007-02 method is placed in the small chamber within an environmentally controlled unit. Air is circulated through the small chambers at a flow rate of 1.0 liter per minute (LPM) for 0.5 hours*. DNPH-silica cartridges are placed on a sampling line from the small chamber to collect emissions. The samples are eluted with 10 mLs of acetonitrile (ACN) then analyzed using a liquid chromatograph with an ultraviolet detector at 360 nm.

*See Method Development document in Appendix A for supporting data.

3.0 DEFINITIONS

BATCH – an analytical batch is a set of prepared samples (i.e. extracts) analyzed together as a group in an uninterrupted sequence. A preparation (extraction) batch is a set of samples which is processed all in one group using the same equipment, reagents and staff within a single work shift.

BLANK - a sample that has not been exposed to the sample stream in order to monitor contamination during sampling, transport, storage, extraction, or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value.

> METHOD BLANK (Extraction Blank) – a new, unused DNPH-cartridge free of analyte and matrix to which all reagents are added in the same

volumes or proportions as used in sample processing, and which is taken through the entire sample preparation process. It is used to monitor the laboratory preparation and analysis systems for interferences and contamination from glassware, reagents, sample manipulations, and the general laboratory environment.

SOLVENT BLANK – a sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps.

CARTRIDGE BLANK – a new, unused DNPH-cartridge from the same lot as those used for samples that is not exposed to the target analyte or sample matrix but is carried through all extraction and analytical steps to determine any possible background contribution from the cartridge. The cartridge blank is used to represent the cleanliness of all samples in a single manufacturing lot.

SAMPLING PURGE BLANK– DNPH cartridge placed on small sampling chamber during the first 0.5 hour system purge prior to collecting a sample. This cartridge is not analyzed and may be used multiple times for this purpose. It is removed and replaced with a new, unused cartridge for sample collection.

CALIBRATION - Calibration refers to the act of evaluating and adjusting the precision and accuracy of measurement equipment using known values (standards).

COMPOSITE WOOD PRODUCTS (CWP) – hardwood plywood, particleboard, and medium density fiberboard.

CONTINUING CALIBRATION VERIFICATION SAMPLE (CCV) – a sample containing analyte at a known concentration obtained from a source other than that of the calibration standards.

ENVIRONMENTAL CHAMBER – an enclosure with controlled temperature and humidity. An environmental conditioning chamber is used to bring samples to a similar state prior to sampling. A separate environmental chamber is used to hold small sampling chambers.

ESTIMATED QUANTITATION LIMIT (EQL) – defined as five times the method detection limit (MDL) and used as the lower limit for reporting data.

FINISHED GOODS – any good or product, other than a panel, containing hardwood plywood, particleboard, or medium density fiberboard.

INTERFERENCE – discrete artifacts or elevated baselines from solvents, reagents, glassware, and other sample processing hardware that may cause misinterpretation of the chromatographic data.

LIMIT OF DETECTION (LOD) or Method Detection Limit (MDL) – the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and statistically different from a blank. It is determined from replicate analyses of a sample in a given matrix containing the analyte.

REPLICATE – a separate analysis of the same sample. The sample extract used for replicate analyses must be chosen at random. Relative percent difference between the sample and its replicate is calculated and must meet specified quality control criteria or be reanalyzed. Replicate analytical results are used to evaluate analytical precision but not the precision of sampling, preservation, or storage internal to the laboratory.

SAMPLE CONDITIONING – to hold samples in an environmental chamber at specified temperature and humidity for a specified time prior to sampling.

SMALL CHAMBER BACKGROUND CHECK - a sample collected to measure background levels in each small chamber. Small chamber background checks consist of 0.5 hours of sampling using a new, unused DNPH cartridge with no sample in the chamber.

SMALL SAMPLING CHAMBER – an enclosure used to hold samples for collection of emissions while air is circulated at a specified flow rate around the sample inside. Multiple small sampling chambers fit into a single environmental chamber.

4.0 INTERFERENCES/LIMITATIONS

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. High levels of formaldehyde in background or supply air may contribute to elevated concentrations. A method blank, solvent blank, small chamber background blank, and cartridge blank must be analyzed with each batch of samples to detect any possible interference. Conditioning chamber and room air samples are taken each quarter for analysis to ensure levels of ambient formaldehyde are below 20 ppb. The temperature and relative humidity of the

environmental chambers and small chambers will be continuously monitored to ensure that these parameters stay within the range specified in ASTM D6007-02.

5.0 EQUIPMENT AND CONDITIONS

5.0.1 INSTRUMENTATION

Agilent 1100 or 1260 Series Liquid Chromatograph
Agilent 1100 or 1260 Variable Wavelength Detector, set at 360 nm
Column: Restek Allure C-18 150 x 4.6 mm, 5µm
Solvent: 60% Acetonitrile/Deionized Water
Column Flow Rate: 1.0 mLPM
Sample volume: 5 µL
Run time: 16 mins
Formaldehyde-DNPH retention time= 4.00 mins

5.0.2. AUXILIARY APPARATUS

1. Caron Environmental Chambers, Marietta, Ohio, Model 6020-1
2. Wasson-ECE pump
3. Aalborg flow controllers
4. Sampling chambers each with a volume of 0.020 m^3 (20.31 x 20.32 x 50.8 cm)
5. NIST traceable temperature/humidity/dew point meter (Control Company, Friendswood, TX, Traceable Humidity/Temperature/Dew Point Meter 4085)
6. Pipettors, 10 mL capacity
7. HPLC vials with septum caps
8. Syringes, 10 mL capacity
9. Aluminum flex tape
10. Supelco DNPH Cartridges S10L, #505358

5.0.3. REAGENTS

1. Acetonitrile, LC-MS grade or better
2. Formaldehyde-2,4-DNPH, Standards prepared from Restek #31837, 500 µg/mL in ACN. Secondary source as controls/check from Supelco, #44-2597

6.0 SAMPLE PREPARATION

6.0.1 SAMPLE RECEIPT

Enforcement Division (ED) staff collect and process the products, either raw boards or finished goods following their prescribed SOP. Samples may be prescreened for formaldehyde using a Field and Laboratory Emission Cell (FLEC meter), when possible. Samples are brought to the laboratory with chain-of-custody (COC) forms identifying each sample and its screening concentration. If the sample identification information does not match the COC record, ED staff must make corrections at the time of delivery or the laboratory may refuse to accept samples until such corrections are made. Samples are stored as received in separate packaging at room temperature until conditioning is performed.

6.0.2 FLOW RATE

The area and cut size of the sample is dependent on the type of composite. The size of the sample is based on the flow to area (Q/A) ratio as described in Table 1 of ASTM D6007. Each small chamber has a volume of 0.021m^3 (20.32 x 20.32 x 50.8 cm). The air flow is 0.06 m^3/hour (the same as the sampling flow rate, 1 LPM) therefore, to meet the specified Q/A ratio the size of the CWP samples are:

PB (particle board) - 180mm x 143 mm
HWPW (hardwood plywood) - 180mm x 143 mm
MDF (medium density fiberboard) - 180 mm x 90 mm.

Flow rates through the small sampling chambers are maintained using a pump and flow controllers (Figure 1).

6.0.3 CONDITIONING

Samples are conditioned in an environmental chamber to standardize them to a uniform temperature and humidity prior to testing. Samples are conditioned for 24 hours ±3 hours at 24 $\pm$ 3°C and 50 $\pm$ 5% relative humidity (Figure 2). In ASTM D6007-02, sample specimen conditioning parameters are specified at these temperature and relative humidity conditions for 2 hours ± 15 minutes. This method further states that alternative conditioning intervals may give better correlation, which ARB has demonstrated through equivalency testing to a large chamber. The temperature and relative humidity of the environmental chamber and small chambers are continuously monitored and recorded to ensure that these parameters stay within the range. The background formaldehyde levels are checked to ensure they do not exceed the proscribed limits.

Samples are prepared for conditioning following all instructions on the COC for special handling (i.e., taping samples together, etc.) to meet

specifications. If the combined area of the cut edges is greater than five percent of the surface area, the edges must be covered with aluminum flex tape prior to conditioning.

