

November 19, 2020

Mr. Jeffrey Meyer
Manager
Division of Air Enforcement
Bureau of Air Compliance and Enforcement – Northern
7 Ridgedale Avenue
Cedar Knolls, NJ 07927

Subject: Covanta Essex Company - Condition (a)1 of Phase II, Section B of Administrative Consent Order EA ID# 200001-07736

Mr. Meyer;

The Administrative Consent Order ("ACO") entered into by Covanta Essex Company ("Covanta Essex") with the Commissioner of the New Jersey Department of Environmental Protection ("Department") on October 9, 2020 included condition (a.1.) of Phase II of Section B compliance Schedule as follows;

Prior to conducting and modeling or health risk assessment COVANTA ESSEX COMPANY shall provide detailed estimates of all emissions associated with the purple plumes including but not limited to, iodine and other associated acid gases and, the methodologies used to estimate the amount and duration of emissions within 45 days of the Effective Date of this ACO.

The attached report is provided to the Department to fulfill this condition of the ACO.

Sincerely,

David Blackmore Facility Manager

#### Attachment

Iodine emissions to ambient air from the Covanta Essex Resource Recovery Facility (prepared by Green Toxicology LLC)

"I certify under penalty of law that I have personally examined and am familiar with the information submitted in this letter and all attached documents and, based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete. I am aware that there are significant civil and criminal penalties, including the possibility of fine or imprisonment or both, for submitting false, inaccurate, or incomplete information."

David Blackmore Facility Manager Date

#### 1.0 Introduction

The New Jersey Department of Environmental Protection ("Department") has required COVANTA ESSEX COMPANY to provide a written report with detailed estimates of all emissions associated with the purple plumes including but not limited to, iodine and other associated acid gases and the methodologies used to estimate the amount and duration of emissions.

### 2.0 Background

The Covanta Essex facility (the Facility) had multiple events in 2019 and early-2020 where a colored plume was recorded as opacity at or above the Operating Permit limit of 10% as a 6-minute block average. The plume was described as a pink color with varying degrees of intensity. Colored plumes have infrequently been observed at certain facilities and have been correlated to iodine due to its known chemical and physical properties including;

- Solid iodine exists as a black crystalline solid with a melting point of 113.7 °C and a boiling point of 184.3 °C.
- It forms a purple vapor when present at certain concentrations

The following information explains the procedures used to estimate the amount of iodine as  $I_2$  in stack flue gas to create a visible colored plume.

#### 3.0 Iodine concentration related to plume formation

The amount of iodine as I<sub>2</sub> to form a colored plume was estimated through several steps;

- 1. identify the operating period in each flue when opacity exceeded the 10% 6-minute standard and a purple plume was observed;
- 2. identify stack flue dimensions, opacity monitor specifications and estimate stack flue characteristics;
- 3. provide information from steps 1 and 2 to an independent third-party expert for evaluation.

Table 1 provides a summary of the results with the estimated I<sub>2</sub> concentration values as "parts per million (ppm)" being an average concentration based on correlations described in subsequent sections.

### 3.1 Flue dimensions and flue gas parameters

The facility design criteria that were used in this evaluation are:

Parameter	Value	Source		
Flue diameter	15.08 feet	Stack Design		
Opacity monitor	Lighthawk 560 Continuous Monitoring Systems, Teledyne Monitor Labs	Equipment specification		
Flue gas temperature	Varies with each event	Stack instrument		
Flue gas flow rate	Varies with each event	Stack flow rate monitor		
Opacity as %	Varies with each event	Stack opacity monitor		

### 3.2 Correlation of stack opacity with iodine concentration

Green Toxicology LLC is an independent consultancy with expertise in a wide variety of environmental and health-based matters. Green Toxicology LLC demonstrated proficiency in analyzing colored plumes by correlating stack opacity with iodine emission factors at the facility operated by Covanta Lancaster, Inc. for the Lancaster County Solid Waste Management Authority (the Lancaster facility). That evaluation was specific to the Lancaster facility including stack flue diameter, flue gas temperature and the type of opacity monitor. Covanta Essex selected Green Toxicology LLC to complete a similar analysis for design and operating conditions at Covanta Essex. The complete report provided by Green Toxicology LLC including methodologies and results is provided as Attachment 1.

