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# Project Summary

# Characterization of Mercury Emissions at a Chlor-Alkali Plant

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**Current estimates indicate that up to 160 short tons (146 Mg) of mercury (Hg) are consumed by the chlor-alkali industry each year. Very little quantitative information is currently available, however, on the actual Hg losses from these facilities. The Hg cell building roof vent is considered to be the most significant potential emission point in chlor-alkali plants, especially when the cells are opened for maintenance. Because of their potential importance, chlor-alkali plants have been identified as needing more accurate measurements of Hg emissions. To obtain a better understanding of the fate of Hg within their manufacturing process, the Olin Corporation voluntarily agreed to cooperate with the U.S. Environmental Protection Agency (EPA) in a comprehensive study of Hg emissions from their Augusta, GA, facility, in collaboration with other members of the Chlorine Institute representing the active chlor-alkali plants in the United States.**

**To investigate the Hg releases from the Olin chlor-alkali facility, the EPA's National Risk Management Research Laboratory, Air Pollution Prevention and Control Division (EPA-APPCD) in Research Triangle Park, NC, organized a special study involving multiple organizations and personnel. However, only the research conducted by EPA-APPCD involving roof vent monitoring and air flow studies conducted in the Olin cell building is discussed in this report.**

**The overall objective of the cell building roof vent monitoring was to determine the total elemental mercury ($Hg^0$) mass flux under a range of typical wintertime meteorological conditions, including both normal operation of the cell building as well as routine maintenance of Hg cells and decomposers. Secondary objectives of the research were to perform an air flow mass balance for the building and to compare various Hg monitoring methods under a variety of sampling conditions. Both objectives were met during the February 2000 field sampling campaign, which showed an average $Hg^0$ emission rate of 0.36 g/min from the roof ventilator as determined over the 9-day monitoring period.**

***This Project Summary was developed by the National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

Current estimates indicate that up to 160 short tons (146 Mg) of Hg are consumed by the chlor-alkali industry each year. Very little quantitative information is currently available, however, on the actual Hg losses from these facilities. The most significant potential emission point in chlor-alkali plants is thought to be the Hg cell building roof vent, especially when the cells are opened for maintenance. Because of their potential importance, chlor-alkali plants have been identified as needing more accurate measurements of Hg emissions.

To better understand the fate of Hg within their manufacturing process, the Olin Corporation voluntarily agreed to cooperate with the U.S. EPA in a comprehensive study of the Hg emissions from their Augusta, GA, facility. This effort was conducted in collaboration with other members of the Chlorine Institute representing active chlor-alkali plants in the United States. Chlorine Institute members have committed to reduce overall $Hg^0$ consumption by 50% (from 1990-95 levels) by the year 2005.

To investigate Hg releases from the Olin chlor-alkali facility, EPA-APPCD in Research Triangle Park, NC, organized a special study involving multiple organizations and personnel, with each major aspect of the study addressed by a separate principal investigator based on the individual area of expertise. However, only the research conducted by EPA-APPCD involving roof vent monitoring and air flow studies conducted in the Olin cell building is discussed in this report.

The overall objective of the field sampling program was to determine the total Hg release from the plant using parallel sampling approaches under typical wintertime meteorological conditions, including both normal operation of the cell building as well as routine maintenance of the electrolytic cells and decomposers. Secondary objectives of the research were to perform an air flow mass balance for the building and to compare various Hg monitoring methods under a variety of sampling conditions. Both objectives were met.

## Experimental Procedures

A combination of measurement methods was used for data collection at the Olin chlor-alkali facility because parallel approaches reduce the overall uncertainty of the estimates and provide useful constraints on measurement accuracy. The methods used were roof vent monitoring, tracer gas analyses, and manual velocity measurements. Each approach is summarized below.

### *Roof Vent Monitoring*

For this study, long-path instruments were used in lieu of extractive sampling using a manifold system to allow measurements to be made on a spatially integrated basis and to eliminate problems with representative sampling typical of point measurements. The primary instrumentation used in roof vent monitoring consisted of:

- Ultraviolet differential optical absorption spectrometer (UV-DOAS) for measurement of gas-phase $Hg^0$ concentrations;
- Optical scintillometer (anemometer) for determination of air velocity; and
- Fourier transform infrared (FTIR) spectrometer for measurement of sulfur hexafluoride ($SF_6$) tracer gas concentrations.

