

IODINE IN WORKPLACE ATMOSPHERES
(IMPREGNATED ACTIVATED BEADED CARBON)



Method Number:	ID-212 (This method supersedes ID-177)
Matrix:	Air
OSHA Permissible Exposure Limits	
Final Rule Limit*:	0.1 ppm (Ceiling)
Transitional Limit:	0.1 ppm (Ceiling)
Collection Device:	An air sample is collected using a calibrated sampling pump and a glass tube containing impregnated activated beaded carbon (IABC). A modified sampling tube (MST) can be used to preclude any iodide-containing particulate, if necessary. Loss of iodine using IABC has been noted when sampling in relative humidities (RHs) > 50%. See Special Precautions below.
Recommended Sampling Rate:	0.5 liter per minute (L/min)
Recommended Minimum Sampling Time:	5 min
Analytical Procedure:	The sampling medium is desorbed using an aqueous solution containing 1.5 mM sodium carbonate (Na_2CO_3) and 1.5 mM sodium bicarbonate (NaHCO_3). An aliquot of this solution is analyzed for iodine (as iodide, I^-) by an ion chromatograph equipped with a pulsed electrochemical detector (PED).
Detection Limit	
Qualitative:	0.0004 ppm as I_2 (2.5-L air sample)
Quantitative:	0.0010 ppm as I_2 (2.5-L air sample)
Precision and Accuracy	
Validation Range:	0.05 to 0.20 ppm
CV_T (pooled):	0.045
Bias:	-0.025
Overall Error:	$\pm 11.5\%$
Method Classification:	Interim Method (See Special Precautions below)
Special Precautions:	1) - Loss of iodine has been noted when sampling in >50% RH. See Sections 2 and 4.6 for details. The loss in relation to humidity is concentration-dependent. Due to the dependence on humidity, this method is considered an interim procedure until alternate sampling can be explored further. 2) - Samples should be shipped for laboratory analysis as soon as possible.
Chemist:	James C. Ku
Date:	May, 1994

* The U.S. Court of Appeals, Eleventh Circuit, has ruled that Final Rule Limits of 29 CFR 1910.1000 be vacated. The Transitional Rule Limits are currently in effect and in the case of iodine the limits are identical in value. The Final Rule definition of a "Ceiling" has been retained (See Federal Register, Vol. 58, No. 124, Wednesday June 30, 1993 p.35339 for further details regarding the ceiling definition).

Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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1. Introduction

This method describes the sample collection and analysis of airborne iodine (I_2). Samples are taken in the breathing zone of workplace personnel, and analysis is performed by ion chromatography (IC) equipped with a pulsed electrochemical detector (PED).

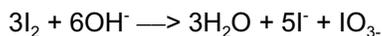
1.1 History

Previously, iodine vapor in the workplace atmosphere was collected in a 1% sodium bisulfite solution and analyzed by an ion specific electrode (ISE) technique (5.1). This method was considered inadequate due to the instability of I_2 in bisulfite solution. Two stopgap methods were later developed, in which any iodine present in the air was collected in 0.01 N sodium hydroxide solution contained in a midjet fritted glass bubbler (MFGB). These samples were then analyzed by ISE (5.2) or IC equipped with an electrochemical detector (ED) (5.3). Because bubblers are inconvenient to use as personal samplers due to spillage or breakage, it was desirable to develop a solid-sorbent sampling method. A method was developed which collected I_2 in the air using activated charcoal impregnated with an alkali metal hydroxide. The base-impregnated charcoal converted I_2 to iodide (I^-) and iodate (IO_3^-) which was then desorbed using a weakly basic solution. An aliquot of the solution was analyzed for I^- by IC or ISE. Unfortunately, background levels of I^- (up to 5 μg) found in the impregnated charcoal were considered unacceptable (5.4).

Impregnated activated beaded carbon (IABC), previously developed (5.5, 5.6) at the OSHA Salt Lake Technical Center (OSHA-SLTC), was used to replace impregnated charcoal sampling tubes (ICST) used for the collection of I_2 . The IABC has a significantly lower background level of I^- (<0.008 μg). This current method was evaluated using IABC as the collection medium.

1.2 Principle

Iodine is collected using IABC sorbent contained in a glass tube. The collected I_2 is converted to I^- and IO_3^- by the treated sorbent based on the following chemical reaction:



The resultant I^- is analyzed by IC-PED. A stoichiometric conversion factor is used to calculate the amount of I_2 collected. The same mechanism is used for iodine collection in impingers containing 1.5 mM sodium carbonate and 1.5 mM sodium bicarbonate solutions. These solutions are used for sampling when the relative humidity >50%.

1.3 Advantages and Disadvantages

- 1.3.1 This method has adequate sensitivity for determining compliance with the OSHA Ceiling Permissible Exposure Limit (PEL) for I_2 exposure.
- 1.3.2 The method is simple, rapid, and easily automated.
- 1.3.3 The method is specific and can determine the I_2 (as I^-) in the presence of other halogen-containing substances.
- 1.3.4 The solid sorbent sampling tube used to collect I_2 is small, portable, and contains no liquid. The tube used to collect only iodine vapor is identical to that used to collect sulfur dioxide in OSHA Method No. ID-200. A modified sampling tube is also available for collecting particulates. The modified tube is similar to the one also recommended in OSHA Method No. ID-200; however, the foam used in the modified SO_2 sampling device must be removed before sampling iodine. See Section 2 for further details.
- 1.3.5 Desorption and preparation of samples for analyses involve simple procedures and equipment.

- 1.3.6 The amount of I₂ (as I⁻) can also be analyzed and confirmed by an ISE technique. This ISE technique is listed as an Appendix to this method.
- 1.3.7 The I⁻ contaminant (background) levels of the IABC sorbent are extremely low, especially when compared to the sampling media previously used in OSHA Method No. ID-177.
- 1.3.8 One major disadvantage of the method is that lower recoveries are noted when samples are taken at high humidities. A 30% loss in recovery was noted at 80% RH when the I₂ concentration was near 0.5 × PEL (see Section 4.6). Due to this humidity problem, the method is considered an interim method until more suitable sampling media can be developed or the humidity problem rectified.
- 1.3.9 Another disadvantage is the skilled maintenance required for the analytical detector. As specified in Section 3.2.1, the detector is equipped with two electrodes, a silver working electrode and a silver/silver chloride reference electrode. The silver working electrode must be polished before it is installed in the amperometric cell. It is also necessary to polish the working electrode whenever a high background current, decreased sensitivity, or other degradation in detector output is observed. Polishing is a time-consuming process requiring skill and care. Recently developed silver/silver chloride reference electrodes require little, if any, maintenance.

1.4 Method Performance

A synopsis of the method performance is presented below. Further information can be found in Section 4.

- 1.4.1 This method was validated over the concentration range of 0.05 to 0.20 ppm. An air volume of 2.5 L and a flow rate of 0.5 L/min were used.
- 1.4.2 The qualitative detection limit was 0.0027 µg/mL or 0.008 µg (as I⁻) when using a 3-mL solution volume. This corresponds to 0.0004 ppm I₂ for a 2.5-L air volume.
- 1.4.3 The quantitative detection limit was 0.009 µg/mL or 0.03 µg (as I⁻) when using a 3-mL solution volume. This corresponds to 0.001 ppm I₂ for a 2.5-L air volume. A 50-µL sample loop and a detector setting of 0.1 microampere (µA) full-scale output were used.
- 1.4.4 The sensitivity of the analytical method, when using the instrumental parameters listed in Section 3.6.3, was calculated from the slope of a linear working range curve (0.1 to 5.0 µg/mL I⁻). The sensitivity was 2.5 × 10⁶ area units per 1 µg/mL. A Dionex Series 4500i ion chromatograph with AI450 computer software was used (Dionex, Sunnyvale, CA).
- 1.4.5. The performance of this method was significantly better than OSHA Method No. ID-177 for I₂ (5.4).
- 1.4.6. The total pooled coefficients of variation (CV_T), bias, and total overall error (OE) are as follows:

$$CV_T (\text{pooled}) = 0.045; \quad \text{bias} = -0.025; \quad OE_T = \pm 11.5\%$$
- 1.4.7 The collection efficiency at 2 × PEL was 100%. Samples were collected from a generated test atmosphere of 0.20 ppm I₂ for 5 min.
- 1.4.8 Breakthrough tests were performed at concentrations of 0.75 ppm I₂. No breakthrough was found for a sampling time of 30 min and an average sample flow rate of 0.5 L/min.
- 1.4.9 Samples can be stored at ambient (20 to 25 °C) temperature on a lab bench for a period of 29 days. Results show the mean sample recovery after 29 days of storage was within ±10% of results at Day 0; however, a loss over time was noted and samples should be

analyzed as soon as possible. There was no significant difference in results for samples stored at room temperature, in a refrigerator, or freezer.

1.5 Interferences

1.5.1 Other gaseous or particulate iodide compounds may interfere in the analysis of I₂ if collected on the IABC. A modified sampling tube (MST) should be used to collect any iodide-containing particulate if suspected to be a problem.

1.5.2 Any substance that has the same retention time as I⁻, when using the ion chromatographic operating conditions described in this method, is an interference. Changing the chromatographic separation conditions (detector settings, column, eluent flow rate, and strength, etc.) may circumvent the interference.

1.6 Uses

Industrial uses and products of iodine (5.7):

unsaturation indicator	x-ray contrast media
dyes	catalysts
production of iodides and iodates	pharmaceuticals
process engraving and lithography	iodized salt
preservatives	photography
disinfectants	food and feed additive
special lubricants for titanium and stainless steel parts	

1.7 Physical and Chemical Properties (5.8)

Iodine exists as dense crystalline grayish-black plates or granules and has a metallic luster and characteristic odor. Iodine readily sublimates, producing a violet vapor.

Iodine (CAS No. 7553-56-2)

Chemical formula	I ₂
Formula weight	253.8
Melting point	113.5 °C
Boiling point	184.4 °C
Vapor pressure	0.0410 kPa (0.309 mmHg) at 25 °C
Vapor density	4.98 times that of air
Solubility	Soluble in alcohol, carbon disulfide, chloroform, toluene, ether, carbon tetrachloride, glycerol, and alkaline iodide solutions. Slightly soluble in water.
Combustibility	Noncombustible

1.8 Toxicology

Information listed within this section is a synopsis of current knowledge of the physiological effects of I₂ and is not intended to be used as a basis for OSHA policy.