The calculation methodology in the Green Toxicology LLC report considered several correlations which are summarized below with Figure 1 illustrating the results.

For high accuracy (<1% of ppm estimate as calculated by the methodology):

$$P = 103.5 \times (-\ln(1 - (K - C)/100)) \times (1 + 0.0018 \times (T - 300))$$

For medium accuracy (<5% of ppm estimate up to 60% opacity)

$$P = 1.0 \times (K - C) \times (1 + 0.009 \times (K - C)) \times (1 + 0.0018 \times (T - 300))$$

For an easy to calculate estimate with less accuracy (<10% of ppm estimate as calculated by the methodology)

$$P = 1.07 \times (K - C)$$
 for  $(K - C) \le 10.5\%$ 

$$P = -2.71 + 1.32 \times (K - C)$$
 for  $10.6\% \le (K - C) \le 35.5\%$ 

$$P = -25.9 + 1.98 \times (K - C)$$
 for  $35.6\% \le (K - C) \le 60\%$ 

These apply within the stated accuracy for all three units for 250<T<350 °F. For each of the above correlations;

K = opacity reading (%)

C = background or drift of opacity meter (%)

T = baghouse outlet temperature (°F)

P = iodine ppm in stack gas

Figure 1 presents iodine concentration as a function of opacity and temperature however flue gas temperature has a comparatively minor impact. The Y-axis is a multiplier that can be used to estimate I<sub>2</sub> concentration directly from opacity. As an example, the I<sub>2</sub> concentration at 10, 20 and 30 % opacity is estimated by the following;

Opacity	Estimated factor	Estimated I2 as ppm
10	1.0	10
20	1.1	22
30	1.2	36

This correlation is an estimate based on the eleven events in Table 1.

## 3.3 Other acid gas emissions

The reaction between I<sub>2</sub> and SO<sub>2</sub> has been well documented in scientific literature and is generally described by the following equation;

$$I_2 + SO_2 + H_2O = unknown products$$

The forward reaction is highly favorable so that all SO<sub>2</sub> would react in the presence of sufficient I<sub>2</sub>. I<sub>2</sub> present at a concentration greater than SO<sub>2</sub> would be present in the stack flue and the source of a potentially visible colored plume.

Equilibrium data for I<sub>2</sub> and iodic acid (HI) identifies that I<sub>2</sub> would be the predominant species of iodine at the inlet to the air pollution control system and stack. If HI was present at the economizer location, that acid gas would be removed by the semi dry scrubbing system.

#### 4.0 Summary and conclusions

An independent third party developed a relationship between iodine (as I<sub>2</sub>) concentration and opacity using facility specific information. That relationship is based on the general principle that iodine vapor absorbs light in the wavelength range monitored by the opacity-measuring continuous emission monitor. The estimated I<sub>2</sub> concentration from this relationship is the basis of the iodine emission factors used in air dispersion modeling analysis.