The long-path instruments were mounted on wooden sampling platforms erected at the east and west ends of the cell building roof vent. Except for the optical anemometer, the signals from all instruments were directed by optical fiber to computerized data acquisition systems located in a trailer parked directly beneath the roof ventilator at the west end of the cell building. For the optical anemometer, the microprocessor and associated laptop computer used for data acquisition were located on the sampling platform itself. Each instrument was set up and calibrated according to the operating manual and/or approved Quality Assurance Project Plan for the study. A Met One Model 062 temperature controller and meteorological station and associated laptop computer were also installed on the west sampling platform to monitor air temperature and relative humidity.

### *Tracer Gas Analyses*

In addition to the roof ventilator, $SF_6$ tracer gas concentrations were also determined in various cell building openings using manually operated Tedlar® bag samplers and a closed-cell Nicolet Magna 760 FTIR spectrometer to analyze the gas samples. Manual bag sampling was accomplished by drawing sample air into the Tedlar® bag over a nominal 24-hr period to obtain levels of $SF_6$ released along the open areas on the basement and cell room floors. Multiple sampling locations were used to obtain a distribution of tracer concentrations at key locations in and around the cell building.

### *Manual Velocity Measurements*

Manual anemometer measurements were performed to evaluate air velocity in the roof vent as an independent check on the optical anemometer as well as to determine the air velocity in various building openings to perform an overall flow balance for the cell building. A hand-held Davis Instruments TurboMeter® propeller anemometer was eventually used for manual velocity measurements. The propeller anemometer was also compared with a hand-held hot wire instrument during selected measurement periods. Propeller anemometer readings were obtained both in the roof ventilator and in cell building openings. For the vent measurements, readings were made at selected locations across the width of the ventilator throat both at the same height as the optical anemometer measurement path and also ~ 20 cm below the throat exit. For the various building openings, anemometer readings were obtained at the approximate geometric center of each opening.

### *Data Reduction and Analysis*

In the roof vent monitoring, $Hg^0$ concentrations measured by the UV-DOAS were plotted as a chronology, and summary statistics were calculated for each 24-hr period. In addition, a second data set consisting of 1-min averages was downloaded for emission rate calculations. A similar calculation procedure was also used for analysis of the optical anemometer results, with an appropriate temperature and pressure correction applied to the optical anemometer results prior to combination with the DOAS data.

The roof vent FTIR measurements generated individual FTIR spectra (64 separate scans every 5 min), and the individual spectra were analyzed by post-processing to determine the concentration of $SF_6$ and other gases of interest. Analysis of the roof vent FTIR data disclosed that the FTIR detector was optically saturated due to poor instrument setup in the field. Because of this detector saturation, the response of the instrument was highly non-linear, making quantitative interpretation of the spectra impossible. Results of manual tracer gas measurements using sample collection into a Tedlar® bag with FTIR measurement are also reported.

### *Manual Velocity Measurements and Flow Balance Calculations*

For the manual velocity measurements in the roof vent, data from a field notebook were plotted with respect to the physical boundaries of the ventilator throat and averages calculated for each set of observations. These averages were then compared to similar values obtained from the optical anemometer data for the same time period. In addition, the data points obtained at both edges of the ventilator were extrapolated by linear regression to the point of zero velocity. These locations were then used to determine the effective flow area of the vent for the emission rate calculations by trigonometric analysis.

For the cell building openings, manual velocity data were multiplied by the cross-sectional area of each opening and combined with the total volumetric flow of the electrically powered ventilation fans to obtain the total air entering the cell building at ambient temperature and pressure. Similar calculations were also performed for the roof vent using the applicable optical anemometer data for the same measurement period and the effective flow area as described earlier. A flow balance for the entire building was then calculated using three techniques:

- The total flow values obtained for the building inlets and roof vent were corrected to standard temperature and pressure conditions, and the two values were compared on a volumetric basis.
- The mass of air entering and leaving the building was calculated, and a similar comparison was made.
- A method developed by the Occidental Chemical Corporation as part of their direct mass balance modeling effort was also used.

## Results

Continuous monitoring was conducted at the roof vent for $Hg^0$ concentration and air velocity from which 1-min average $Hg^0$ emission rates were calculated. In addition, continuous monitoring was also attempted for $SF_6$ tracer gas as a separate measure of the air flow rate from the vent.

### *$Hg^0$ Monitoring Results*

Raw 30-second averages generated by the UV-DOAS were reduced to produce daily plots of $Hg^0$ monitoring results as well as summary statistics calculated for each day. The measured $Hg^0$ concentration varied over an order of magnitude from ~ 73 to 7.3 mg/m$^3$. The overall average for the study period was 24 mg/m$^3$ of $Hg^0$. Similar plots and statistics were also created from analysis of the 1-min optical anemometer data. The air velocities measured by the optical anemometer varied from 0.24 to 1.5 m/s with an overall average for the monitoring period of 0.93 m/s.