1.8.1 Iodine is considered a greater physiological irritant and more corrosive than bromine or chlorine (5.9). Occupational routes of exposure for I₂ are inhalation, skin contact, and eye contact.

1.8.2 Symptoms of I₂ exposure (5.10, 5.11, 5.12)

Inhalation: Nasal passage irritation, headache, tightness in chest, chronic pharyngitis, rhinitis, possible pulmonary edema.

Skin: Rash, cutaneous hypersensitivity, skin burns.

Eyes: Burning, stinging sensations, blepharitis, lacrimation.

- 1.8.3 Excretion: Iodine absorbed by the lungs is physiologically converted to iodide and eliminated primarily in the urine.

2. Sampling (See Interferences, Section 1.5, and Notes in Section 2.1.2 before sampling.)

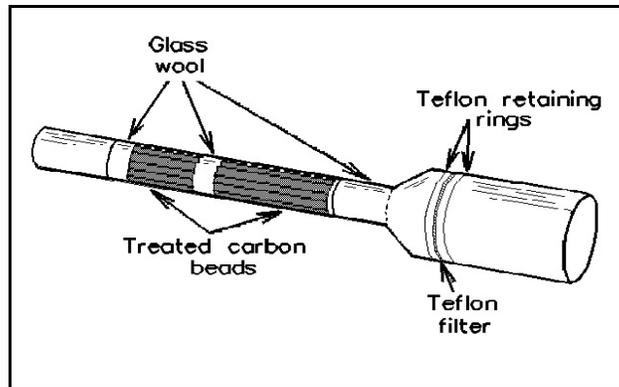
Wipe samples are normally not taken for iodine. If wipe sampling is necessary, the ability to perform this will have to be conducted on a case-by-case basis. Contact the OSHA-SLTC for further sampling information.

2.1 Equipment - Air Samples

- 2.1.1 Calibrated personal sampling pumps capable of sampling within $\pm 5\%$ of the recommended flow rate of 0.5 L/min are used.
- 2.1.2 Solid sorbent sampling tubes are prepared using glass tubes, glass wool plugs, and IABC. Commercially available sampling tubes consist of glass tubes packed with 100-mg IABC front and 50-mg backup sections (Cat. No. 226-80, SKC Inc., Eighty Four, PA). The IABC is held in place with glass wool and a stainless steel retainer clip.

Notes:	a) IODIDE PARTICULATE: If there is reason to suspect the sampled air could contain iodide particulate, a modified sampling tube (MST) should be used to exclude the particulate. See Section 2.1.6 for more details. <u>Most industrial operations that use iodine in their processes do not normally also use iodide salts.</u>
	b) RELATIVE HUMIDITY: If the relative humidity is $\geq 50\%$, impinger samplers should be used. A 20% loss of iodine at 80% RH (25 °C) and 1 \times PEL has been noted when using SKC Cat. no. 226-80 tubes. It is unknown what loss of iodine occurs above 80% RH. Please note the following equipment is used: 1) Midget impingers, (order no. 7531, Ace Glass Co., Vineland, NJ). 2) Sample shipment vials: Scintillation vials, 20-mL (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon® cap liners. 3) Collection solution: 1.5 mM Na ₂ CO ₃ + 1.5 mM NaHCO ₃ Dissolve 0.159 g sodium carbonate (Na ₂ CO ₃) and 0.126 g sodium bicarbonate (NaHCO ₃) in 1-L deionized water. Use at least reagent grade chemicals.

- 2.1.3 A stopwatch and bubble tube or meter are used to calibrate pumps.
- 2.1.4 A battery-operated or sling psychrometer, or a water vapor detector tube is used to measure the relative humidity prior to sampling.
- 2.1.5 Various lengths of polyvinyl chloride (PVC) tubing are used to connect sampling media to pumps.
- 2.1.6 Sampling in presence of iodide-containing particulates. Filter media normally used for collecting or precluding particulate (i.e., polyvinyl chloride, mixed-cellulose ester, etc.) should not be used as prefilters due to the possibility of reaction with iodine. If the workplace air being sampled is suspected of containing particulate which could interfere (i.e. iodides), a MST device containing a Teflon® filter as shown below should be used to exclude particulate. (Note: If impingers are used, the IABC and glass wool are removed from the rear of the MST and only the glass jacket/ Teflon filter and retaining rings are connected in front of the impinger.) The sampled air should always travel in the direction shown below:



<-----<Sample Flow<----->

Type II - Modified Sampling Tube (MST)

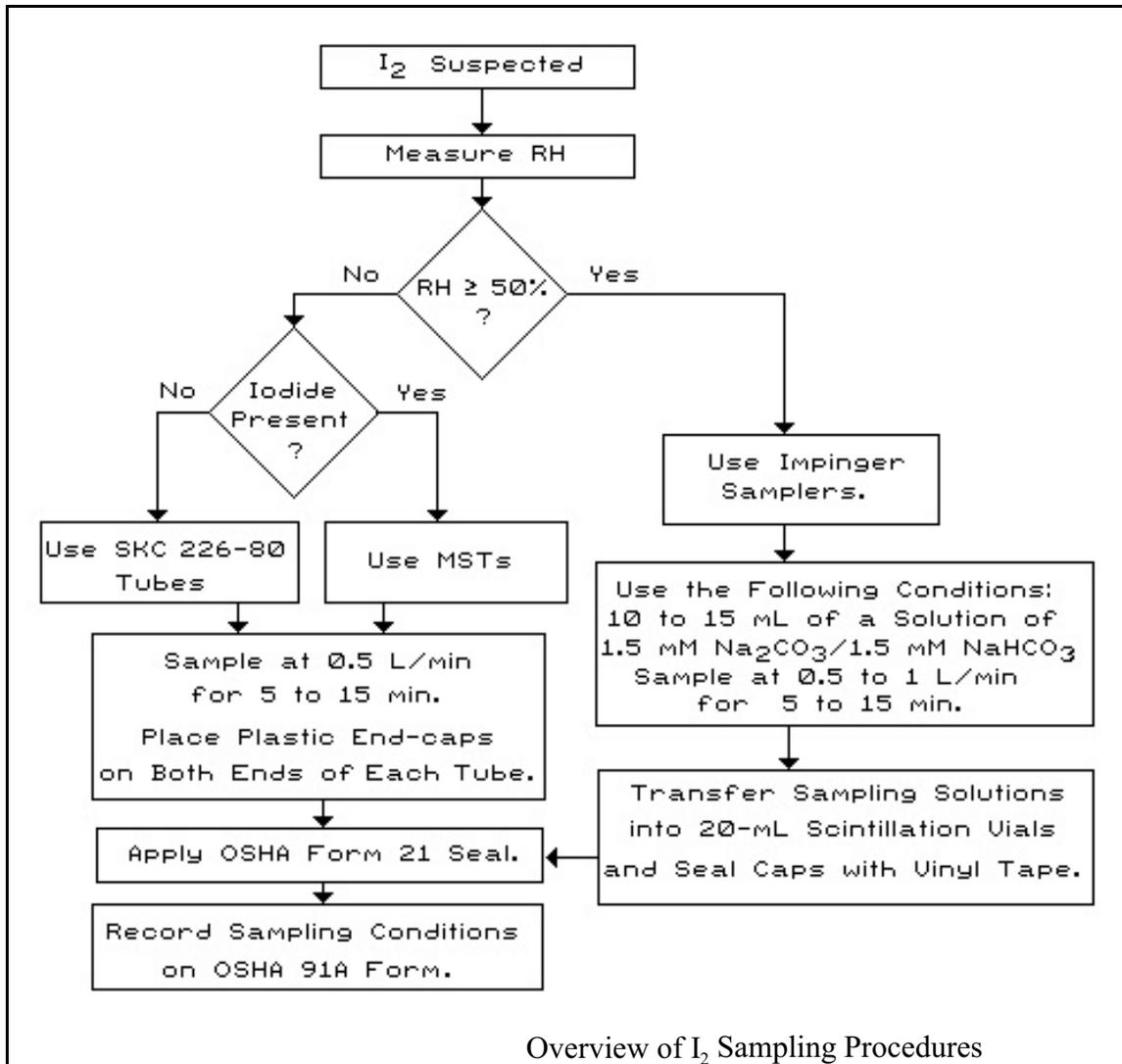
Note: This MST (Forrest Biomedical, Salt Lake City, UT) is the same sampling device (Type II) discussed in OSHA Method ID-200 (5.6) for sulfur dioxide with one exception: The foam normally used as spacers in the tube are replaced with glass wool. Foam can absorb the iodine.

2.2 Equipment - Bulk Samples

Scintillation vials, 20-mL (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon® cap liners. If possible, submit bulk samples in these vials. Tin or other metal cap liners should not be used because the metal and iodine may react.

2.3 Sampling Procedure - Air Samples

The following flow chart is an overview of the sampling protocol for iodine.



- 2.3.1 Determine the humidity at the sampling site using a psychrometer, detector tube, or other suitable device. Loss of iodine has been noted at high humidities. This loss is concentration-dependent, and at iodine levels near the PEL the loss in recovery is approximately 20%. An alternate method employing impinger solutions should be used when sampling in high humidities (>50% RH) as described above. See Section 4.6 for further details regarding the humidity- and concentration-dependent loss of iodine.
- 2.3.2 Connect the sampling tube (or impinger) to the calibrated pump. If sampling tubes are used, make sure sampled air enters the large section (100 mg) of IABC first. Place the sampling device on the employee such that air is sampled from the breathing zone.
- 2.3.3 Use a flow rate of 0.5 L/min and a sampling time between 5 to 15 min. Take additional samples as necessary.
- 2.3.4 After sampling, place plastic end caps tightly on both ends of the tube and apply OSHA Form 21 seals in such a way as to secure the end caps. If impingers were used, transfer solutions to 20-mL scintillation vials and apply seals. Record the sampling conditions such as sampling time, air volume, etc. on the OSHA 91A form. When other compounds are known or suspected to be present in the air, record such information and transmit with the samples.

- 2.3.5 Use the same lot of IABC tubes for blank and collected samples. Handle the blank sorbent tube (or solution if impingers are used) in exactly the same manner as the sample tubes except that no air is drawn through it. Submit at least one blank tube for each batch of ten samples.