Table 1 Estimate of iodine in flue gas correlated with opacity

Reference	erence Unit Date		Time <sup>(1)</sup>	% Opacity <sup>(2)</sup>	l <sub>2</sub> Mass Emission Rate <sup>(3)</sup> (g/sec)	I <sub>2</sub> as ppm	
	Unit1	1/14/2019	-	-	-	-	
1	Unit2	1/14/2019	17:12	8.6	7.2	8.8	
	Unit3	1/14/2019	16:10	9.2	8.2	10.6	
	Unit1	1/28/2019	-	- 1	-	-	
2	Unit2	1/28/2019	-	- 1	-	-	
	Unit3	1/28/2019	17:25	17.7	15.2	19.7	
	Unit1	5/2/2019	-	- 1	-	-	
3	Unit2	5/2/2019	15:53	7.0	4.8	7.7	
J	Unit3	5/2/2019	-		-	-	
111	Unit1	6/3/2019	-	- 1	-	-	
4	Unit2	6/3/2019			11.4	21.8	
	Unit3	6/3/2019	18:56	19.7	7.2	10.2	
5	Unit1	6/16/2019	4:03	6.4	4.4	6.3	
	Unit2	6/16/2019	-	- 1	-	-	
	Unit3	6/16/2019	-	- 1	-	-	
	Unit1	6/19/2019	13:00	6.0	4.13	5.3	
6	Unit2	6/19/2019	12:24	29.7	27.0	38.4	
	Unit3	6/19/2019	12:28	24.4	23.0	27.8	
	Unit1	6/24/2019	5:08	9.7	8.6	10.4	
7	Unit2	6/24/2019	1:15	9.2	6.4	9.9	
	Unit3	6/24/2019	-	1 - 1	-	-	
8	Unit1	8/7/2019	-	-	-	-	
	Unit2	8/7/2019	-	-	-	-	
	Unit3	8/7/2019	9:40	8.7	5.5	6.8	
	Unit1	9/20/2019	-	- 1	-	-	
9	Unit2	9/20/2019	-	1.2	-	-	
	Unit3	9/20/2019	18:04	6.7	5.8	7.1	
	Unit1	10/10/2019	14:46	16.5	12.4	18.9	
10	Unit2	10/10/2019	-	-	-	-	
	Unit3	10/10/2019	-	-	•	-	
	Unit1	2/5/2020	18:52	6.6	3.7	5.4	
11	Unit2	2/5/2020	-	-	-	-	
	Unit3	2/5/2020	-	-	-	-	

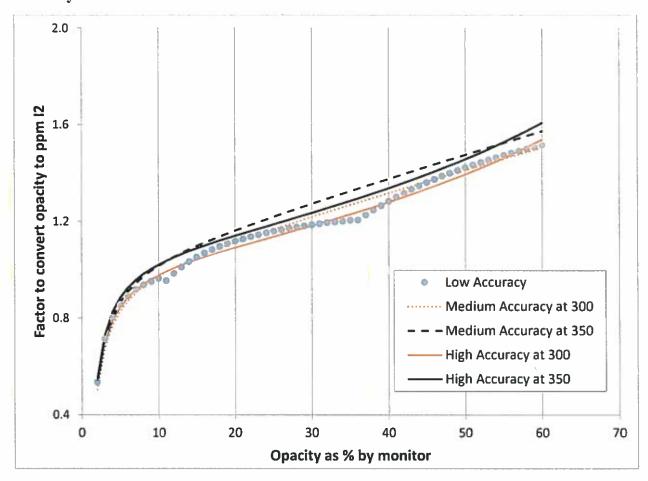
<sup>(1)</sup> Starting time for 60-min maximum emissions.

<sup>(2)</sup> Average opacity over 60-min period corresponding to emission rate.

<sup>(3) 60-</sup>min maximum emissions.

<sup>(4)</sup> AERMOD can only model 60-minute periods that begin on the hour. Since the mass emission rate time period does not begin right on the hour, modeling was conducted for the two "model hours" that captured the actual 60-minute period.

Figure 1. Illustration of correlations: High and medium accuracy at 300 and 350 F and low accuracy



# **Attachment 1:**

Iodine emissions to ambient air from the Covanta Essex Resource Recovery Facility (prepared by Green Toxicology LLC)



#### Memorandum

To:

Brian Bahor and Gary Pierce, Covanta

From:

Edmund A.C. Crouch, Ph.D.