Samples are placed in the conditioning chamber standing on edge and at least six (6) inches apart. This placement ensures that the maximum surface area is exposed and maximizes air flow around the samples. See Figure 3. Samples are placed in the conditioning chamber according to their formaldehyde screening concentrations, which should be indicated on the COC. When a prescreen test indicates a high emitting sample, the high emitting samples (>0.15 ppm) are not conditioned with low emitting samples (<0.07 ppm) to avoid cross contamination. The time is recorded when the batch of samples is in place. Samples must be placed in the sampling chamber immediately upon removal from the conditioning chamber but may remain in the conditioning chamber for up to seven days.

6.0.4 SAMPLE COLLECTION

Sampling consists of a 0.5 hour system purge and a 0.5 hour sample collection as specified below.

1. Small Chamber Background Check

   Prior to sampling, a small chamber background check is collected to measure background levels in each small chamber. Small chamber background checks consist of 0.5 hours of sampling using a new, unused DNPH cartridge with no sample in the chamber. After DNPH background blanks are removed, each conditioned sample is placed in one of the small chambers. The sample fits in the small chamber so the maximum surface area is exposed. See Figure 4. The small chambers are placed in a separate environmental chamber maintained at 25 $\pm$ 1°C and 50 $\pm$ 4% relative humidity (Figure 5).

2. Sampling Purge Blank

   Sampling in the small chamber is for 0.5 hour with an air flow of 1.0 LPM (0.06 m^3/hour). The first 0.5 hour sampling using a blank pre-sampling cartridge purges the chamber system. This cartridge is a spent cartridge and may be reused for this purpose multiple times. This cartridge is not analyzed. Changing the pre-sampling cartridge on a monthly basis is recommended. This purge blank ensures

that only the product sample currently in the chamber is represented by the collected emissions.

3. Sampling

A new cartridge is placed on the sampler for sample collection. Again, sampling in the small chamber is for 0.5 hour with an air flow of 1.0 LPM. During sample collection the formaldehyde (H_2CO) reacts with the DNPH on the cartridge to form the hydrazone derivative. Emissions from one specimen per batch are collected and analyzed in replicate. A batch consists of all of the samples contained in the small sampling chambers that are sampled simultaneously.

6.0.5 SAMPLE EXTRACTION

Sample extraction must be done within thirty days of sample collection per the cartridge manufacturer's recommendation. If this extraction hold time is exceeded, results may be biased low and should be flagged or invalidated.

Sample extraction consists of eluting the H_2CO-DNPH derivative from the sampling cartridge using 10 mLs of acetonitrile and collected in a 10 mL volumetric flask. The volume is adjusted to 10mLs with Acetonitrile to account for approximately 0.5 mL dead volume capacity of the cartridge. The extract is transferred to an HPLC vial for analysis. If not analyzed immediately after extraction, extracts are stored at 4^oC until analysis and would be allowed to reach room temperature prior to analysis.

7.0 SAMPLE ANALYSIS

7.0.1 HOLD TIME

Sample extracts must be analyzed within 180 days of extraction. If this analytical hold time is exceeded, results may be biased low and should be flagged or invalidated.

7.0.2 SOLVENT BLANK

Solvent blanks are analyzed with each batch of samples. The blank must be free of interferences that may affect the formaldehyde peak. A solvent blank is analyzed before and after the calibration and all other QC samples, with every ten samples, before and after the calibration

verification sample (CCV), except at the end of the analytical batch in which the solvent blank is only analyzed before the CCV.

7.0.3 SMALL CHAMBER BACKGROUND CHECK

A check consisting of 0.5 hour sampling of each small chamber to determine background concentration is collected and analyzed with each batch of samples. The formaldehyde background in the small chambers must not be greater than 20 ppb. If the formaldehyde background in the small chambers is greater than 20 ppb, sample results from that small chamber are invalid and must be re-analyzed.

7.0.4 INSTRUMENTATION

Samples are analyzed using high performance liquid chromatograph with an ultraviolet detector (HPLC-UV) at 360 nm.

8.0 QUALITY ASSURANCE

8.0.1 CALIBRATION

1. Weekly

   A five-point calibration curve is made ranging from 0.05-1.0 µg/mL as free formaldehyde, with r^2 at least 0.999. A calibration will be run at least weekly, after any maintenance is performed on the HPLC-UV, or when the continuing calibration verification (CCV) is outside the control limits.

2. Daily

   A daily calibration must be performed prior to analyzing samples. This may consist of a single point or multi-point calibration.

8.0.2 CONTINUING CALIBRATION VERIFICATION (CCV)

A continuing calibration verification sample (0.2 µg/mL standard), also known as a check sample or control standard) is run to verify the calibration, at the beginning of each analytical run, after every ten samples, and at the end of the analytical batch. This check sample must be from a different source than the calibration standard. The value of the CCV must be within $\pm 3\sigma$ ($\pm$ three times the standard deviation) or $\pm$10% of the expected value, whichever is greater. If the CCV is outside this limit,

the CCV and all samples in the batch following the last valid CCV need to be reanalyzed. A recalibration may be performed.

8.0.3 CONTROL CHARTS

Control charts are used to show that the system (sampling, extraction, and analysis) is within expected limits, to signal systematic departures, and to identify inconsistencies in precision. Charts are created using the results of the CCV analyses. Upper and lower control limits and warning limits are established after at least 20 CCV values have been obtained. Control limits are calculated as $\pm 3\sigma$ (± 3 times the standard deviation) from the mean of the multiple measurements and warning limits are $\pm 2\sigma$ (± 2 times the standard deviation). All CCV results must fall within the control limits. Trends and exceedences must be evaluated for corrective action.

8.0.4 ENVIRONMENTAL CHAMBERS TEMPERATURE AND RELATIVE HUMIDITY

Temperature and humidity for each environmental chamber is continuously recorded. An independent check of temperature and relative humidity within the environmental chambers is made on a quarterly basis with a NIST traceable temperature/humidity/dew point meter. The meter currently used is from Control Company (Friendswood, Texas) Traceable Humidity/Temperature/Dew Point Meter 4085 (Temperature Range: –40.00 to 104.0°C; Humidity Range is 5.00 to 95.00% RH). Calibration must be performed annually on this meter.

Temperature and humidity readings must be documented at the start and end of each conditioning and sampling period.

8.0.5 FLOW RATES

Mass flow controllers must be calibrated at least annually. Flow rates must be recorded at the start and at the end of each sampling period. Flows must not vary by more than $\pm$ 0.05 lpm from the beginning to the end of the sampling period for the sample to be considered valid.

8.0.6 REPLICATES

One sample chosen at random is collected in replicate (two cartridges sampling 0.5 hours each from the same specimen) with each sampling batch. If the difference between analyses exceeds 20%, the analyst should evaluate the cause of the discrepancy (i.e., inadequately set

cartridge, loose sampling line, or other mechanical issues) and make appropriate corrections. The sample and its replicate should be reanalyzed, as necessary.

8.0.7 BLANKS

The method blanks, solvent blanks, and cartridge blanks should have no interfering peaks in the area of the formaldehyde that might cause integration problems. One method blank (extraction blank) must be prepared with each batch of samples extracted. Any concentrations greater than the limit of detection (LOD) in the method blank are reported but no blank correction is made.

One cartridge from each manufacturing lot must be extracted and analyzed prior to using any cartridges from that lot. The result from the method blank (extraction blank) analysis may be used to determine any possible background contribution from the cartridge, and thus, the appropriateness of using cartridges from any particular lot.

8.0.8 SAMPLE STABILITY AND HOLDING TIMES

Studies conducted by ARB have shown DNPH sample extracts to be stable for 180 days when stored at $4^{o}C$. Sample results may not be accurate if extracts are analyzed after this time.

9.0 DATA MANAGEMENT AND REPORTING

9.0.1 CONCENTRATION CALCULATION

The concentration of free formaldehyde is calculated according to:

Conc ($\mu g/m^3$) = Extract Conc ($\mu g/mL$) X 10 mL / Air Volume (0.03 m^3)

Conc (ppm) = Conc ($\mu g/m^3$) x ppm/1000 ppb x 0.814

No blank corrections or background corrections are made to calculated concentrations.

9.0.2 LABORATORY INFORMATION MANAGEMENT SYSTEM

All data is entered into a secure, limited access, laboratory information management system (LIMS) database. LIMS performs the functions of

data storage, data processing, and report generation. All changes made to data contained in LIMS are electronically tracked.