2.4 Sampling Procedure -Bulk Samples

Bulk samples can be taken to assist in resolving any potential interferences or to confirm the presence of free iodine in the workplace.

- 2.4.1 Take a representative sample of the bulk material in the workplace. Transfer the bulk material into a 20-mL scintillation vial and seal the cap with vinyl or electrical tape. Securely wrap an OSHA-21 seal length-wise from vial top to bottom.

- 2.4.2 The type of bulk sample should be stated on the OSHA 91A and cross-referenced to the appropriate air sample(s).

2.5 Shipment

- 2.5.1 Immediately send the samples to the laboratory with the OSHA 91A paperwork requesting iodine analysis.

- 2.5.2 Ship any bulk samples separately from air samples. Enclose Material Safety Data Sheets if available. Check current shipping restrictions and ship to the laboratory by the appropriate method.

3. Analysis

Note: If the instrumentation in Section 3.2.1 is unavailable, samples can be prepared and analyzed using an ion specific electrode (ISE) technique. Directions are given in the Appendix of this method. Due to the greater specificity of an IC-PED, this ISE procedure is only recommended if an IC-PED system is unavailable.

3.1 Safety Precautions

- 3.1.1 Refer to appropriate IC instrument manuals, PED maintenance manual (especially for electrode maintenance), and any Standard Operating Procedures (SOP) for proper instrument operation (5.13).
- 3.1.2 Observe laboratory safety regulations and practices.
- 3.1.3 Some chemicals are corrosive. Use appropriate personal protective equipment such as safety glasses, goggles, face shields, gloves, and lab coat when handling corrosive chemicals.

3.2 Equipment

- 3.2.1 Ion chromatograph (Model 4000i or 4500i Dionex, Sunnyvale, CA) equipped with a pulsed electrochemical detector (PED) containing a silver working electrode and silver/silver chloride reference electrode.

[Note: A combination PED/conductivity detector (Dionex, part no. 42039) was used to validate this method. The conductivity detector is not used for this method; however, having both detectors present in one package is advantageous because of increased applications.]

- 3.2.2 Automatic sampler (Dionex Model AS-1) and sample vials (0.5 mL).

- 3.2.3 Laboratory automation system: Ion chromatograph interfaced with a data reduction system (AI450, Dionex).

- 3.2.4 Separator and guard columns, anion (Model HPIC-AS5 and AG5, Dionex).
- 3.2.5 Disposable syringes (1 mL).
- 3.2.6 Syringe prefilters, 0.5- μ m pore size (part no. SLSR 025 NS, Millipore Corp., Bedford, MA).

Note: Some syringe prefilters are not cation- or anion-free. Tests should be performed with blank solutions first to determine contamination and suitability with the analyte.

- 3.2.7 Miscellaneous volumetric glassware: Micropipettes, pipettes, volumetric flasks, Erlenmeyer flasks, graduated cylinders, and beakers.
 - 3.2.8 Scintillation vials, glass, 20-mL.
 - 3.2.9. Equipment for eluent degassing (vacuum pump, ultrasonic bath).
 - 3.2.10 Analytical balance (0.01 mg).
- 3.3 Reagents - All chemicals should be at least reagent grade.
- 3.3.1 Principal reagents:
 - Sodium carbonate (Na_2CO_3)
 - Sodium bicarbonate (NaHCO_3)
 - Sodium nitrate (NaNO_3)
 - Potassium iodide (KI)
 - Potassium iodate (KIO_3)
 - Deionized water (DI H_2O)
 - 3.3.2 Desorbing solution (1.5 mM Na_2CO_3 + 1.5 mM NaHCO_3): Dissolve 0.318 g Na_2CO_3 and 0.252 g NaHCO_3 in 2.0 L DI H_2O .
 - 3.3.3 Eluent (0.02 M NaNO_3):

Dissolve 3.40 g NaNO_3 in 2.0 L DI H_2O . Sonicate this solution and degas under vacuum for 15 min before use.
 - 3.3.4 Iodide (I^-) stock standard (100 $\mu\text{g}/\text{mL}$): Dissolve and dilute 0.1308 g of KI to 1.0 L with DI H_2O . Prepare monthly.
 - 3.3.5 Iodide (I^-) standard solutions, 10, 1, and 0.1 $\mu\text{g}/\text{mL}$:

Pipette appropriate volumes of the 100 $\mu\text{g}/\text{mL}$ I^- stock standard into volumetric flasks and dilute to the mark with desorbing solution. Prepare monthly.

3.3.6 Iodate (IO₃⁻) stock standard (100 µg/mL):

Dissolve and dilute 0.1224 g of KIO₃ to 1.0 L with DI H₂O. Prepare monthly (Note: This standard is only used if confirmation of iodine is necessary in addition to the iodide analysis. Dilute to concentrations in Section 4.12 with desorbing solution. See Sections 4.11 and 4.12 for more details.).

3.4 Working Standard Preparation - Prepare monthly.

Prepare I⁻ working standards in desorbing solution. A suggested scheme for preparing a series of working standards using 10-mL final solution volumes is shown below:

Working Std (µg/mL)	Std Solution (µg/mL)	Aliquot (mL)	Eluent Added (mL)
0.1	0.1	*	*
0.2	1.0	2.0	8.0
0.5	1.0	5.0	5.0
1.0	1.0	*	*
2.0	10.0	2.0	8.0
5.0	10.0	5.0	5.0

* Already prepared in Section 3.3.5.

3.5 Sample Preparation

IABC samples: Follow Sections 3.5.1 to 3.5.3 below.

Impinger samples: Follow Section 3.5.4 only.

Note: If the MST device discussed in Section 2.1.6. is used, the prefilter is not analyzed for iodine.

3.5.1 Carefully remove and discard the rear glass wool plug from each glass tube without losing any IABC sorbent.

Note: The sorbent should always be removed from the glass tube via the opposite end of collection (i.e., 50-mg IABC backup section is removed first). This will minimize the possibility of contamination from any collected particulate.

3.5.2 Carefully transfer each IABC section from a sample tube into a separate 25-mL Erlenmeyer flask or 20-mL scintillation vial.

3.5.3 Pipette 3.0 mL of desorbing solution into each flask.

Note: Alternate sample volumes can be used and are dependent on the analytical sensitivity desired. For most industrial hygiene samples, 3-mL volumes will allow for detection of iodine within the range of standards specified. Cap each flask or vial tightly and allow each solution to sit for at least 60 min. Occasionally swirl each solution.

3.5.4 Impinger samples: Measure and record the solution volume of each sample using individual graduated cylinders.

3.6. Analysis

3.6.1. Pipette or pour a 0.5- to 0.6-mL portion of each standard or sample solution into separate automatic sampler vials. Place a filtercap into each vial. The large filter portion of the cap should face the solution.

3.6.2. Load the automatic sampler with labeled samples, standards, and blanks.

3.6.3. Set up the ion chromatograph in accordance with the SOP (5.13).

Note: An SOP is a written procedure for a specific instrument. It is suggested that SOPs be prepared for each type of instrument used in a lab to enhance safe and effective operation.

Typical operating conditions for a Dionex 4000i or 4500i with a PED and an automated sampler are listed below:

Ion Chromatograph

Eluent: 0.02 M NaNO₃
 Column temperature: ambient
 Anion precolumn: AG5
 Anion separator column: AS5
 Amperometry Output range: 0.1 μA
 Sample injection loop: 50 μL

Pump

Pump pressure: ≈900 psi
 Flow rate: 2 mL/min

Chromatogram

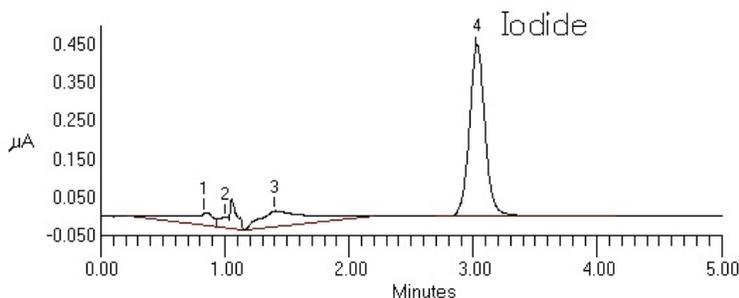
Run time: 5 min
 Peak retention time: ≈3.00 min for I⁻

3.6.4 Follow the SOP for further instructions regarding analysis (5.13).

3.7 Calculations

3.7.1 After the analysis is completed, retrieve the peak areas or heights. Obtain hard copies of chromatograms from a printer. An example chromatogram of a solid sorbent sample collected at an iodine concentration of approximately 2 × PEL for 5 min is shown below:

Pk. Num	Ret Time	Component Name	Concentration	Height	Area
1	0.83		0.000	33671	638475
2	1.00		0.000	28118	423885
3	1.40		0.000	41691	1158425
4	3.02	IODIDE	1.779	431769	3964487



3.7.2 Prepare a concentration-response curve by plotting the peak areas or peak heights versus the concentration of the I⁻ standards in μg/mL.

3.7.3 Perform a blank correction for each IABC front and backup section. Subtract the μg/mL I⁻ blank value (if any) from each sample reading if blank and sample solution volumes are the same. If a different solution volume is used, subtract the total μg blank value from each total μg sample value.

3.7.4 Calculate the air concentration of I₂ (in ppm) for each air sample:

$$A = (\mu\text{g/mL I}^-) \times (\text{Sol Vol}) \times (\text{GF})$$

$$\text{ppm I}_2 = \frac{(A) \times (\text{Mol Vol})}{(\text{AV}) \times (\text{Mol Wt})}$$

where:

$A = \mu\text{g I}_2$

$\mu\text{g/mL } f = \text{Amount found (from calibration curve)}$

$\text{Sol Vol} = \text{Solution volume (mL) from Section 3.5.3 (or 3.5.4)}$

$GF = \text{Gravimetric factor} = 3\text{I}_2/5\text{I} = 6/5 = 1.2$

$\text{Mol Vol} = \text{Molar volume (L/mol)} = 24.45 \text{ (25 }^\circ\text{C and 760 mmHg)}$

$\text{AV} = \text{Air volume (L)}$

$\text{Mol Wt} = \text{Molecular weight for I}_2 = 253.8 \text{ (g/mol)}$

3.8 Reporting Results

Add the backup section ppm I₂ result (if any) to the front section result for each IABC sample. Report results to the industrial hygienist as ppm I₂.