Date:

June 25, 2020

Subject:

Iodine emissions to ambient air from the Covanta Essex Resource Recovery

Facility

#### Introduction

The Covanta Essex resource recovery facility has experienced multiple episodes of atmospheric releases of iodine in sufficient quantities to cause purple colored plumes, with corresponding opacities measured at up to 50% over brief time-intervals. I have evaluated the levels of iodine emissions required to cause the measured increases in opacity, based on measurements of iodine optical-absorption cross-section and characteristics of the opacity monitors, combined with minute-by-minute continuous emission monitor readings of stack gas characteristics (opacity, temperature, and flow rate).

#### Estimation of iodine emissions based on stack gas characteristics

# Methodology

Emissions of iodine are estimated by realizing that iodine vapor absorbs light in the wavelength range monitored by the opacity-measuring continuous emission monitor (CEM). Literature studies on the absorption of light by iodine vapor are used to construct a relationship between light extinction and the concentration of iodine in stack-gas as a function of light wavelength and temperature. This relationship in turn is used in conjunction with the specific light characteristics of the opacity CEM to derive a relationship between CEM opacity measurement, temperature, and the concentration of iodine in stack gas. This relationship is then used to infer stack-gas concentrations of iodine from recorded CEM measurements of opacity and temperature. Subsequent multiplication of the concentrations by flowrates results in estimates of mass emission rates.

### Extinction coefficient for iodine vapor

The wavelength dependence of the extinction coefficient (equivalently, the absorption cross-section) for iodine vapor at room temperature (295 K) and in air at atmospheric pressure has been accurately measured by Saiz-Lopez et al. (2004) at high resolution in the relevant wavelength interval (Figure 1). These measurements clearly resolve the band structure, and

agree<sup>1</sup> reasonably well on average with earlier lower-resolution measurements at room temperature (extrapolated to zero pressure) by Tellinghuisen (1973; see Figure 1), and with earlier work. Sulzer and Wieland (1952) also provide lower resolution measurements at temperatures of 423 K, 873 K, and 1323 K, together with a theoretical analysis of the major contributing component to the extinction coefficient in the relevant wavelength range. This theoretical analysis omits various smaller contributions (e.g. providing the band structure) but allows extrapolation between temperatures and provides a smooth interpolation across the band structure — see the curves shown as "Theory" in Figure 1. The Sulzer and Wieland (1952) curve shape for the extinction (absorption) coefficient  $\varepsilon$  as a function of wavelength  $\lambda$  and temperature T is given by:

$$\varepsilon(T,\lambda) = \varepsilon_o \left(\frac{\lambda_0}{\lambda}\right)^2 \sqrt{\tanh\left(\frac{\theta}{2T}\right)} \exp\left\{-\tanh\left(\frac{\theta}{2T}\right) \left(\frac{1/\lambda - 1/\lambda_0}{1/\Delta\lambda}\right)^2\right\}$$

where  $\lambda$  is the wavelength and T is the absolute temperature. Fitting the Saiz-Lopez et al. (2004) data (minimizing the sum of squared differences for all points measured between 450 and 630 nm) gives the constants:

 $\varepsilon_0 = 278.54 \, \text{m}^2 \, \text{mole}^{-1}$ 

 $\lambda_0 = 529.67 \text{ nm}$ 

 $\Delta \lambda$  = 8654.6 nm

with  $\theta$  = 308.62 K based on Sulzer and Wieland (1952).<sup>3</sup>

### Opacity meter response

The wavelength-dependence of the opacity meter responses in Units 1, 2, and 3 are provided at the 10 nm intervals measured as part of the standard quality control procedures for these instruments (all units use Lighthawk 560 Continuous Monitoring Systems, Teledyne Monitor Labs, 2006a, b, c). The measurements were performed on representative samples from the manufacturing production runs, not on the installed instruments themselves; the same sample was used for the Unit 1 and 2 instruments, with a different (later) sample for Unit 3. The LED

<sup>&</sup>lt;sup>1</sup> The agreement shown in Figure 1 is not as good as that indicated by Saiz-Lopez et al. (2004) in their paper, but I have not been able to locate the discrepancy. This agreement requires assuming that all earlier workers reported extinction coefficients with units based on moles of atomic iodine, rather than the moles of iodine vapor shown in Figure 1.