The 1-min average $Hg^0$ emission rates calculated from the monitoring data were plotted for the 9-day study period with summary statistics calculated from these data shown in Table 1. As indicated by Table 1, the $Hg^0$ emission rate varied over about 2 orders of magnitude from 0.08 to 1.22 g/min. An overall average for the monitoring period of 0.36 g/min was also determined.

### *Tracer Gas Results*

Tracer gas results include both roof vent monitoring conducted using the open-path FTIR and manual bag sampling conducted in various building openings.

- Roof Vent Monitoring: Results of the FTIR measurements at the roof vent were found to be unusable for determination of volumetric air flow due to optical saturation of the detector. However, three common greenhouse gases (carbon monoxide, nitrous oxide, and methane) were found in measurable quantities in the roof vent effluent; exact source(s) of these gases could not be determined from available data.

**Table 1.** Summary of Calculated $Hg^0$ Emission Rates

| | $Hg^0$ Emission Rate (g/min) | | | | | |
|---|---|---|---|---|---|---|
| Date | Maximum | Minimum | Mean | Standard Deviation | Number of Observations (n)[a] | Total Daily Emissions (g/day)[b] |
| 2/17/00 | 0.82 | 0.24 | 0.38 | 0.076 | 747 | N/A |
| 2/18/00 | 0.58 | 0.15 | 0.33 | 0.075 | 1339 | 481 |
| 2/19/00 | 0.64 | 0.10 | 0.26 | 0.085 | 1364 | 370 |
| 2/20/00 | 1.22 | 0.13 | 0.35 | 0.19 | 1368 | 510 |
| 2/21/00 | 0.88 | 0.12 | 0.27 | 0.11 | 1311 | 387 |
| 2/22/00 | 0.69 | 0.12 | 0.31 | 0.080 | 1340 | 453 |
| 2/23/00 | 0.65 | 0.08 | 0.30 | 0.090 | 1300 | 438 |
| 2/24/00 | 0.83 | 0.24 | 0.46 | 0.12 | 1130 | 662 |
| 2/25/00 | 0.87 | 0.33 | 0.58 | 0.11 | 450 | N/A |
| Mean | 0.80 | 0.17 | 0.36 | ___ | ___ | 472 |

[a] Dimensionless.
[b] Sum of measured 1-min values adjusted to a standard day of 1440 min to account for missing data. Rounded to three significant figures.

**Table 2.** Results of Air Flow Balance Calculations for the Olin Cell Building[a]

| Date | Volume Balance (% Closure) | Mass Balance (% Closure) | OxyChem DMB Results[b] (% Closure) | Mass Balance % Difference |
|---|---|---|---|---|
| 2/24/00 | 82 | 82 | 79 | 2.9 |
| 2/25/00 | 100 | 99 | 100 | -0.9 |

[a] Rounded to two significant figures.
[b] Occidental Chemical Corporation direct mass balance (DMB) method as provided by Michael Shaffer.

- Manual Bag Sampling: The average concentration of $SF_6$ for the low release days was just above the detection limit for the instrumentation. The average concentration for the high release days was below the method detection limit. Although the concentrations of $SF_6$ measured on February 20, 2000, were less than 5 times the method detection limit, the concentrations detected were significantly higher, on average, than any other sampling day, suggesting minimal Hg transport during this sampling period.

### *Air Flow Study Results*

Air flow was determined for the cell building using manual velocity measurements, with associated air flow balance calculations.

- Roof Vent Monitoring: Air velocity measurements, performed manually using a propellor anemometer as well as an optical anemometer in the same time period, showed that the average air velocities determined by the two methods were within $\pm$ 10%, quite acceptable considering the differences in measurement technique. Based upon these measurements, the measurement path of the optical anemometer was considered to be located at a point representative of the average velocity and thus appropriate for use in the emission rate calculations.
- Air Flow Balance: The results of the cell building flow balance calculations are shown in Table 2 for the three methods used. Unusually good closure was obtained in each of the three flow balance calculations performed, and the three methods also correlate well with each other. The high degree of closure of these flow balances lends further credibility to the air velocity measurements made by the optical anemometer in the roof

ventilator to adequately characterize the air flow from the cell building.

## Discussion

No specific pattern could be discerned from the daily plots of the $Hg^0$ emission rate determined from the roof vent monitoring conducted in this study. An attempt was made to correlate various episodic events where the emission rate rose for a period of time and then dropped back to some nominal level with either process operation or maintenance events using plant records, but this analysis failed to find any useful association. Although the concentration of $Hg^0$ was found to be relatively homogeneous across the lateral dimension of the roof vent, such was found not to be the case along the longitudinal dimension. The differences observed constitute yet another argument supporting spatially integrated readings in lieu of point sampling with a manifold system. Another observation made during the study involved the impact of the high electromagnetic field on instrument operation. For future studies of this type, optical modems and cables should be used for the optical anemometer to allow logging of the data at a remote location to reduce the amount of lost data and make troubleshooting much easier for the operator.