4. Backup Data

This method has been validated for a 2.5-L, 5-min sample taken at a flow rate of 0.5 L/min. The method validation was conducted near the OSHA Ceiling PEL of 0.1 ppm I₂. The sampling media used during the validation consisted of two-section tubes packed with 100-mg of IABC for the front and 50 mg for the backup sections. Tubes were obtained commercially from SKC (Lot no. 810, Cat. no. 226-80, SKC Inc., Eighty Four, PA).

The validation consisted of the following experiments and discussion:

1. An analysis of 20 spiked samples was performed (7 samples each at 2 × and 1 ×, and 6 samples at 0.5 × the Ceiling PEL) to evaluate desorption efficiency (DE).
2. A sampling and analysis of 18 samples (6 samples each at 2 ×, 1 ×, and 0.5 × Ceiling PEL) collected from dynamically generated test atmospheres at 50% RH to determine bias and overall error.
3. A determination of the sampling media collection efficiency at approximately 2 × Ceiling PEL).
4. A determination of potential breakthrough.
5. An evaluation of storage stability at room (20 to 25 °C), refrigerator (0 to 4 °C), and freezer (-10 to -14 °C) temperatures for 80 collected samples.
6. A determination of any significant effects on results when sampling at different humidities.
7. A determination of the qualitative and quantitative detection limits for I₂.
8. Comparison of sampling methods: IABC versus Impinger.
9. Evaluation of a prefilter/cassette assembly and a modified sampling tube for use during sampling.
10. Evaluation of the previous OSHA sampling device, an impregnated charcoal sampling tube (SKC, Lot 411, Cat. No. 226-67).
11. Confirmation of iodine using the disproportionation product iodate (IO₃⁻).
12. A determination of the qualitative and quantitative detection limits for IO₃⁻.
13. Summary.

A generation system was assembled, as shown in Figure 1, and used for all experiments except the analysis and detection limit determinations. All samples were analyzed by IC-PED. All known concentrations of generated test atmospheres were calculated from the I₂ diffusion rate.

All results were calculated from concentration-response curves and statistically examined for outliers. In addition, the analysis (Section 4.1) and sampling and analysis results (Section 4.2) were tested for homogeneity of variance. Possible outliers were determined using the Treatment of Outliers Test (5.14). Homogeneity of variance was determined using Bartlett's test (5.15). Statistical evaluation was conducted according to the Inorganic Methods Evaluation Protocol (5.16). The overall error (OE) (5.16) was calculated using the equation:

$$OE_i\% = \pm(|bias_i| + 2CV_i) \times 100\% \text{ (at the 95\% confidence level)}$$

where i is the respective sample pool being examined.

Block Diagram of the Laboratory Generation System

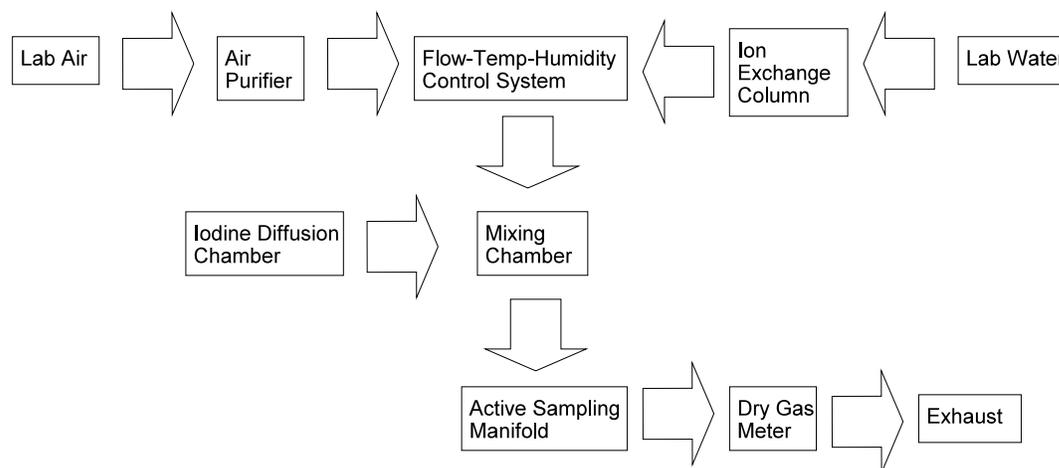


Figure 1

4.1 Spiked Sample Analysis

Twenty samples were prepared by adding known amounts of I^- (as KI) stock solution to the IABC tubes to determine desorption efficiencies (DEs) for the analytical portion of the method.

4.1.1 **Procedure:** Sampling tubes containing IABC were spiked using a 25- μ L syringe (Hamilton Microliter/Gastight Syringe, Hamilton Co., Reno, NV). Spikes were 2.25, 4.50, and 9.00 μ g I^- . These levels correspond approximately to 0.5, 1, and 2 \times the Ceiling PEL for a 5-L air sample collected at a 0.5-L/min flow rate. [Note: 5 L (10-min sample) was used as an intermittent point between a 5 to 15-min sample. The spiked sample analysis test is conducted first to determine analytical merits of the method. It was unknown whether this method could collect iodine as a 5-min sample when this test was conducted and 10-min was chosen from past experience.]

4.1.2 **Results:** Desorption efficiencies are presented in Table 1. As shown, the average DE is very close to 1.0. No DE corrections are necessary for I_2 collection using IABC tubes.

Table 1
Iodine (as I^-) Analysis - Desorption Efficiency (DE)

Level	N	Mean DE	SD	CV ₁
0.5 \times PEL	6	1.048	0.072	0.069
1 \times PEL	7	0.997	0.017	0.017
2 \times PEL	7	1.001	0.023	0.023
All Levels	20	1.015	0.042	0.041*

* = CV₁ (pooled)

4.2 Sampling and Analysis

To determine the precision and accuracy of the method, known concentrations of I_2 were generated, samples were collected and then analyzed.

4.2.1 Procedure:

a) Test atmospheres of I₂ were generated using a permeation/diffusion chamber (Model 450 Dynacalibrator, Metronics, Santa Clara, CA) and a dynamic generation system. To generate I₂ vapor, I₂ resublimed crystal was placed in a diffusion tube, and heated to 70 ± 0.1 °C. The I₂ vapor was diluted with filtered, humidified air using the system shown in Figure 1 and as discussed below.

b) Dynamic generation system

A Miller-Nelson Research Inc. flow, temperature, and humidity control system (Model HCS-301, Monterey, CA) was used to control and condition the dilution airstream. All generation system fittings and connections were Teflon. The I₂ concentrations were varied by adjusting the dilution airstream volume. The dilution airstream was adjusted using the mass flow controller of the Miller-Nelson system. For this experiment, the system was set to generate test atmospheres at 50% RH and 25 °C.

c) The total flow rate of the generation system was measured using a dry test meter.

d) Solid-sorbent samples were taken from the sampling manifold using constant-flow pumps. Gilian Gil-Air SC pumps (Gilian Instrument Corp., W. Caldwell, NJ) were used. Pump flow rates were approximately 0.5 L/min and sampling time was 5 min. Generation system concentrations were approximately 0.5, 1, and 2 times the OSHA Ceiling PEL.

4.2.2 **Results:** The results are shown in Table 2. The spiked sample (Table 1) and test atmosphere sample (Table 2) results each passed the Bartlett's test and were pooled to determine a CV_T for the sampling and analytical method.

Table 2
Iodine Sampling and Analysis - Ceiling PEL Determination

Level	N	Mean	SD	CV _s	OE (±%)
0.5 × PEL	6	0.987	0.045	0.046	10.5
1 × PEL	6	0.942	0.033	0.035	12.8
2 × PEL	6	0.997	0.043	0.043	8.90
All Levels	18	0.975	-	0.042*	10.9**

* = CV_s (pooled)

** = OE₂

The total pooled coefficients of variation (CV_T), bias, and total overall error (OE_T) are as follows:

CV_T (pooled) = 0.045; bias = -0.025; OE_T = ±11.5%

(Note: CV_T values include data from Section 4.1 and are calculated using equations specified in references 5.15 and 5.16)

4.3 Collection Efficiency

Procedure: Six commercially-prepared sampling tubes were used for collection at a concentration of approximately 2 × the OSHA Ceiling PEL for 5 min at 0.5 L/min (50% RH and 25 °C). The amounts of I₂ vapor collected in the first section (100 mg of sorbent) and second section (50 mg) were determined. The collection efficiency (CE) was calculated by dividing the amount of I₂ collected in the first section by the total amount of I₂ collected in the first and second sections.

Results: The results in Table 3 show a CE of 100%. No I₂ was found in the second sorbent section for the CE experiment and indicates the sorbent can adequately collect iodine near the PEL.

Table 3
Collection Efficiency
(2 × PEL, 25 °C & 50% RH)

Sample No.	ppm I ₂ First Section	ppm I ₂ Second Section	% Collection Efficiency

1	0.201	ND	100.0
2	0.185	ND	100.0
3	0.194	ND	100.0
4	0.210	ND	100.0
5	0.192	ND	100.0
6	0.196	ND	100.0

- Notes: (a) Sampled at approximately 0.5 L/min for 5 min.
(b) Samples desorbed using a sample solution volume of 3.0 mL
(c) ND = None detectable (<0.0004 ppm I₂)

4.4 Breakthrough

(Note: Breakthrough is defined as >5% loss of analyte through the sampling media at 50% RH)
Procedure: The same procedure as the CE experiment (Section 4.3) was used with two exceptions: The generation concentration was increased to a level approximately 7 × the Ceiling PEL, and samples were taken at approximately 0.5 L/min for 30 min.

The amount of breakthrough for each sampling tube was calculated by dividing the amount collected in the second section by the total amount of I₂ collected in the first and second sections.

Results: No breakthrough of I₂ into the second section was found, and indicates the sorbent has adequate retention of iodine at concentrations higher than expected in industrial workplaces. Results are shown in Table 4.