<sup>&</sup>lt;sup>2</sup> This curve is a Gaussian on a frequency scale. It is written here on the wavelength scale of Figure 1.

 $<sup>^3</sup>$   $\theta$  has a theoretical interpretation, but changes in its value simply change the estimated values for the other constants without affecting the curve fit.

light source should provide a smooth spectrum (with no narrow band structure or peaks), so interpolation of these measurements (shown on Figure 1) should be accurate. Six point Lagrange interpolation to 0.5 nm intervals was used for the Unit 1 and 2 response, and four point for the Unit 3 response.<sup>4</sup> Figure 1 shows that the opacity CEM response matches the absorption characteristics of iodine vapor well, so CEM measurements should be sensitive to sufficiently high iodine concentrations.

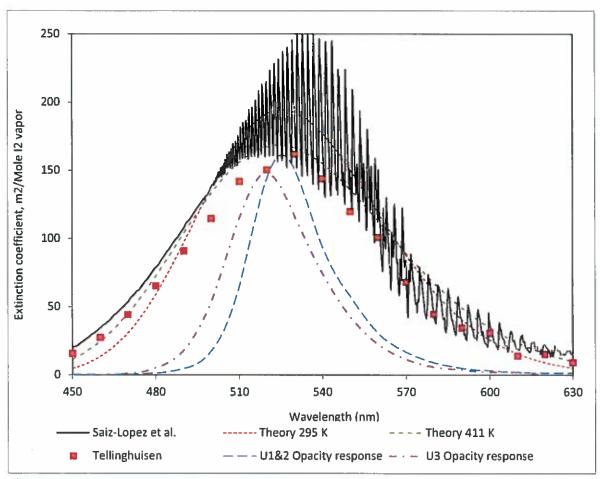


Figure 1 Extinction coefficient for I<sub>2</sub> vapor at 295 K, theoretical curve (see text) at 295 K and 411 K, and the opacity meter responses in Units 1, 2, and 3 (arbitrary units, but with equal areas under the curves).

<sup>&</sup>lt;sup>4</sup> The overall response was given at 10 nm intervals from 360 to 750 nm for units 1 and 2, although the response was less than 1% of the maximum outside the range 480 to 630 nm. For unit 3, the overall response was given as zero outside the range 470 to 610 nm. The different interpolation orders were chosen to give smooth transitions at the end-points of the useful ranges, and variations in interpolation order have negligible effect on the result.

### Overall opacity sensitivities to iodine vapor

The sensitivities of the opacity meter to iodine vapor were obtained by convolving the opacity meter responses with the extinction coefficient for iodine at the temperature of the stack gas. With the opacity meter responses shown, the band structure in the extinction coefficient will be averaged, and suitably accurate estimates may be obtained by using the smooth approximate theoretical curves of Sulzer and Wieland (1952). These theoretical curves match the average extinction coefficient over the wavelength range of the opacity meter response with reasonable accuracy at 295 K, and have the advantage of allowing extrapolating to higher temperatures (where the height and width of the curve and the band structure are all modified). Performing these convolutions<sup>5</sup> for stack temperatures in the range of 250 °F to 350 °F gives the wavelength integrated extinction coefficients (absorptivities) shown in Figure 2. The curves are quadratic fits to values calculated at 5 °F intervals, which values deviate negligibly from these curves.

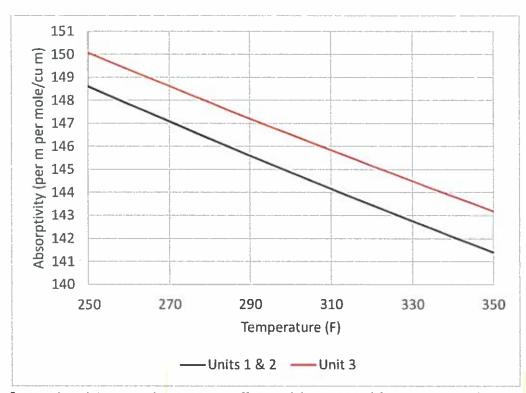


Figure 2 Wavelength integrated extinction coefficients (absorptivities) for Units 1, 2, and 3.