9.0.3 FINAL REPORTS

Final reports generated by LIMS and submitted to clients will include the following, based upon information provided by ED staff and through laboratory protocol:

Conditioning information:
- date performed,
- temperature,
- humidity,
- duration,
- conditioning background level

Sampling information:
- date performed,
- temperature,
- humidity,
- air flow rate,
- duration,
- testing background level

Analytical results with:
- sample identification,
- wood type,
- analysis date

Figure 1.1
Small Chamber Sampling System
Wasson-ECE Pump and Flow Controllers

Figure 1.2
Environmental Chamber

Figure 1.3
Samples in Environmental Conditioning Chamber

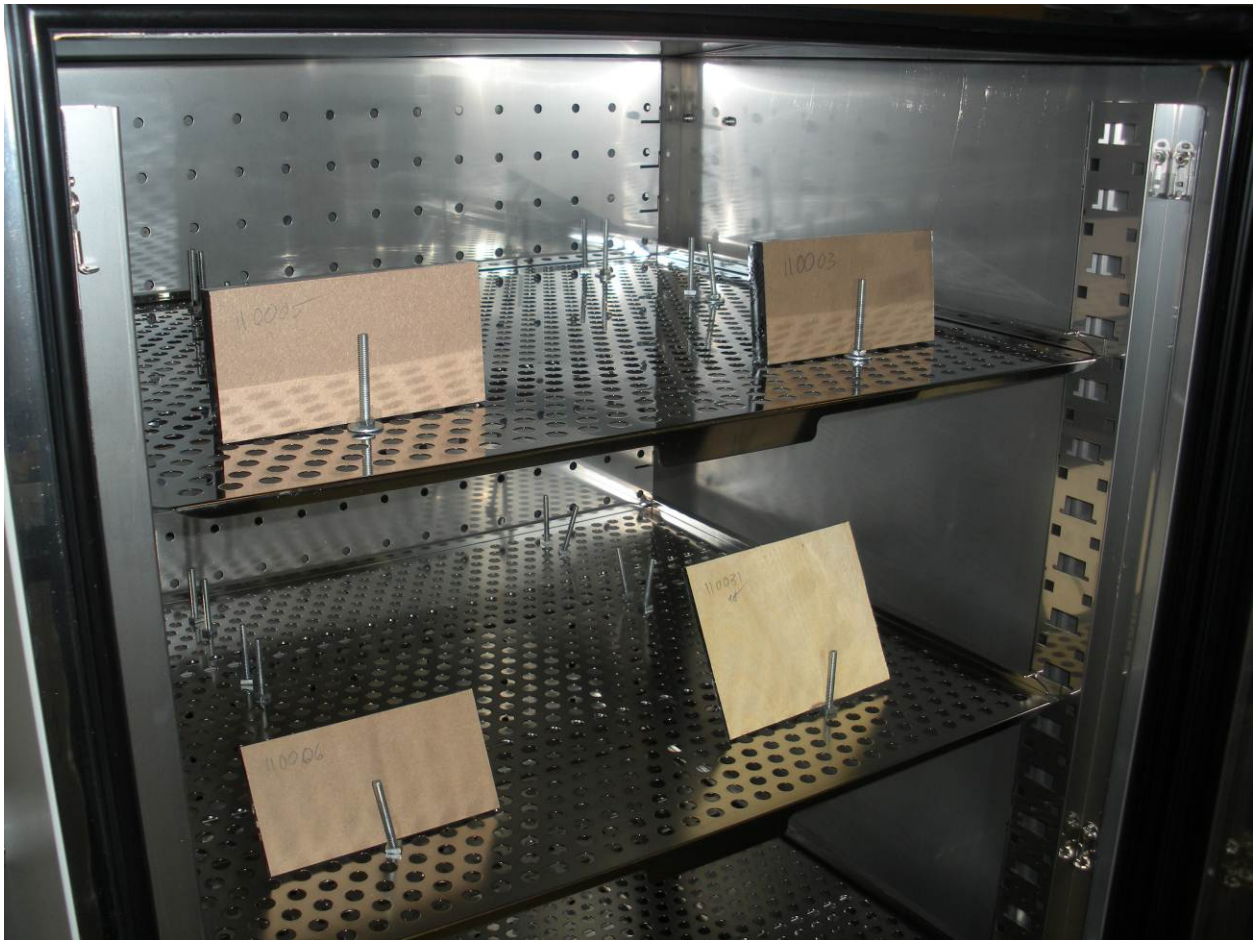


Figure 1.4
Taped Sample in Small Sampling Chamber

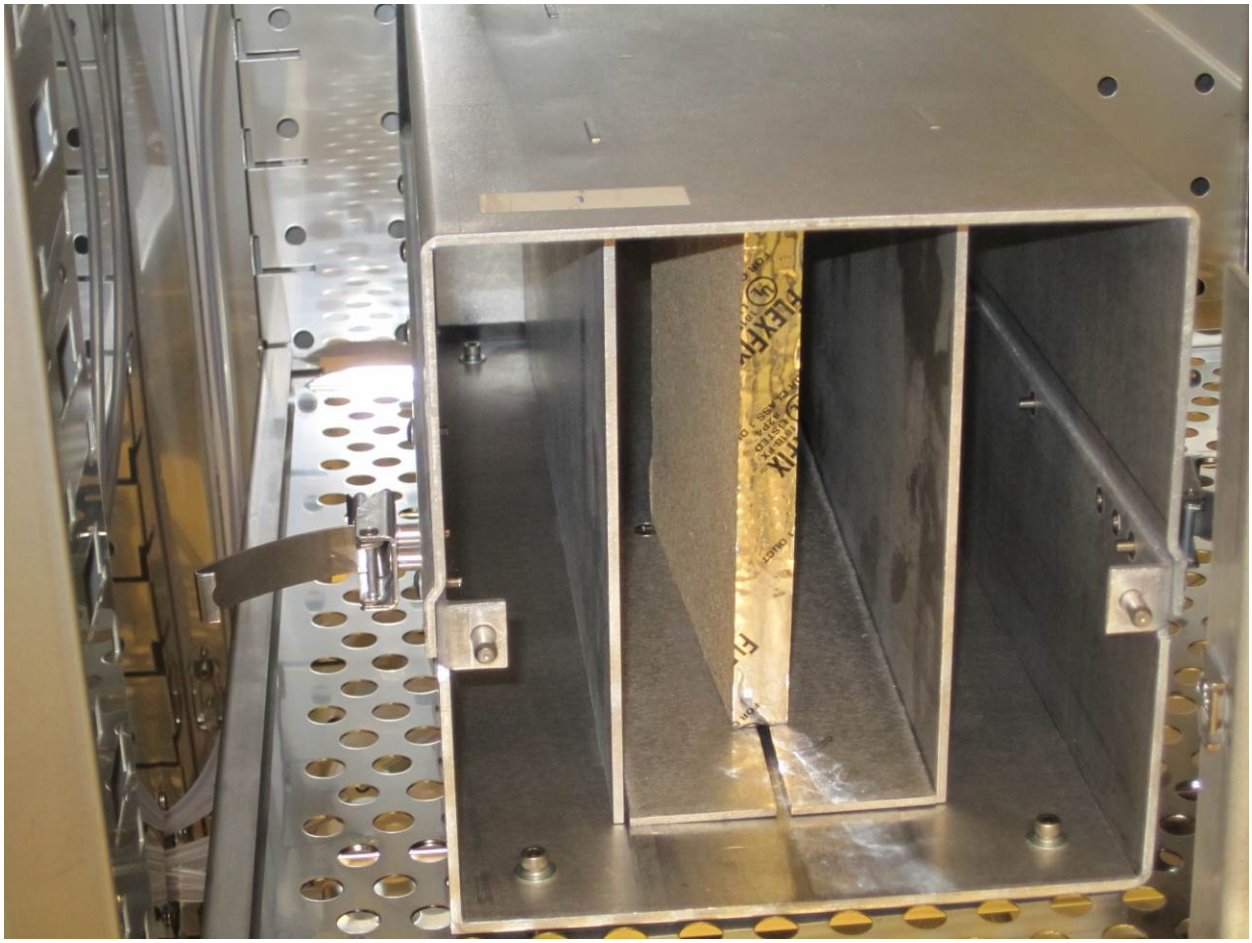


Figure 1.5
Environmental Chamber with Small Sampling Chambers Inside

APPENDIX A

Method Development for Sampling and Analysis of Formaldehyde in Composite Wood Products by High Performance Liquid Chromatography with UV Detection

California Environmental Protection Agency

Air Resources Board

Method Development for Sampling and Analysis of Formaldehyde in Composite Wood Products by High Performance Liquid Chromatography with UV Detection

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

6/21/10

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

The current method is for the analysis of formaldehyde in composite wood products by high performance liquid chromatography using ultra-violet detection (HPLC-UV). The air sampling procedure is based on ASTM D6007-02: *"Standard test method for determining formaldehyde concentrations in air from wood products using a small-scale chamber".* The air sampling uses 2,4-dinitrophenylhydrazine (DNPH) silica cartridges to capture the formaldehyde. Cartridges are eluted with acetonitrile and samples analyzed as the DNPH-derivative. The analytical procedure is based on ASTM D5197-03: *"Standard test method for determination of formaldehyde and other carbonyl compounds in air (active sampler methodology)"*.