Table 4
Breakthrough Study
(25 °C and 50% RH)

Sample No.	ppm I ₂		% Collection Efficiency
	First Section	Second Section	
1	0.201	ND	0
2	0.185	ND	0
3	0.194	ND	0
4	0.210	ND	0
5	0.192	ND	0
6	0.196	ND	0

- Notes: (a) Sampled at approximately 0.5 L/min for 30 min
(b) Due to the large concentration generated and the analytical sensitivity, the front IABC sections of sampling tubes were desorbed using larger sample solution volumes of 20.0 mL. The 2nd sections were desorbed using the recommended volume of 3 mL.
(c) ND = None detectable (<0.0004 ppm I₂)

4.5 Storage Stability

Procedure: Two tests were conducted to assess storage stability. The first was a preliminary study of room temperature storage (20 to 25 °C) after I₂ collection. Twenty-four samples were taken near the OSHA Ceiling PEL of 0.1 ppm. After collection, all samples were stored under normal laboratory conditions (20 to 25 °C) on a lab bench and were not protected from light. Six samples were initially desorbed and analyzed, then six samples were desorbed and analyzed after various periods of storage (5, 15, and 30 days).

In order to assess if sample storage is temperature-dependent for iodine samples, an additional test was conducted to determine if refrigeration could improve recoveries. This test was conducted by generating 56 samples, including 6 control samples (used for day 0). The samples were separated into 3 groups, consisting of 5 or 6 samples per storage period. A group was stored at either room (20 to 25 °C), refrigerator (0 to 4 °C), or freezer (-10 to -14 °C) temperatures. The same analytical procedure as the previous storage test was used. Samples were analyzed after 0, 5, 15, and 29 days.

Results: As shown in Table 5a, the results of the preliminary test conducted at room temperature show the mean of samples analyzed after 30 days displayed a 12% loss when compared to the value of day 0.

Table 5a - Preliminary Test

Storage Stability - Iodine (1 × PEL, 25 °C, and 50% RH)

Day	N	Mean	SD	CV	Recovery (%)
0	5	0.114	0.005	0.045	99.1
5	6	0.109	0.004	0.037	94.8
15	6	0.096	0.007	0.073	83.5
30	6	0.100	0.003	0.027	87.0

Table 5b shows the results of the second study at different temperatures. The recovery shows 9.5% less of the value of day 0 after a 29-day storage at room temperature, and losses of 15.5% and 14.7% at refrigerator and freezer temperatures, respectively. Therefore, an improvement in recoveries was not noted when samples are stored at reduced temperatures. A significant reduction in recovery over 30 days was not noted using the previous charcoal treated sampling media in OSHA Method No. ID-177 (5.4) or in the bicarbonate/carbonate solutions used as impinger collection or as analytical standards. The carbon bead used for this collection procedure appears to be responsible for the loss and further work will have to be performed to determine the extent and mechanism.

Table 5b - Storage Stability
Room, Refrigerator, and Freezer Temperatures
(Known I₂ Concentration = 0.116 ppm at 50% RH)

Day	Temperature	N	Mean	SD	CV	Recovery (%)
0	Room	6	0.114	0.003	0.025	98.3
5	Room	5	0.109	0.009	0.081	94.0
	Refrigerator	5	0.109	0.008	0.075	94.0
	Freezer	5	0.108	0.007	0.063	93.1
	Room	6	0.101	0.008	0.074	87.1
15	Refrigerator	5	0.102	0.004	0.042	87.9
	Freezer	5	0.101	0.003	0.034	87.1
	Room	6	0.103	0.004	0.035	88.8
29	Refrigerator	6	0.096	0.004	0.047	82.8
	Freezer	6	0.097	0.008	0.086	83.6
	Room	6	0.103	0.004	0.035	88.8

Figure 2 shows results from both studies and linear curve fits of the recovery data over time. The loss over time shows that samples should be analyzed as soon as possible, preferably within 1 or 2 weeks after sampling.

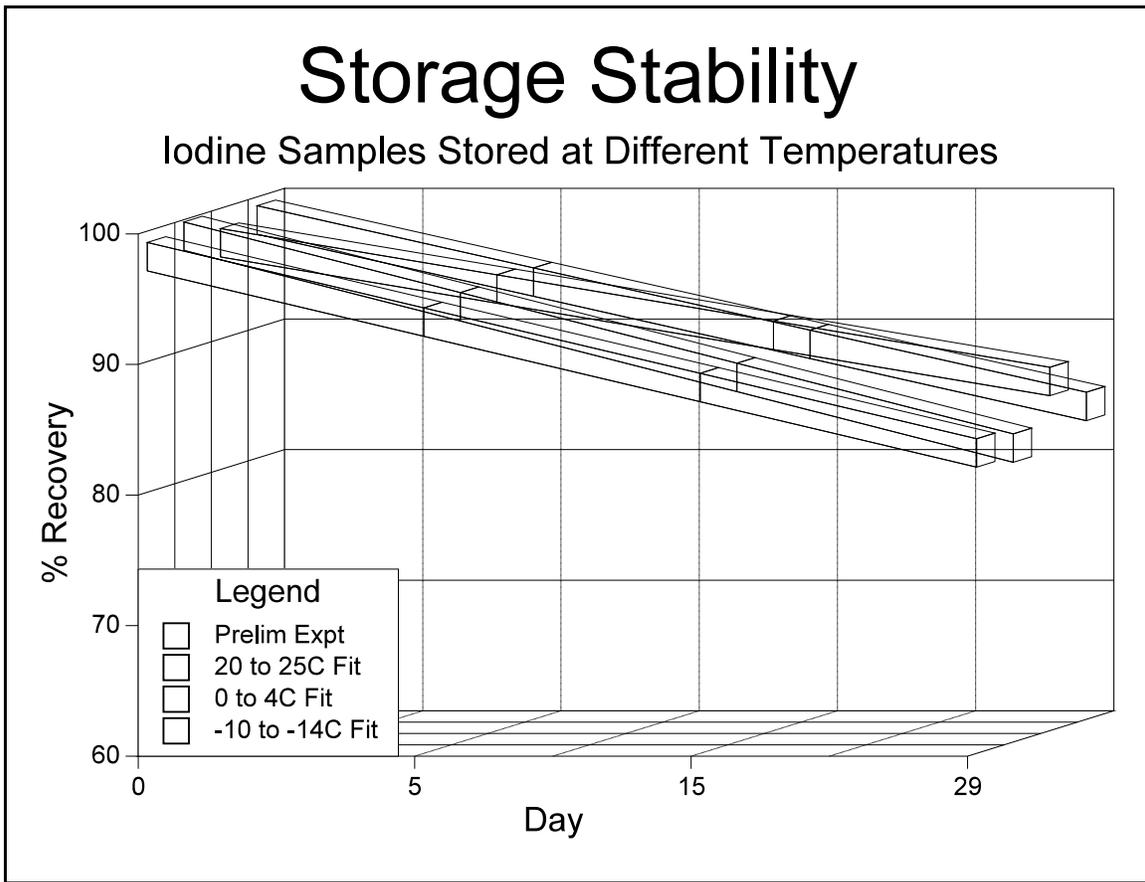


Figure 2

4.6 Humidity Study

Procedure: A study was conducted to determine any effect on results when samples are collected at different humidities. Samples were taken using the generation system and procedure described in Section 4.2. Test atmospheres were generated at 25 °C and at approximately 0.5, 1, and 2 × the OSHA Ceiling PEL. Relative humidities of 25%, 50%, and 80% were used at each concentration level tested. All tests were conducted by taking IABC samples side-by-side with impinger samples containing an aqueous collecting solution mixture of 1.5 mM Na₂CO₃ and 1.5 mM NaHCO₃. Impingers were used at first instead of bubblers to minimize any back pressure which could result from sampling rates of approximately 1 L/min and dual sampling trains. Two impingers in series were thought to be necessary for iodine collection; however, after a few experiments it was determined iodine collection efficiency using one impinger was adequate.

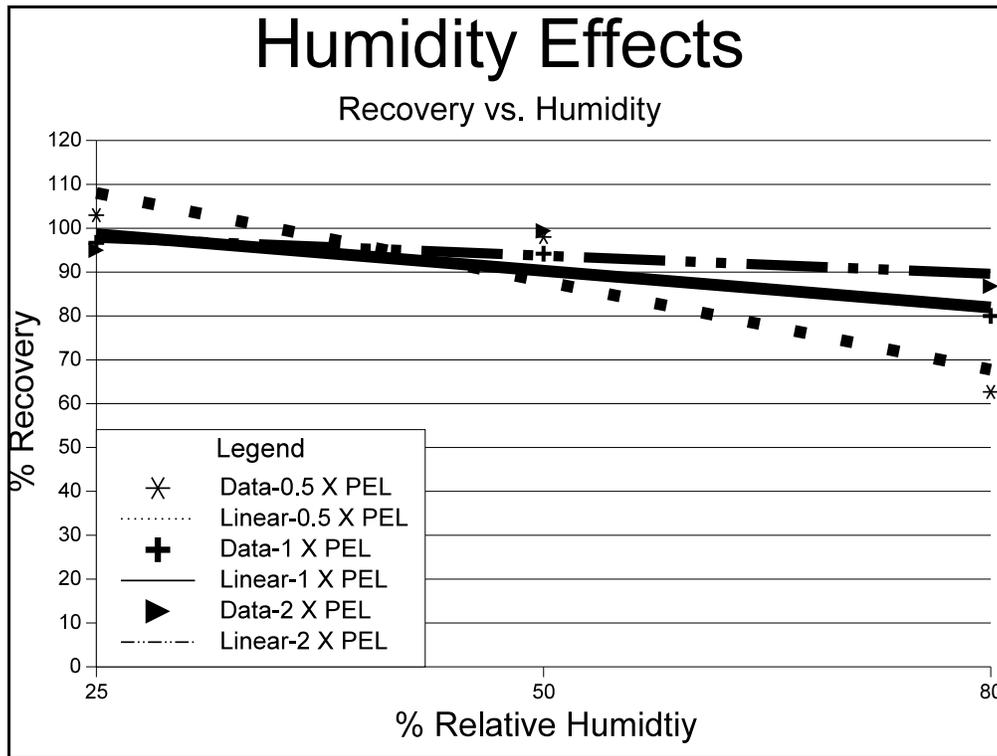


Figure 3

Results: Results of the humidity tests are listed in Table 6 (results of impinger samples taken at 80% RH are also shown for comparison) and shown in Figures 3 through 5. An F test was used to determine if any significant effect occurred when sampling at different RHs. As shown, at the 99% confidence level, the calculated F values are larger than critical F values (5.16) for all the concentrations tested, and a significant difference in results occurred across the RH ranges tested. Figures 3 and 5 show a dependence on RH occurs and samples collected at higher RHs tend to display lower recoveries.