## Conclusions and Recommendations

Conclusions drawn from the use of the equipment, methods, and data analysis procedures to determine the total $Hg^0$ release and volumetric air flow from the Olin chlor-alkali cell building are presented below.

- $Hg^0$ concentrations measured by the UV-DOAS varied over an order of magnitude from ~73 to 7.3 mg/m³. The overall average for the 9-day study period was 24 mg $Hg^0$/m³.
- $Hg^0$ emission rates measured in the roof ventilator varied from 0.08 to 1.2 g/min. An overall average for the monitoring period of 0.36 g/min was calculated.
- A comparison between the concentration of $Hg^0$ measured by the UV-DOAS and similar measurements conducted using a hand-held instrument across the width of the roof vent showed that the $Hg^0$ concentrations were relatively consistent across the vent and compare reasonably well to the average concentration obtained with the UV-DOAS.
- Comparison of roof vent monitoring data obtained by the UV-DOAS and point measurements made using a Tekran Model 2537A automated Hg analyzer at the entrance to the vent exhibited a relatively high degree of scatter with only about 63% of the variance explained by linear regression. The data do, however, show comparable trends in concentration of $Hg^0$ with time. Scatter in the data is potentially due to a combination of factors including differences in analysis method, non-representative sampling, and sampling line losses.
- The $SF_6$ tracer gas results obtained using the long-path FTIR in the roof vent were found to be unusable for the purpose of determining volumetric air flow due to optical saturation of the detector. Results of the 24-hr, time-integrated bag sampling showed $SF_6$ tracer gas concentrations either at or below the instrumental detection limit except for one sampling period on February 20, 2000.
- The average roof vent air velocity measured by a hand-held anemometer as compared to that obtained by the optical anemometer showed that the two methods agreed within ± 10%.
- Very good closure (79 to 100%) was obtained for each of the three air flow balance calculations performed for the cell building. The three methods also correlate well with each other, and the high degree of closure of these flow balances lends further credibility to the air velocity measurements made by the optical anemometer in the roof ventilator.
- No specific pattern could be discerned from daily plots of $Hg^0$ emission rates. Various episodic events were observed during the study where the emission rate rose for a period of time, then dropped back to some nominal level which could not be correlated to either process operation or maintenance events using plant records.
- Although the concentration of $Hg^0$ was found to be relatively homogeneous across the lateral dimension of the roof vent, concentrations of $Hg^0$ were not consistent along the length of the ventilator.

On the basis of the results obtained for this study, the following recommendations are applicable:

- This study was conducted at one chlor-alkali plant, in a time window of approximately 2 weeks. For more thorough characterizations of operations in this industry, extended monitoring at a single location and/or monitoring at more plants is recommended to better characterize maintenance events and other operational transients.
- Roof vent instrumentation may be a useful tool for process monitoring in some facilities to identify problems in the operation of the cells that may require corrective action. The long-term suitability of these instruments must be established, however, by additional on-site evaluations.
- The high electromagnetic field at the facility has an adverse effect upon instrument operation. For future studies of this type, optical modems and cables should be used to allow logging of data at a remote location to reduce data loss and make troubleshooting much easier for the operator.
- The variation in $Hg^0$ concentrations along the length of the ventilator vs. the homogeneous values observed for $Hg^0$ across the lateral dimension argue strongly for the use of spatially integrated measurements rather than point sampling with a manifold system.
- Roof vent tracer gas data from this study were not usable. Since the use of a tracer is well accepted for determining flow rates, the possibility of use of tracer gas for future flow measurement studies should not be abandoned. Greater care is needed, however, to verify proper instrument setup and operation.
- Different tracer gases such as $CF_4$ could be used using UV-DOAS, making concurrent sampling and analysis of Hg and tracer gas highly desirable. Additional research is also recommended to determine the best way to diffuse the tracer gas into the cell room.
- Additional measurements of non-elemental (oxidized) forms of Hg should also be conducted to determine their overall environmental significance.

*__John S. Kinsey__ is also the EPA Project Officer (see below).*

*The complete report, entitled "Characterization of Mercury Emissions at a Chlor-Alkali Plant, Volumes I and II," will be available at http://www.epa.gov/ORD/NRMRL/Pubs/600R02/007 or as Order No. PB2003-100241; Cost: $98.00, subject to change from:*

*National Technical Information Service*
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