2. SUMMARY OF METHOD DEVELOPMENT

A section of composite wood sized to meet the air flow and surface area requirements as defined in ASTM D6007-02 is placed in a small chamber within a larger environmentally controlled chamber. DNPH-silica cartridges are placed on a sampling line from the small chamber for 0.5 hours at a flow rate of 1.0 liters per minute (LPM). The samples are eluted with 10 mLs of acetonitrile (ACN). A liquid chromatograph with a ultra-violet detector at 360 nm is used for analysis.

In the method development stage of the composite wood testing, it was necessary to ascertain the following:

- **Instrument reproducibility.** The stability of the HPLC/UV system to maintain the calibration over the long term with control checks to monitor the system.
- **Standardization of board conditioning time.** The boards received may have been exposed to a variety of differing environmental conditions, including but not limited to areas of higher temperature and/or humidity. In order to have uniform testing conditions of the boards at a fixed temperature and humidity as well as to maximize sampling throughput an optimal conditioning time is determined. A minimal conditioning time of 2 hours is recommended in ASTM D6007-02.
- **Storage stability.** A series of boards are tested monthly to establish reproducibility of analysis and stability of the boards in long term storage.
- **Cross contamination study.** The potential effects of contamination from higher emitting boards that might be placed in the conditioning chamber with low emitting boards were evaluated.

3. INSTRUMENT REPRODUCIBILITY

The reproducibility of the instrument and analytical method was established by analyzing multiple 5.0 µL injections of H2CO-DNPH derivatized standard at three concentrations (low, mid, and high). The concentrations used were 0.05, 0.2, and 1.0 µg/mL (as free formaldehyde). The low standard was run seven times to give acquire additional data for determining the MDL/EQL. Mid and high concentrations were run five times for instrument reproducibility.

Table 1: Instrument reproducibility

	Low (0.05 µg/mL)	Med (0.2 µg/mL)	High (1.0 µg/mL)
Response	0.0666 0.0670 0.0662 0.0674 0.0664 0.0673 0.0662	0.2168 0.2164 0.2167 0.2158 0.2168	1.0217 1.0092 1.0073 1.0107 1.0086
Average	0.0667	0.2165	1.0115
Standard Deviation	0.0005	0.0004	0.0058

4. MINIMUM DETECTION LIMIT

The instrumental detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level standard (Table 1 above), the method detection limit (MDL) and the estimated quantitation limit (EQL) for formaldehyde is calculated by: MDL = 3.14*(std dev values), where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. The instrumental MDL is 0.02 µg/sample (0.002 µg/mL). EQL, defined as 5*MDL, is 0.10 µg/sample (0.01 µg/mL) based on a 10.0 mL extraction volume. The instrumental MDL and EQL corresponds to 0.6 ppb and 3.0 ppb, respectively.

5. COLLECTION AND EXTRACTION EFFICIENCY (RECOVERY)

Currently no extraction efficiencies have been made on the cartridge analysis. The dead volume capacity of the cartridge is 0.5 mL. The cartridge is washed with 10 mLs, a 20-fold rinse which removes all derivatized formaldehyde. The loading capacity of the cartridges is approximately 75 µg. The average formaldehyde background level of a DNPH cartridge is 0.012 µg/mL.

6. CONDITIONING TIME

The conditioning of the boards to a defined temperature and relative humidity is necessary before testing. The wood products come from across the state and may have been kept in varying environmental conditions, indoors or outdoors. When received in the laboratory the samples are in 9 mil plastic bags and kept at room temperature until ready for testing. The ASTM D6007-02 states a minimal conditioning time of 2 hours at 24 $\pm$ 3ºC and 50 $\pm$ 5% relative humidity. Currently both the sampling and conditioning chambers are set at 25 ºC and 50% relative humidity.

To optimize conditioning time necessary for testing, as well as optimizing for through-put in a production laboratory, samples were analyzed over a period of one to ten days.

Preliminary analysis was with boards identified as M37, a medium density fiber board. The board was a 4 x 8 foot panel with various cuts sent to the laboratory. The boards were tested prior to conditioning (day 0), then at 1, 2, 3, 4, 7, and 10 days. Figure 1 graphs the results over the 10 days of sampling. Averaging the data for a formaldehyde result to the whole panel (dotted line in graph) ranged from 237 ppb for day 1 to 220 ppb for day 7. The overall percent difference for the average between day 1 and day 7 is 7.2%. The percent difference between day 1 and day 7 for the individual boards averaged 6.6%, ranging from 0.6-13.2%. The difference between the 7 day and 10 day sampling averaged 6.2%, ranging from 2.6-9.6%.

A second set of low-emitting boards, designated as M41, were analyzed prior to conditioning (day 0) and at 1, 2, 3, 4, and 7 days. Figure 2 graphs the results for the 7 days of testing. The average formaldehyde concentration in M41 was 42 ppb at day 1 and 34 ppb at day 7 (dotted line in graph). The percent difference of the average is 19%, ranging individually 11.4-25.8%.

A third series of boards evaluated the conditioning time of deconstructed panels. Laminated particle board panels identified as PB 42, PB 43, PB 44, and PB 45 were cut in three sections labeled A, B, and C; within each of these were cut samples 1-9. Samples were paired, as example, A1/A2 where both sides were laminated, A3/A4, A5/A6, and A7/A8 were laminated on 1 side and planed to various depths, and A9 was split in half. The boards were sampled on day 1, 2, 3, and 7. PB 44 was only run for 3 days. The results of the sampling are shown in figures 3-6. The sample pairs of PB 42,43,44-(A,B,C)1/2, where both sides are laminated, was low, averaging 33, 30, and 38 ppb, respectively for the day 1 conditioning. After the 7 days, the formaldehyde concentrations were relatively unchanged. PB 45-(A,B,C)1/2 was much higher in concentration, averaging 111

ppb after day 1, and 101 ppb after day 7. The concentration of the formaldehyde for the pairs 3/4, 5/6, and 7/8 varied depending on the board and the location of the sample within the board. The change in concentration between day 1 and day 7 conditioning ranged from 1.6-21% for all the boards. The concentration for the split boards, 9, averaged 211-236 ppb at day 1 and 152-171 ppb at day 7 (PB 44-(A,B,C)9 only had 3 days, with 220 ppb. These boards had the largest difference in concentrations between the day 1 and day 7 ranging 24-27% for the 7 days.

Concentrations of formaldehyde can vary greatly within a given board, ranging 3-16%. The concentration of formaldehyde between similar boards can also vary considerably from 1 to 15%. These variations are at least comparable to what is observed in concentrations from day 1 and day 7, ranging 5-14%. The variation is a bit higher for the higher emitting 9 boards averaging about 20% between day 1 and day 7. From these results a one day conditioning time should be appropriate for the sampling analysis.

The wide range of formaldehyde values may also be a result of where in the 4 x 8 panel the smaller samples are taken. Analysis of a series of HWPW boards early in the method development shows a wide variation in the concentration of formaldehyde across the boards as well as between boards. Figure 7 shows the layout of the boards cut for the analysis. The average formaldehyde concentration for the boards ranged from 48.3 ppb to 78.5 ppb. These are boards that were purchased at the same time, same location. The variation within a board ranges to 30%. What is observed is that formaldehyde concentration can vary dramatically within and between boards from the same processing lot.