<sup>&</sup>lt;sup>5</sup> Numerical convolution at 0.5 nm wavelength intervals using the trapezoidal rule.

### Calculation of iodine emission rates

lodine emission rates E (grams/second) were estimated from the stack gas opacity K (%), wavelength integrated extinction coefficient H(T) ( $m^2$ /mole from Figure 2) at the stack temperature T (°F), and the stack flow rate (actual) V ( $m^3$ /sec), using

$$E = \frac{-\ln(1 - (K - C)/100)}{LH(T)}VM$$

where C (%) is a cut-off opacity to account for drift of the opacity meter and background opacity from other materials, L (m) is the opacity meter optical path length through the stack gas (2.337 m for Units 1 and 2, 2.318 m for Unit 3), and M is the molar weight of diatomic iodine vapor (253.81 g/mole). All opacity-values above the cut-off C were assumed to be due to iodine.

#### Results

#### Total emissions and maximum emission rates

A total of 15 emission events were modeled, each one consisting of one or more peaks of opacity over periods extending up to several hours, with summary results shown in Table 1 for total mass of iodine emitted during the day, and maximum emission rates averaged over 1 minute, 15 minutes, and 1 hour, and the initial minute for the given maximum.<sup>6</sup> The cut-off opacity selected for each event was estimated empirically by selecting a value that just suppressed any estimate of emissions outside the event in an approximately 24-hour period containing the event. The selections were made by visual observation of graphs of opacity and emission estimates (see appendix). The various estimates are probably uncertain to at least 10% due to the limited precision of the opacity meters, which report opacity to 0.1%, and the potential drift of these meters such that positive opacity may be reported as 0% (see, for example, the lack of a longer tail to the opacity and emission curve for the event in Unit 2 on 05-02-19). In addition, there is an uncertainty of unknown size in the theoretical analysis above, in that it has not been tested empirically; such uncertainty could be evaluated by injection of iodine in known quantities into the stack gas after the baghouse and measuring the resulting opacity.

<sup>&</sup>lt;sup>6</sup> Note that the U2 01-14-19 times look a little odd compared with the rest, but examination of the figure for that case makes the reason clear — the initial spike in concentration gives the highest 1 and 15 minute averages, but the more sustained but lower later peaks give the highest 1 hour average.



Unit & date emiss	Total emissions	Maximum emission rate averages (grams/second)		Time of initial minute for given maximum			Cutoff	
	(kg)	1 min	15 min	60 min	1 min	15 min	60 min	(%)
U1 02-05-20	34.8	7.9	6.4	3.7	19:04	18:56	18:52	1.6
U1 06-16-19	34.2	9.7	7.9	4.4	04:13	04:11	04:03	0.5
U1 06-24-19	32.6	53.2	26.4	8.6	05:20	05:15	05:08	0.9
U1 10-10-19	45.8	35.8	25.3	12.4	14:52	14:49	14:46	0.0
U2 01-14-19	49.3	16.5	12.8	7.2	16:24	16:18	17:12	0.0
U2 05-02-19	17.5	9.7	8.2	4.8	16:08	16:06	15:53	0.0
U2 06-03-19	82.0	33.3	21.6	11.4	20:57	19:38	19:29	0.0
U2 06-19-19	157.9	61.8	46.6	27.0	12:48	12:45	12:24	0.0
U2 06-24-19	38.9	10.8	9.3	6.4	01:35	01:25	01:15	0.0
U3 01-14-19	30.7	24.9	19.8	8.2	16:24	16:19	16:10	0.7
U3 01-28-19	75.1	28.0	23.4	15.2	18:16	18:12	17:25	0.4
U3 06-03-19	35.1	19.1	13.1	7.2	19:07	18:59	18:56	1.2
U3 06-19-19	139.6	56.8	37.3	23.0	12:58	12:55	12:28	0.9
U3 08-07-19	21.0	8.8	8.0	5.5	10:00	09:54	09:40	2.2
U3 09-20-19	31.1	13.4	9.3	5.8	18:15	18:12	18:04	0.0