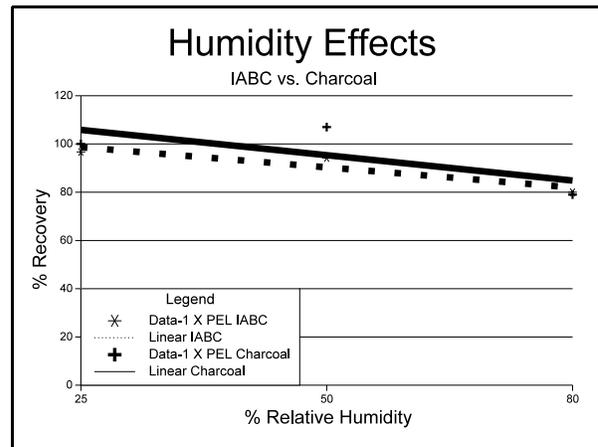


Figure 4

The loss over humidity levels appears to follow a linear trend as shown in Figures 3 and 4. Figure 4 shows an almost identical loss occurs when using the treated charcoal sampler listed in OSHA Method No. ID-177 (5.4). A dependence on concentration is also readily apparent when examining the recoveries for Figure 5. This loss versus concentration appears to follow a logarithmic function (concentrations above 2 x PEL are extrapolated). Loss of iodine is more readily evident at low concentration and high RHs than higher concentrations and high RHs. The lower recoveries were not readily evident at low concentrations when samples were collected in impingers containing

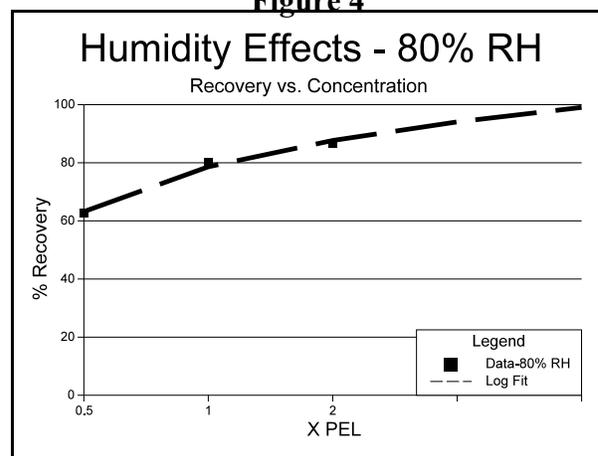


Figure 5

weakly basic solutions. Tests were not conducted above 80% RH due to difficulties associated with generating higher humidity levels in the laboratory. It is unknown what losses will occur at RH levels above 80%. If low concentration and high humidity situations are anticipated ($\geq 50\%$ RH) prior to sampling, sample collection using impingers will give increased recoveries; however, the inconvenience of collection using these devices is a serious disadvantage.

Although impingers were used for this test, bubblers will most likely give better results than impingers due to increased dispersion of the sample into the bubbler solution. The increased collection efficiency of bubblers over impingers for the same substance and collection solution has been demonstrated in previous studies of formaldehyde (5.18). As previously discussed in Section 1, two stopgap methods were developed using bubblers containing basic collection solutions. Adequate recoveries were noted using this approach. Further testing of bubblers may be necessary to demonstrate improved collection of iodine over impingers.

Table 6
Humidity Test - Iodine - 25 °C

Level	% RH	N	Mean	SD	CV	Taken	Recovery (%)	F _{crit}	F _{calc}
0.5 × PEL	25	6	0.063	0.008	0.134	0.061	103	6.36	33.5
	50	6	0.049	0.002	0.046	0.050	98.0		
	80	6	0.037	0.005	0.129	0.059	62.7		
	80*	3	0.058	0.005	0.086	0.061	95.1		
1 × PEL	25	6	0.116	0.006	0.050	0.120	96.7	6.52	10.5
	50	5	0.113	0.004	0.039	0.120	94.2		
	80	6	0.092	0.014	0.152	0.115	80.0		
	80*	3	0.109	0.002	0.018	0.115	94.8		
2 × PEL	25	6	0.210	0.014	0.068	0.221	95.0	6.36	14.0
	50	6	0.196	0.009	0.043	0.197	99.4		
	80	6	0.184	0.008	0.042	0.212	86.8		
	80*	3	0.183	0.004	0.022	0.212	86.3		

*Samples were taken with impingers containing collecting solution (1.5 mM Na₂CO₃/NaHCO₃), which was same as desorbing solution used in preparing working standards (see Section 3.4).

4.7. Qualitative and Quantitative Detection Limit Study

A modification of the National Institute for Occupational Safety and Health (NIOSH) detection limit calculations (5.19, 5.20) was used to calculate detection limits.

Note: For this experiment, a comparison of samples with and without the sampling media present was used to determine limits, and a separate recovery study was not conducted as mentioned in the NIOSH protocol. The recovery study was not conducted so as not to confound the difficulty of generating very low concentration samples with the comparison of spiked samples with and without the sampling media.

Procedure: Two sets of low concentration samples were prepared by spiking desorbing solutions (Section 3.3.2) with aliquots of aqueous standards prepared from KI (Section 3.3.4.) at five different concentrations. One set of samples was spiked at five different levels without the IABC sorbent present while the other set included IABC in each solution prior to spiking. Both sets of samples were analyzed using a 50- μ L sample injection loop and a PED setting of 0.1 μ A.

Results: The IABC spiked sample results are shown in Table 7 for qualitative and quantitative detection limits, respectively. Both sets of samples gave virtually identical detection limits, indicating in this case, sampling media did not have a significant effect on the detection limit. The qualitative detection limit is 0.003 μ g/mL as I⁻ at the 99.8% confidence level. The quantitative detection limit is 0.009 μ g/mL as I⁻. Using a 2.5-L air volume and a 3-mL sample solution volume, the qualitative and quantitative detection limits are 0.0004 ppm and 0.001 ppm, respectively as I₂.

Table 7
Qualitative and Quantitative Detection
Limits
I₂ (as μ g/mL, I⁻) Level

Sample No.	0.002 PA	0.005 PA	0.010 PA	0.020 PA
1	3244	5918	18190	36081
2	3501	9682	18624	37305
3	2598	6929	20428	35622
4	3002	10842	20398	38262

PA = Integrated Peak Area (as I⁻)

The blank and 0.001 µg/mL integrated peak areas were all equal to zero.

The response of the low-level calibration samples were plotted to obtain the linear regression equation ($Y = mX + b$), and the predicted responses (\hat{Y}_i) at each X.

Using the equations:

$$S_y = [\sum(\hat{Y}_i - Y_i)^2 / (N - 2)]^{1/2}$$

$$Q1 = (3S_y + B - b) / m$$

$$Q2 = 3.33 Q1$$

where:

B = the mean blank response

b = intercept of the regression

m = analytical sensitivity or slope as calculated by linear regression

S_y = the standard error of the regression

N = the number of data points

Q1 = qualitative detection limit

Q2 = quantitative detection limit

$$B = 0; b = -546.3833; m = 1,887,623; S_y = 1,496; N = 16 \text{ and } Y = b + mX = -546.3833 + 1,887,623X$$

Therefore,

$$Q1 = (3S_y + B - b) / m = 2.667 \times 10^{-3} \mu\text{g/mL as I}^-$$

$$Q1 \Rightarrow 8.00 \times 10^{-3} \mu\text{g as I}^- \text{ (3-mL sample volume).}$$

$$Q1 \Rightarrow 3.70 \times 10^{-4} \text{ ppm I}_2 \text{ (2.5-L air volume).}$$

$$Q2 = 3.33 Q1 = 1.23 \times 10^{-3} \text{ ppm I}_2 \text{ (2.5-L air volume).}$$

Using the International Union of Pure and Applied Chemistry (IUPAC) approach as discussed in prior methods (5.20) gave a detection limit (Q2) of 5.5×10^{-4} ppm I₂ when using the data presented above.

4.8 Comparison of Sampling Methods

Procedure: In order to compare the performance of this method, the IABC and impinger samples were collected side-by-side from the generation system at approximately 1 × PEL. The impinger collection solution is specified in Section 4.6. All samples were analyzed by IC-PED.

Results: Table 8 shows the results of comparison study. As shown, the IABC and impinger results are in good agreement.

Table 8
Comparison Study - IABC vs Impinger
(Known Concentration = 0.115 ppm I₂) (25°C, and 50% RH)

	N	Mean	SD	CV	Recovery, %
IABC	6	0.113	0.004	0.035	98.3
Impinger	6	0.111	0.002	0.019	96.5

- Notes:
- Sampling Time = 5 min
 - Flow Rate = 0.525 L/min for IABC samples.
= 0.942 L/min for impinger samples.
 - Sample solution volume for desorbing IABC samples = 3.0 mL
Sample solution volume for impinger samples = 10.0 mL

4.9 Evaluation of a Prefilter and a Modified Sampling Tube

As previously discussed, particulate iodide compounds may interfere with the determination of iodine in workplace atmospheres. Past research regarding aerosols (5.21) has indicated that particulate in the air sampled may penetrate any glass wool plugs and the sorbent when using conventional sampling tubes. Different types of prefilters have been used to assist in capturing particulate before entry into the sampling tube. A study was conducted to evaluate the possibility of I₂ reacting with a prefilter/cassette or a MST device to capture iodides or other particulate.

Procedure: Evaluations were performed using either IABC sampling tubes with prefilter sampling assemblies (5-μ pore size, 25-mm diameter PVC filter/carbon-filled polypropylene cassette), or MSTs with Teflon filter [similar to Type II tubes for SO₂ (OSHA Method No. ID-200) without polyurethane foam] for particulate and vapor collection.

A test was conducted by taking six IABC samples without prefilters side-by-side with six IABC samples connected to prefilters. Another test was performed by taking six IABC samples side-by-side with six MSTs. All samples were taken at a flow rate of about 0.5 L/min for 5 min. The generation system concentration was approximately at the Ceiling PEL for iodine.

Results: The results of the comparison of IABC samples taken, with and without prefilters, and MSTs are displayed in Table 9. As shown, a difference in the amount of I₂ collected was noted between the prefilter/IABC and IABC, and not noted between MST and IABC. The PVC prefilter/cassette does appear to slightly react with I₂ when using the sampling conditions stated in Section 2. The PVC filter/cassette assembly is not recommended for particulate sample collection when also sampling I₂. The MST device may be used for collection of I₂. Glass wool is used for separation in the sampling tube rather than foam. Some foams will absorb or react with iodine and subsequently contribute to lower recoveries.