The conditioning time of overnight or 18-24 hours for the boards for analysis was chosen to maximize throughput of samples for a production lab. A 2 hour conditioning time as mentioned in the ASTM would be too short to be efficient in production. A seven day conditioning time is prohibitive time-wise for analysis in a efficient manner. From the data of the boards a greater variation is observed within boards than between a day 1 and day 7 analysis.

7. CROSS CONTAMINATION STUDY

A study looked at the potential of contamination of lower emitting boards while being conditioned in the presence of higher emitting boards. For this study board M39 which averaged 307 ppb (range 262-380 ppb) is used as the high emitting contaminating board and M40 the lower emitting board exposed.
Table 2 shows the results of the testing and the conditions used. A sampling of the conditioning chamber was made prior to the analysis of the boards. The

background concentration of formaldehyde was 69 ppb with the boards in the chamber. Another sampling an hour after the boards were removed another showed the concentration had dropped to 11 ppb.

Table 2: Cross contamination study.

Board	Formaldehyde, ppb	Comments
M40 Edge 1 2 3	21.5 20.2 19.6	The edge samples were conditioned 24 hours.
M40-B1 M40-D2 M40-F4	17.1 17.5 16.7	Samples conditioned for 24 hours.
M40-E2 M40-E3 M40-E4	29.6 29.6 28.8	24 hour conditioning in the presence of 9 high emitting M39 boards.

Another set of M40 boards were placed between M39 boards in a 9 mil plastic bag for a week prior to testing. The M40 boards were then removed and conditioned 24 hours for testing. The boards were placed back in the conditioning chamber for another 24 hours and tested. Table 3 shows the results of the testing of these boards.

Table 3: Cross contamination study, part 2.

Boards	Formaldehyde, ppb	Comments
M40-B3 M40-D3 M40-F1	57.4 58.9 55.2	One week storage in presence of high emitting boards.
M40-B3 M40-D3 M40-F1	44.0 49.2 43.8	Additional 24 hours conditioning.

A third set of contamination testing was done where edge piece of M40 were received “boxed” in with M39 pieces to maximize exposure to the higher boards. Another set of M40 boards were received alternating between M39 boards. The samples were conditioned 24 hours and tested. The results for these samples are reported in Table 4.

Table 4: Cross contamination study, part 3.

Boards	Formaldehyde, ppb	Comments
M40-Edge1	137.6	Edge pieces "boxed" in with M39 boards.
2	122.6	
3	120.2	
M40-B3	85.2	M40 boards placed between M39 boards.
M40-D4	83.7	
M40-F2	76.0	

The baseline concentration of formaldehyde for M40 boards averaged 17.3 ppb after the 24 hour conditioning. Concentrations were higher by over 50% when the boards were exposed to the higher emitting boards while in the conditioning chamber. The formaldehyde concentration is higher for any of the boards that were exposed for a longer period of time or placed in closer proximity with the high boards. The data does indicate that the potential of cross contamination may be an issue with samples for enforcement if packaged together. There will be multiple samples from the same source or product; the boards will be packaged individually, which should minimize any storage contamination. The lab will attempt to condition samples from the same product or batch and any potentially high emitting products will be conditioned with similar ones.

8. Storage Stability

A series of samples cut from boards identified as M35 and PB36 were analyzed over a 9 month period to see how the boards held up in long term storage. A set of 3 boards from each panel was brought in by Enforcement periodically over the time for analysis. The results of the analysis are shown in Figure 8. Over the 9 month study the concentration of formaldehyde in M35 dropped by 28%, going from 143 ppb to 103 ppb. The concentration in PB36 showed a similar loss going from 158 ppb to 106 ppb, a loss of 33%. The analysis showed the boards to be fairly stable for about 4 months before dropping. What the study suggests is that boards left at room temperature for extended length of time (more than 4 months) may result in lower formaldehyde concentrations when tested.

9. Safety

The procedures discussed here do not address all of the safety concerns associated with chemical analysis or the mechanical preparation of the boards. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Figure 1: Conditioning time analysis of board M37.

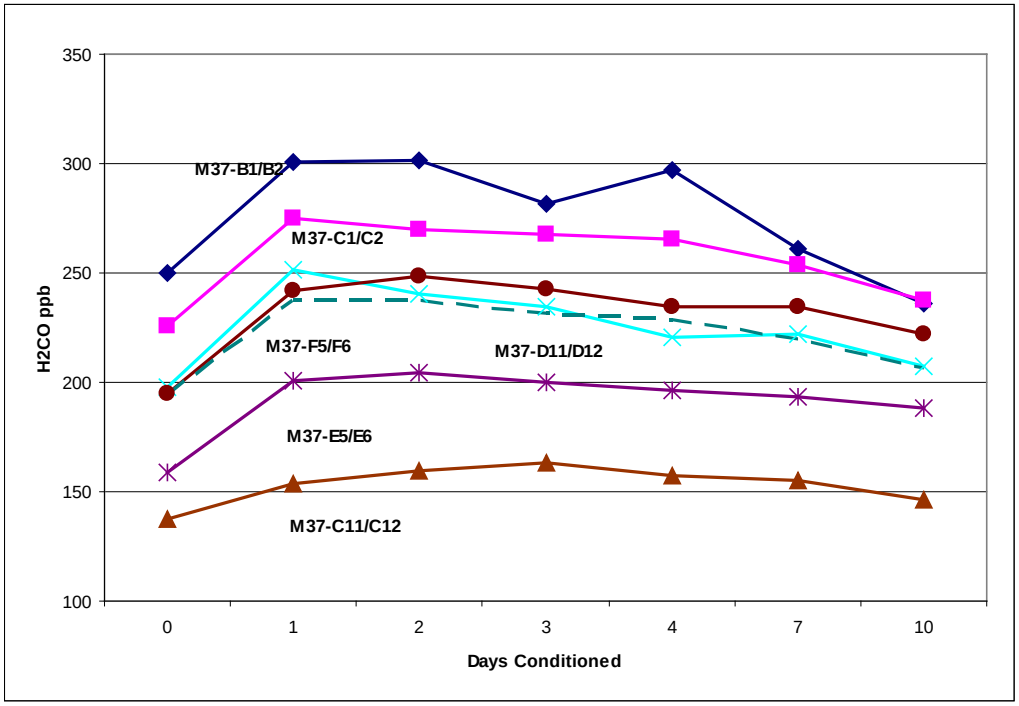


Figure 2: Conditioning time analysis of board M41.

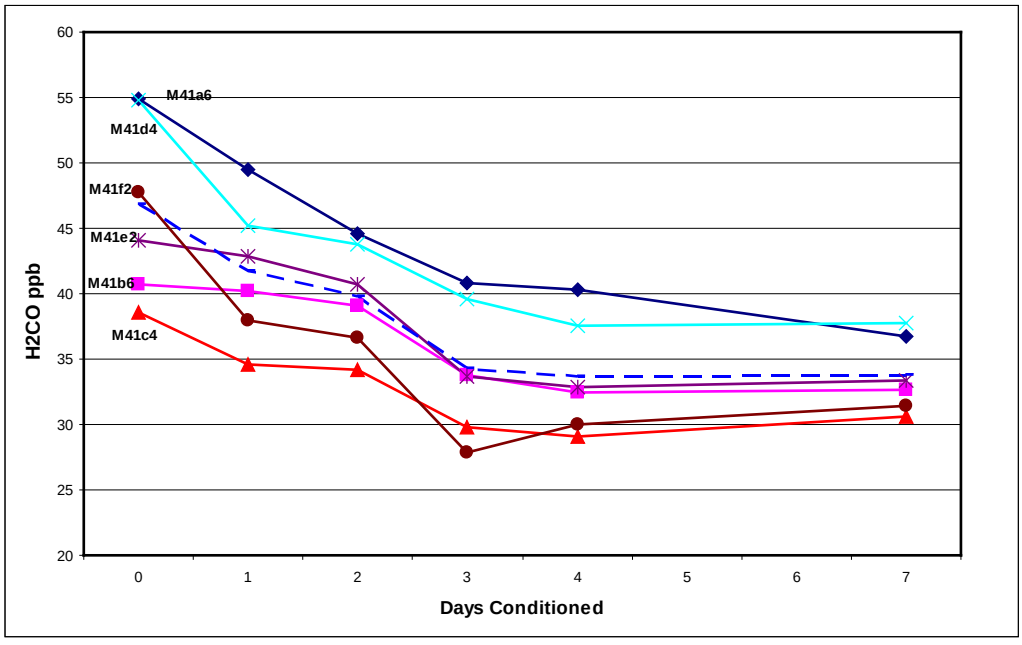


Figure 3: Conditioning time analysis of board PB 42.