Table 1 Summary results of emission modeling for 15 iodine emission events

I understand that these emission rates will be translated via air dispersion modeling into estimated impacts to ambient air, and hence to estimated risks to public health.

Graphs of opacity and emission rate estimates versus time for these events are included in the appendix.

Conversion of opacity reading to iodine volume mixing ratio

Using the methodology described allows a calculation of the iodine volume mixing ratio (measured in ppm) in the stack gas based on the opacity reading, as follows.

Let

K =opacity reading (%)

C = background or drift of opacity meter (%)

T = baghouse outlet temperature (°F)

P = iodine ppm in stack gas

For high accuracy (<1% of ppm estimate as calculated by the methodology):

$$P = 103.5 \times (-\ln(1 - (K - C)/100)) \times (1 + 0.0018 \times (T - 300))$$



For medium accuracy (<5% of ppm estimate up to 60% opacity)

$$P = 1.0 \times (K - C) \times (1 + 0.009 \times (K - C)) \times (1 + 0.0018 \times (T - 300))$$

For an easy to calculate estimate with less accuracy (<10% of ppm estimate as calculated by the methodology)

$$P = 1.07 \times (K - C)$$
 for  $(K - C) \le 10.5\%$   
 $P = -2.71 + 1.32 \times (K - C)$  for  $10.6\% \le (K - C) \le 35.5\%$   
 $P = -25.9 + 1.98 \times (K - C)$  for  $35.6\% \le (K - C) \le 60\%$ 

These apply within the stated accuracy for all three units for 250<T<350 °F (the slight difference in LED light sources is almost exactly cancelled by the slight difference in light path length).

#### References

- Saiz-Lopez A, Saunders RW, Joseph DM, Ashworth SH, Plane JMC. 2004. Absolute absorption cross-section and photolysis rate of I<sub>2</sub>. Atmos Chem Phys 4(5):1443–1450.
- Sulzer von P, Wieland K. 1952. Intensitätsverteilung eines kontinuierlichen Absorptionsspektrums in Abhängigkeit von Temperatur und Wellenzahl. Helv Phys Acta 25(6):653–676. [In German].
- Teledyne Monitor Labs Inc. 2006a. Manufacturer's certificate of conformance with design specifications per 40CFR60, Appendix B, Performance Specification 1, Published August 2000. LightHawk 560 Continuous Monitoring System (COMS). For Covanta Energy, Unit 1, Serial Number: 5602654. August 2014.
- Teledyne Monitor Labs Inc. 2006b. Manufacturer's certificate of conformance with design specifications per 40CFR60, Appendix B, Performance Specification 1, Published August 2000. LightHawk 560 Continuous Monitoring System (COMS). For Covanta Energy, Unit 2, Serial Number: 5602655. August 2014.
- Teledyne Monitor Labs Inc. 2006c. Manufacturer's certificate of conformance with design specifications per 40CFR60, Appendix B, Performance Specification 1, Published August 2000. LightHawk 560 Continuous Monitoring System (COMS). For Covanta Essex Company, Unit 4, Serial Number: 5602790. August 2015. [Note: this instrument is installed in Unit 3; it was given the designation "Unit 4" due to a misunderstanding.]
- Tellinghuisen J. 1973. Resolution of the visible-infrared absorption spectrum of I₂ into three contributing transitions. J Chem Phys 58(7):2821–2834.



# **APPENDIX**

Graphs of opacity and estimated emission rate for each atmospheric iodine-release event