Table 9
Comparison Study - Known Concentration = 0.105 ppm I₂
With/Without Prefilter and Modified Sampling Tube (25 °C and 50% RH)

	N	Mean	SD	CV _s	Recovery, %
IABC (WOPF)	6	0.103	0.004	0.036	98.1
IABC (WPF)	6	0.077	0.004	0.050	73.3
MST	6	0.100	0.005	0.054	95.2

Notes:

- (a) IABC (WOPF) = Impregnated activated beaded carbon without a prefilter/cassette assembly.
IABC (WPF) = Impregnated activated beaded carbon with a prefilter/cassette assembly.
MST = Modified sampling tube as described in Section 2.1.6.
- (b) The MST device: The dimensions of the front portion of the glass jacket are 12-mm o.d., 10-mm i.d., and 25-mm long and is used to retain the Teflon particulate-collecting filter. The second part of the glass tube contains the two sorbent sections for I₂ collection (100 mg IABC front and 50 mg backup). The dimensions of the second part are 6-mm o.d., 4-mm i.d., and 50-mm long. After sampling, both sampling tube ends are sealed with plastic caps.
- (c) Teflon prefilter analyzed after sampling contained 0.008 ± 0.001 ppm as I₂.
- (d) Sampling Time = 5 min
Flow Rate = 0.526 to 0.544 L/min
- (e) Sample Solution Volume for Desorption = 3.0 mL

4.10 Evaluation of Impregnated Charcoal Sampling Tube (OSHA Method No. ID-177) vs. the IABC tube

Procedure: A side-by-side test using the previous OSHA sampling device for I₂ was conducted. The prior device was a glass tube containing base-impregnated charcoal (SKC Inc., Cat. No. 226-67) and glass wool plugs. Lot number 411 was chosen for the test. The I₂ vapor was collected by taking six impregnated charcoal sampling tubes (ICST) side-by-side with six IABC tubes using the generation system and sampling conditions are stated as follows for both sampling media:

- (a) Sampling Time = 15 min
- (b) Flow Rate = 0.526 to 0.544 L/min
- (c) Desorption Vol = 3.0 mL

Results: Results are listed in Table 10. As shown, the average blank value for SKC lot no. 411 contains 5.50 μg of I₂. This is equivalent to 0.21 ppm of I₂ if a 2.5-L air volume is used in

calculations, and indicates serious contamination of this lot. Table 10 also shows results of I₂ collected in these tubes with/without blank correction.

Table 10
Evaluation of Impregnated Charcoal Sampling Tube
(Known Concentration = 0.105 ppm I₂)
(25 °C and 50% RH)

	N	Mean	SD	CV	Recovery, %
ICST (BT)	6	5.50 µg	0.37 µg	0.067	-
ICST (WOBC)	6	0.162 ppm	0.010 ppm	0.060	154.3
ICST (WBC)	6	0.096 ppm	0.010 ppm	0.107	91.4
IABC (BT)	6	ND	-	-	-
IABC	6	0.103 ppm	0.004 ppm	0.036	98.1

- Notes: (a) ICST (BT) = Blank Impregnated Charcoal Sampling Tube
 (b) ICST (WOBC) = Impregnated Charcoal Sampling Tube without blank correction.
 (c) ICST (WBC) = Impregnated Charcoal Sampling Tube with blank correction.
 (d) IABC (BT) = Blank Impregnated Activated Beaded Carbon tube
 (e) ICSTs were taken from SKC lot 411.
 (f) ND = None detectable (<0.01 µg I₂)

As shown, the IABC and impregnated charcoal recoveries are similar, provided blank corrections are made to the impregnated charcoal results.

4.11 Confirmation of I₂ from IO₃⁻ Peak

The collected I₂ is converted to I⁻ and IO₃⁻ by the IABC sorbent as shown by the chemical reaction discussed in Section 1.2. If IO₃⁻ can also be analyzed, additional evidence of the presence of I₂ can be obtained.

Procedure: A previous analysis using IC has demonstrated that the IO₃⁻ peak had interferences, presumably from the KOH used to impregnate the sorbent, and from other anions, such as fluoride (F⁻), and chlorite (ClO₂⁻). To analyze IO₃⁻, an alternate analytical procedure was used to minimize interference problems. In order to demonstrate the disproportionation product IO₃⁻, I₂ samples were prepared by dissolving small amounts of pure I₂ (U.S.P., J.T. Baker Chemical Co., NJ) in the collecting solution (1.5 mM Na₂CO₃ and 1.5 mM NaHCO₃). Two different detectors (conductivity or UV) were tried for analysis of IO₃⁻. Samples were analyzed for IO₃⁻ using each detector separately.

Typical operating conditions for a Dionex 4000i or 4500i with a conductivity or UV detector and an automated sampler are listed below:

Ion Chromatograph - IO₃⁻ Analysis

Eluent: 1.0 mM Na₂CO₃/1.0 mM NaHCO₃
 Column temperature: ambient
 Anion precolumn: AG5
 Anion separator column: AS5
 Anion self-regeneration suppressor: ASRS-1 (4 mm)*
 Conductivity output range: 1 µS*
 UV output range: 0.1 AU**
 Wavelength: 200 nm**
 Rise time: 5.0 s**
 Sample injection loop: 50 µL

*Conductivity detector only

**UV detector only

Pump - IO₃⁻ Analysis

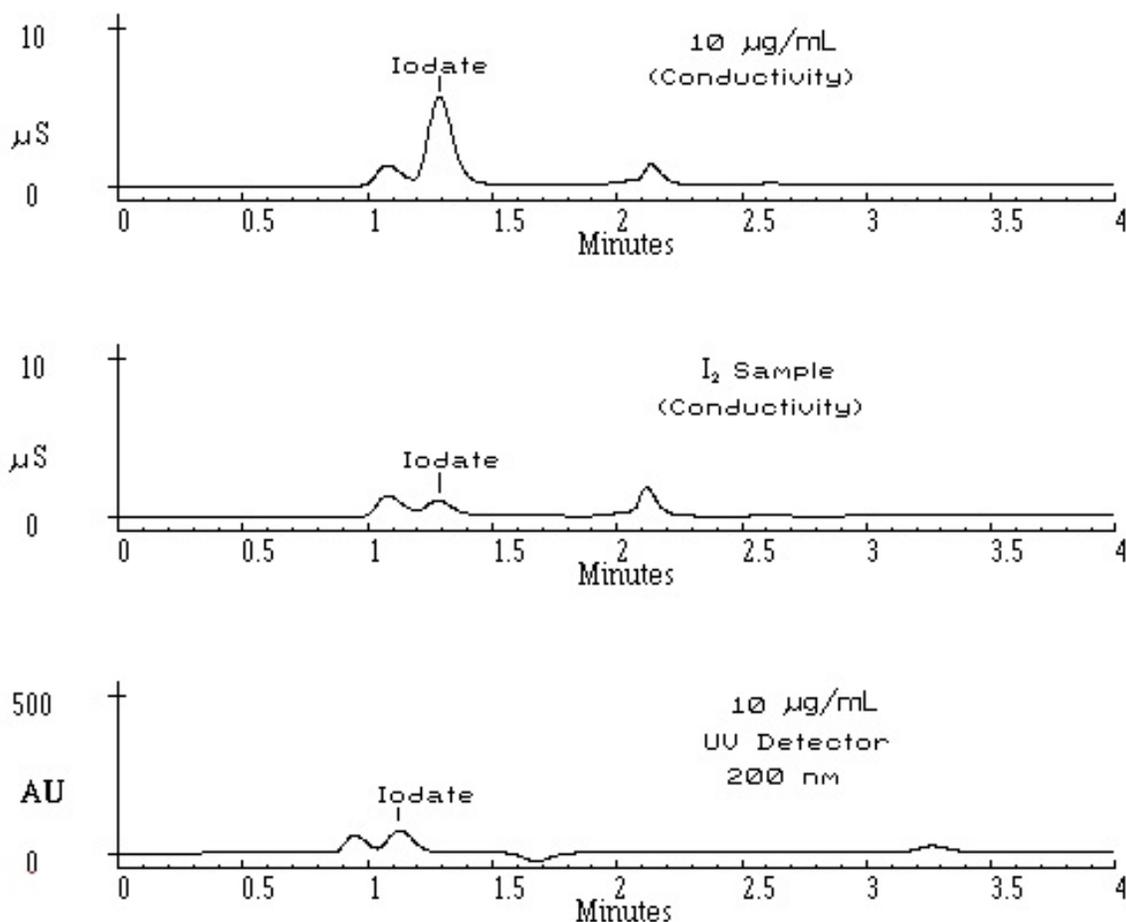
Pump pressure: ~900 psi
 Flow rate: 2 mL/min

Chromatogram - IO₃⁻ Analysis

Run time: 4 min

Peak retention time: ≈ 1.2 min for IO_3^- .

Results: A $10 \mu\text{g/mL}$ IO_3^- standard and an I_2 sample using conductivity and UV detectors are presented in Figure 3.



µS = MicroSiemens
AU = Absorbance Unit

Figure 3

The preliminary determination of IO_3^- using either detector appears satisfactory; however low sensitivity for IO_3^- was evident. A further study to determine detection limits was also conducted as discussed in Section 4.12.

4.12 Qualitative and Quantitative Detection Limit Study for Iodate

Procedure: Low concentration samples of IO_3^- were prepared by spiking desorbing solutions (Section 3.3.2) with aliquots of aqueous standards prepared from KIO_3 (Section 3.3.6). These samples were analyzed using a $50\text{-}\mu\text{L}$ sample injection loop and a conductivity detector setting of 0.1 MicroSiemens (μS). The modified NIOSH method previously discussed in Section 4.7 was used.

Results: The results are shown in Table 11 for qualitative and quantitative detection limits, respectively. The qualitative detection limit is $1.01 \mu\text{g/mL}$ as IO_3^- at the 99.8% confidence level. The quantitative detection limit is $3.36 \mu\text{g/mL}$ as IO_3^- . Using a 2.5-L air volume and a 3-mL sample solution volume, the qualitative limit is 0.17 ppm and the quantitative limit is 0.57 ppm as I_2 .