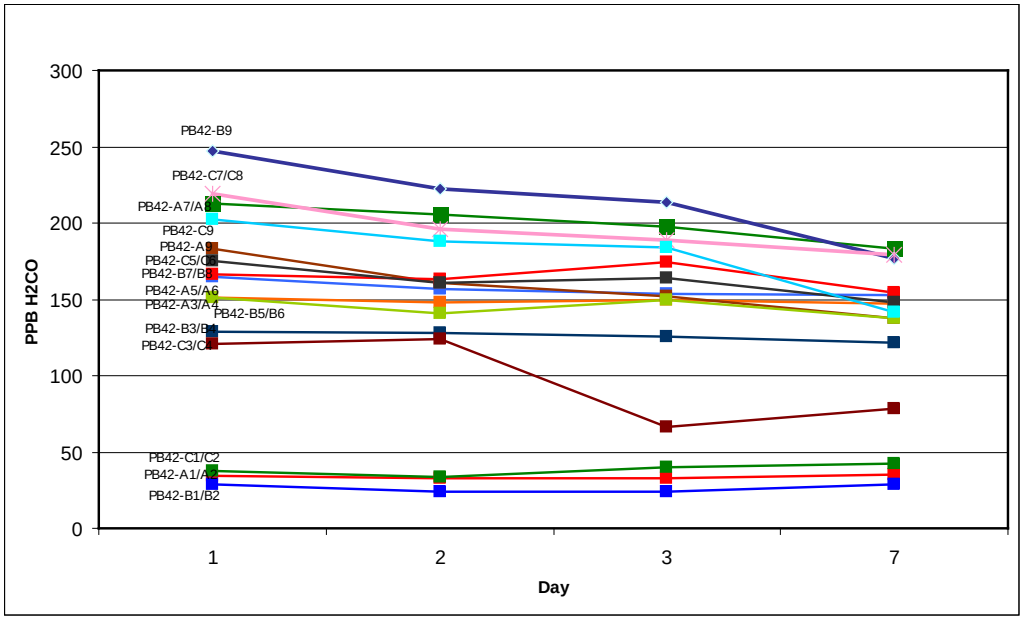


Figure 4: Conditioning time analysis of board PB 43.

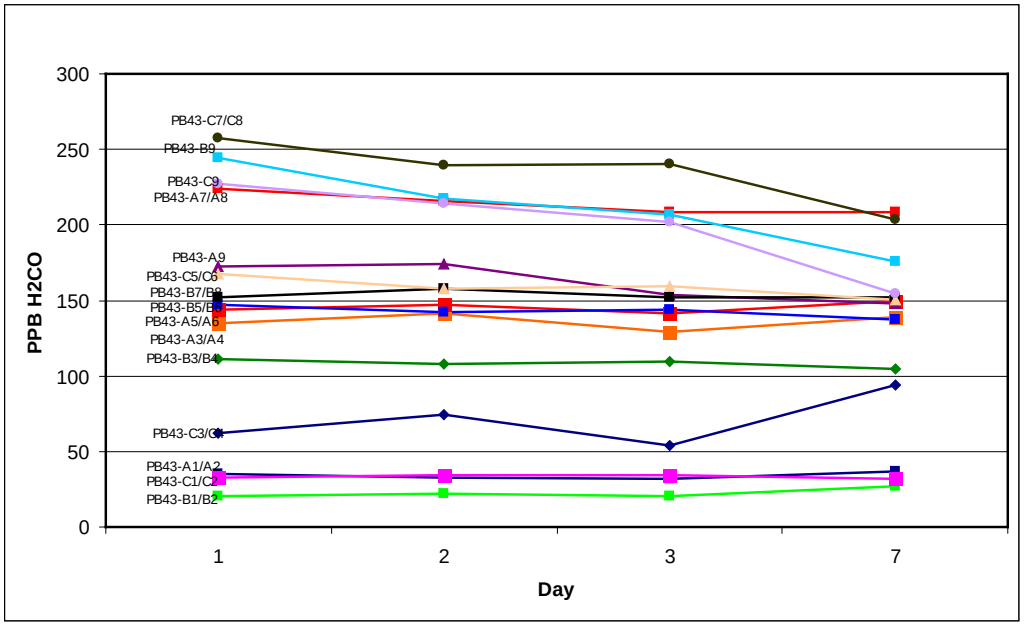


Figure 5: Conditioning time analysis of board PB 44.

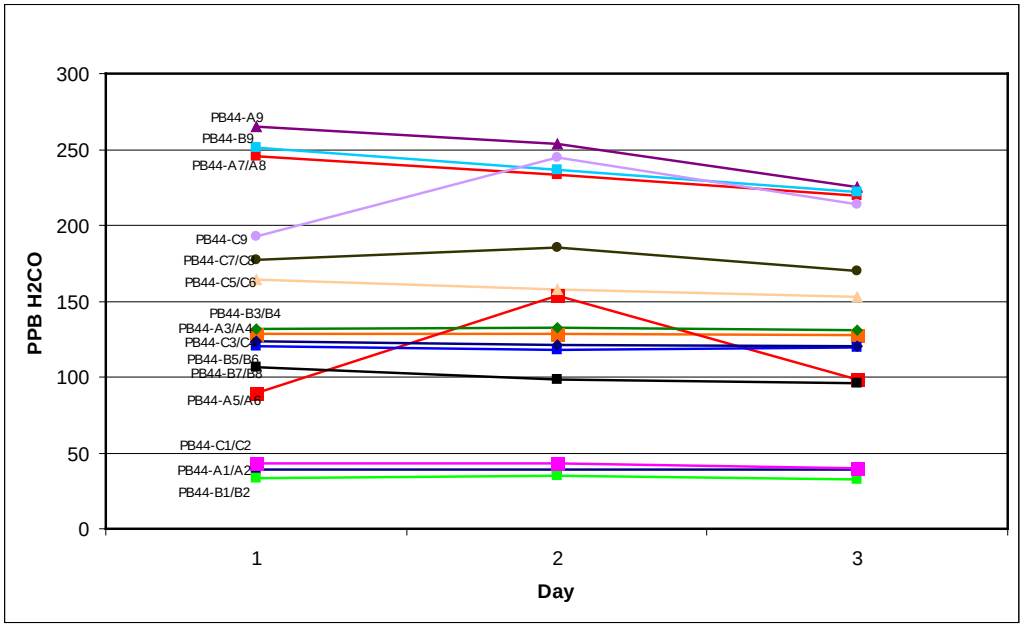


Figure 6: Conditioning time analysis of board PB 45.

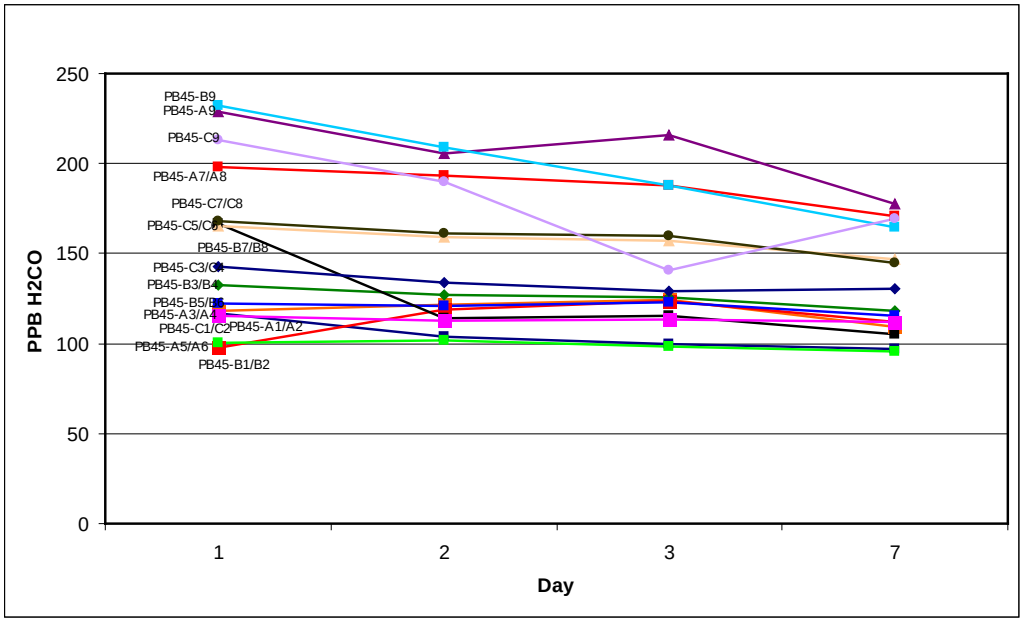
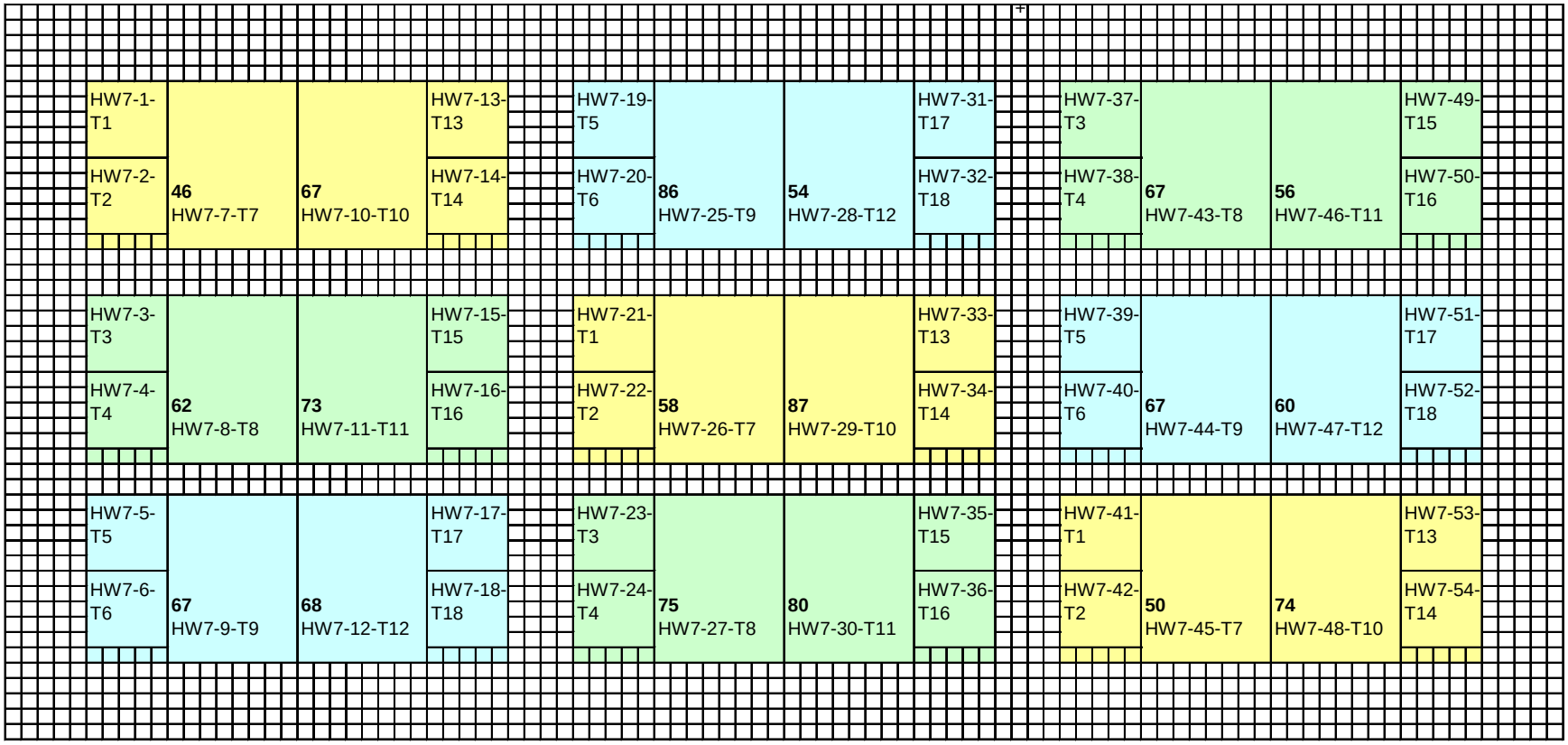
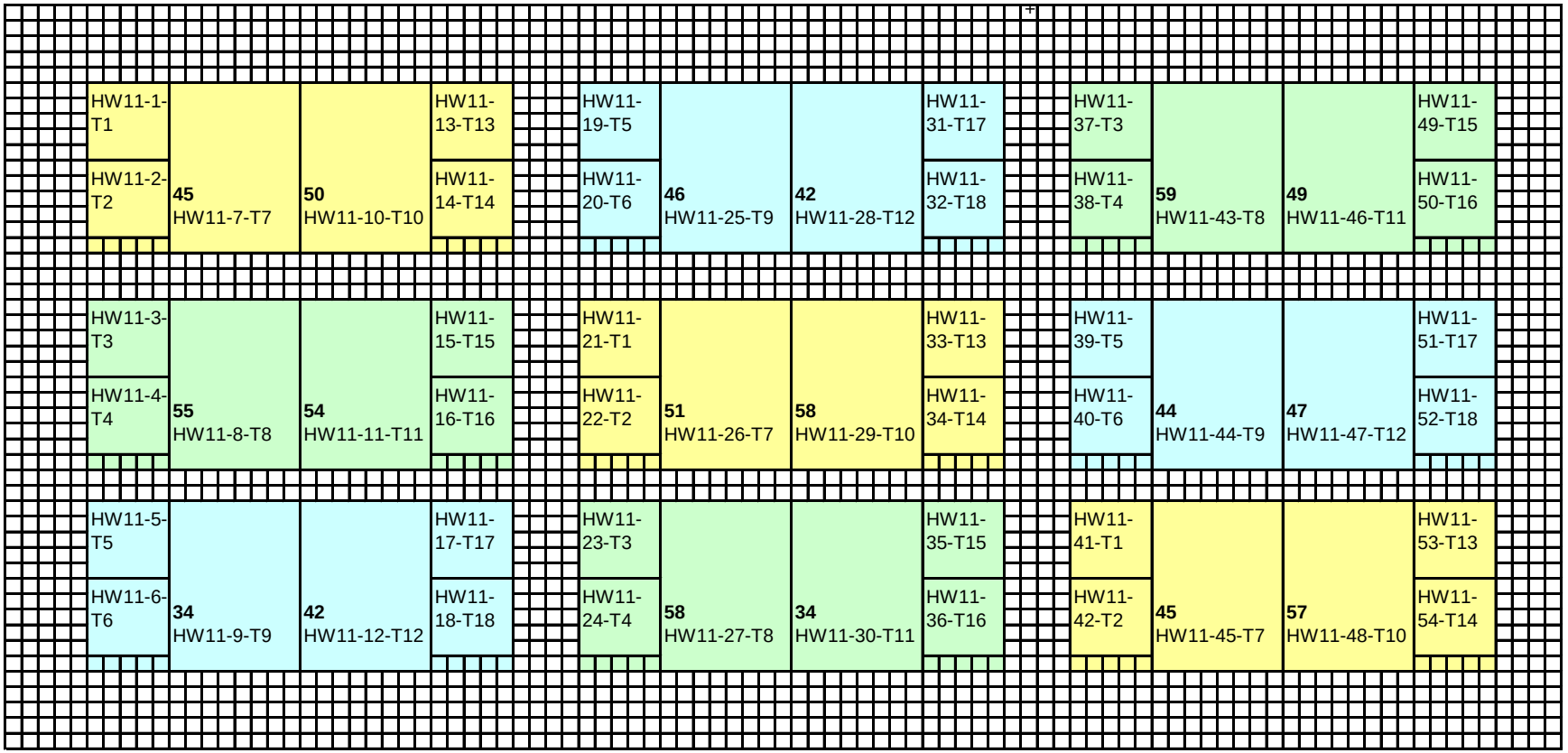


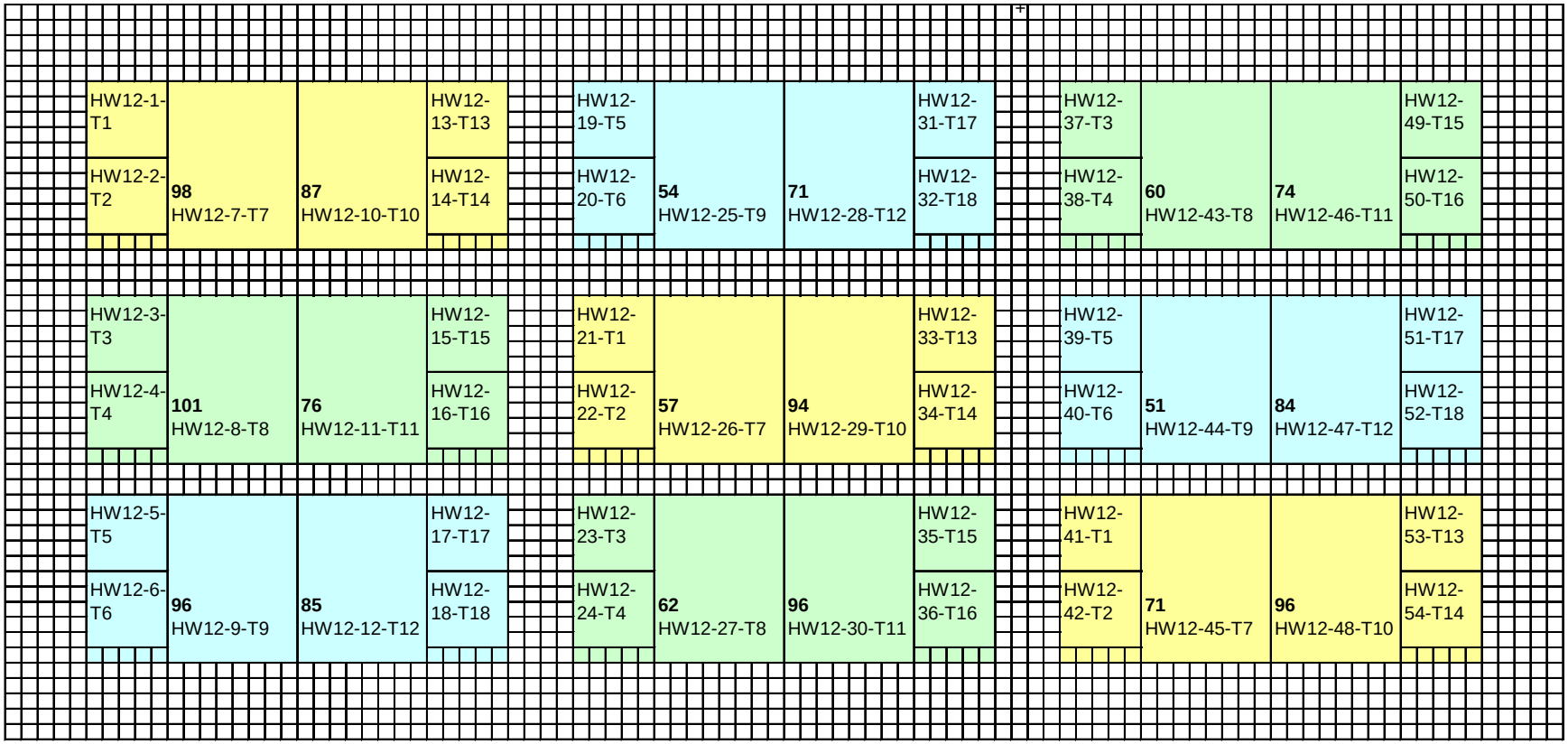
Figure 7: Whole board layout, early testing boards.



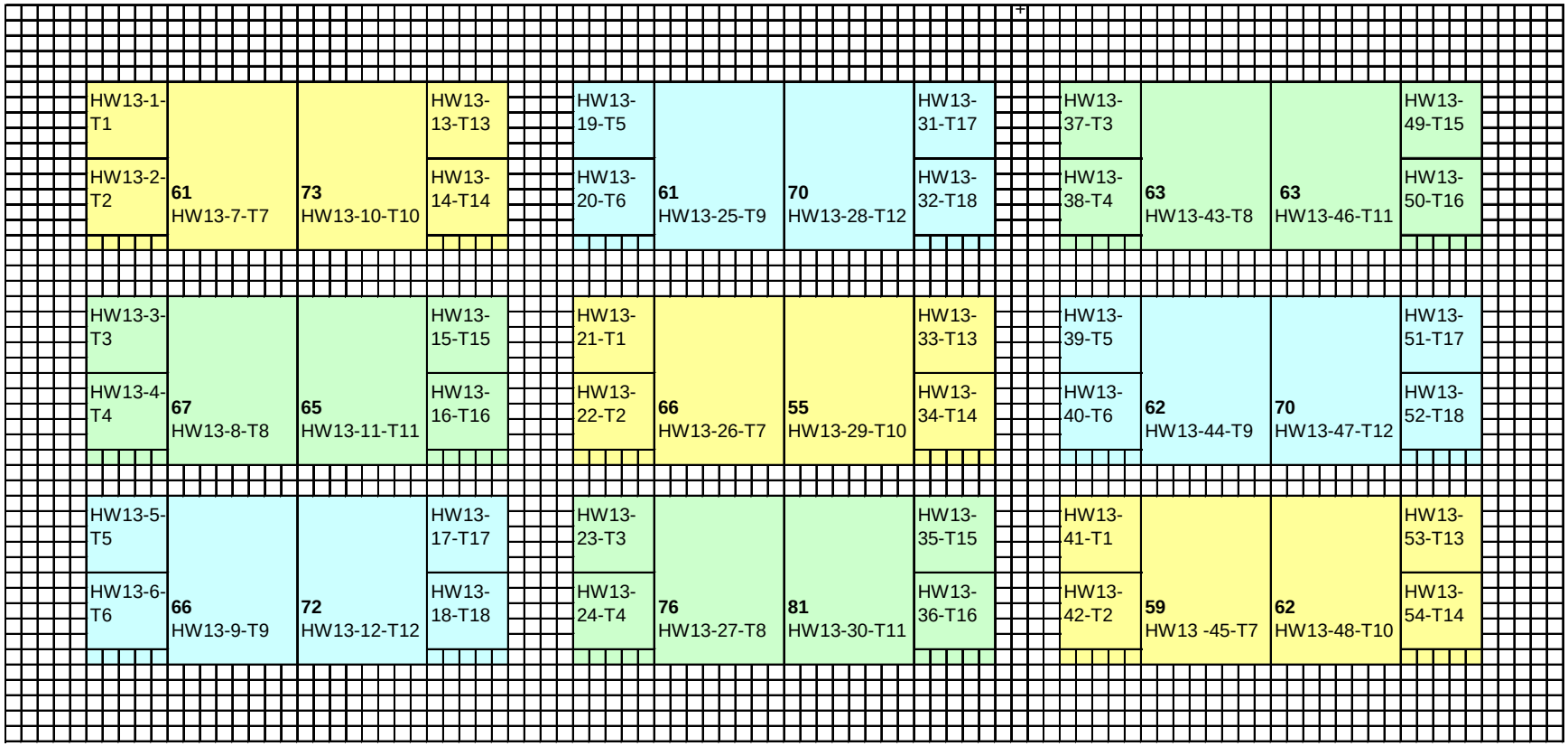
Overall average: 66.5 ppb; range 46-86 ppb.



Overall average: 48.3 ppb; range 34-59 ppb.



Overall average: 78.5 ppb; range 51-101 ppb.



Overall average: 66.2 ppb; range 59-81 ppb.

Figure 8: Storage stability study M35 and PB36.