Table 11
Qualitative and Quantitative Detection Limits

Sample No.	IO ₃ ⁻ Level		
	1.0 µg/mL PA	2.0 µg/mL PA	3.0 µg/mL PA
1	7.73	20.36	34.02
2	7.65	23.77	31.51
3	7.42	16.63	32.85
4	11.74	20.68	27.65
5	6.21	17.09	30.25
6	10.68	18.02	37.92

PA = Integrated Peak Area (IO₃⁻)/10,000

The blank and 0.1, 0.2 and 0.5 µg/mL integrated peak areas, and their standard deviations (Std Dev) were all equal to zero.

The response of the low-level calibration samples were plotted to obtain the linear regression equation ($Y = mX + b$), and the predicted responses (\hat{Y}_i) at each X.

Using the equations:

$$S_y = [\sum(\hat{Y}_i - Y_i)^2 / (N - 2)]^{1/2}$$

$$Q1 = (3S_y + B - b) / m$$

$$Q2 = 3.33 Q1$$

Therefore,

$$Q1 = (3S_y + B - b) / m = 1.01 \mu\text{g/mL as IO}_3^-$$

$$Q1 \Rightarrow 3.04 \mu\text{g as IO}_3^- \text{ (3-mL sample volume).}$$

$$Q1 \Rightarrow 0.17 \text{ ppm I}_2 \text{ (2.5-L air volume).}$$

$$Q2 = 3.33 Q1 = 0.57 \text{ ppm I}_2 \text{ (2.5-L air volume).}$$

The ability to confirm the presence of I₂ using IO₃⁻ is compromised by the low sensitivity noted here. If there is sufficient quantity of I₂ in the collected air samples, the IO₃⁻ analysis using the conditions specified in Section 4.11 can be used. Samples could be taken for longer periods of time to collect sufficient amounts of IO₃⁻ for detection; however, this would defeat the monitoring criteria that iodine is regulated as a Ceiling unless separate short- and long-term samples are taken. Also, if a bulk material is available, the I₂ content could also be examined by assessing both I⁻ and IO₃⁻ results, provided there is sufficiently high concentration of I₂ in the bulk.

4.13 Summary

The validation results indicate the method meets both the NIOSH and OSHA criteria for accuracy and precision (5.15, 5.16). Performance during collection efficiency, breakthrough, and storage stability tests is adequate. Unfortunately, it appears that recovery is humidity-dependent and decreases as humidity increases. Further study is needed to determine the cause; therefore, this method is considered an interim method. The low recovery at higher RHs is similar to results found in the previous OSHA method for iodine (5.4). At higher RHs, samples can be taken using a collecting solution/impinger system, especially if low I₂ concentrations are expected; however, the inconvenience of collection is readily apparent when using bubblers. Detection limits (as I⁻) are adequate when samples are taken for 5 min at 0.5 L/min. In principle, the collected I₂ can also be calculated from an IO₃⁻ analysis using the appropriate stoichiometric factor. Unfortunately, high detection limits and interferences limit the application of the IO₃⁻ for the determination of I₂. Confirmation of I₂ can occur if concentrations exceed detection limits stated in Section 4.12 or more sensitive analytical technology is developed and used.

5. References

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Appendix

Analysis of Samples by Ion Specific Electrode (ISE)

Samples may also be analyzed by ISE or in place of IC; however, interferences particular to ISE may have to be considered. The following procedure addresses the analysis of IABC or impinger samples by ISE.

Detection Limit and Range (ISE)

1. The quantitative detection limit is 0.25 µg of iodide in a 25-mL sample solution. This corresponds to 0.004 ppm iodine for a 7.5-L air volume.
2. The range is from 0.25 µg to 0.25 g iodide based on a 25-mL solution volume. This corresponds to either 0.3 µg to 0.3 g iodine or 0.004 to 4,000 ppm iodine for a 7.5-L air volume.

Interferences [ISE - also see Iodide Ion Specific Electrode (Model 94-53a) Instruction Manual, Orion Research Inc., Boston, MA or other manufacturer instruction manuals if a different iodide electrode is used.]

1. Either sulfide and cyanide, if present in the sampled atmosphere, will give a negative interference; however, this can be resolved by adding a nickel (Ni^{2+}) solution to the samples before analysis.
2. The maximum allowable ratios of interfering ions to iodide are 1×10^6 , 5×10^3 , and 1×10^5 moles/L for chloride, bromide, and thiosulfate, respectively. These are extremely high concentrations and normally should not be seen when sampling industrial environments.
3. Iodide ions may form complexes with some metal ions which will ultimately result in lower iodide recoveries. This problem can be resolved by using a "known (standard) additions" method.

Equipment (ISE)

1. Ion Specific Electrode (ISE) and filling solution, iodide (Model 94-53a, Orion Research Inc., Cambridge, MA).
2. Single junction reference electrode and filling solution (Model 90-01, Orion Research Inc.).
3. Millivolt/pH meter, capable of relative mV, pH, standard addition or concentration measurements (Model EA 940 Expandable Ionanalyzer, Orion Research Inc.).
4. Stirrer, electronic, or magnetic with Teflon stirring bars.
5. Miscellaneous laboratory glassware: Volumetric flasks, pipettes, beakers, disposable beakers, 25-mL Erlenmeyer flasks, etc.

Reagents (ISE - All chemicals should be at least reagent grade)

Sodium nitrate (NaNO_3),
Sodium hydroxide (NaOH),
Potassium iodide (KI),
Sodium iodide (NaI)

1. Deionized water ($\text{DI H}_2\text{O}$)
2. Sodium hydroxide, 0.01 N: Dissolve 0.4 g NaOH and dilute to 1-L with $\text{DI H}_2\text{O}$.
3. Ionic Strength Adjuster (ISA) - Sodium nitrate, 5 M: Dissolve 42.5 g NaNO_3 in 100 mL $\text{DI H}_2\text{O}$.
4. Nickel (Ni^{2+}) solution, 1,000 $\mu\text{g/mL}$: A commercially prepared 1,000 $\mu\text{g/mL}$ solution of nickel common for atomic absorption purposes can be used.
5. Standard stock solution, 1,000 $\mu\text{g/mL}$ iodide: Place 1.31 g KI or 1.18 g NaI in a 1-L volumetric flask. Add about 500 mL $\text{DI H}_2\text{O}$, swirl to dissolve, and dilute to the mark with $\text{DI H}_2\text{O}$.
6. Working iodide standard solutions, 100, 10, 1, and 0.1 $\mu\text{g/mL}$: Pipette appropriate volumes of 1,000 $\mu\text{g/mL}$ stock solution into volumetric flasks and dilute to volume with 0.01 N NaOH . The 100 $\mu\text{g/mL}$ standard is used for known additions as discussed below.

Analysis (ISE - Known Additions)

Known Additions Spike Preparation:

1. Standard Spike, 100 $\mu\text{g/mL}$ is added to all samples and standards.

Note: The concentration of this spike should normally be at least 10 times the expected sample concentration. If concentrations of iodine are expected to be large ($> 10 \mu\text{g/mL}$) or small ($< 0.2 \mu\text{g/mL}$), the spike and standards used should be adjusted accordingly.

Sample Preparation: For IABC samples follow Steps 1 to 3 below. For impinger samples, follow Steps 4 and 5 only.

IABC Samples:

1. Carefully remove and discard the rear glass wool plug from each glass tube without losing any IABC sorbent.

Note: The sorbent should always be removed from the glass tube via the opposite end of collection (i.e. 50-mg IABC backup section is removed first). This will minimize the possibility of contamination from any collected particulate.

Carefully transfer each IABC section from a sample tube and place into a separate 25-mL Erlenmeyer flask or 20-mL scintillation vial.

2. Add 1 mL of 1,000 $\mu\text{g/mL Ni}^{2+}$ solution and pipette 24 mL of 0.01 N NaOH into each flask.
3. Cap tightly, shake vigorously, and allow the solution to sit for at least 1 h.

Impinger Samples Only:

4. Transfer impinger sample solutions to separate 25-mL volumetric flasks.
5. Add 1 mL of 1,000 $\mu\text{g/mL Ni}^{2+}$ solution to each flask and dilute to volume with 0.01 N NaOH.

Electrode Check:

1. Set up the mV meter and electrodes according to the manufacturers instruction manuals or Standard Operating Procedure (SOP).
2. Place 100 mL DI H_2O and 2 mL ISA (5 M NaNO_3) into a 250-mL beaker. Use the relative mV scale setting on the mV meter and then place electrodes (reference and iodide) in the solution.
3. Pipet 1.0 mL of the 1,000 $\mu\text{g/mL}$ stock I^- standard into the solution while stirring. Allow reading to stabilize, then record the mV of the solution.
4. Add 10 mL of the 1,000 $\mu\text{g/mL}$ iodide stock standard while stirring. Read the mV of the solution when stable. Correct electrode operation is indicated by a difference of 55 to 59 mV (assuming the solution temperature is between 20 to 25 $^\circ\text{C}$).

Analytical Procedure

1. If available, use a standard additions program intrinsic within the instrument to calibrate and convert readings directly to concentration values. If an automated program is not available, record the mV reading prior to standard addition (E_o) and after addition (E_s). The "standard addition" normally is a 2.5-mL aliquot of 100 $\mu\text{g/mL}$ iodide working standard (see note on previous page for information).
2. Rinse the electrodes, blot dry, and place in a 25 mL sample or working standard solution. Add 0.5 mL of ISA. Allow time for the reading (E_o) to stabilize.
3. Using a glass or automatic pipet, add 2.5 mL of the 100 $\mu\text{g/mL}$ Standard Spike, and allow time for the reading to stabilize. Take a final reading (E_s or concentration for automated programs).
4. Analyze a standard in the concentration range of the samples after every fifth or sixth sample and at the end of the analysis.

Note: The ISE can be affected by changes in temperature. Standards and samples should be at the same temperature before analyzing. Fluctuations in the ambient temperature during analysis can sometimes be compensated for by slope adjustment. Refer to manufacturer instruction manuals for further details.

Calculations (ISE)

1. Determine the total μg iodine content of each sample and blank using a concentration-response (concentration units versus μg) linear regression curve if readings were measured in concentration units. If mV readings were taken, plot the mV readings using an appropriate standard additions program. An example of equations used for standard additions can be found in ISE user manuals.

2. The concentration of iodine in the air sample is expressed in ppm:

$$\text{ppm I}_2 = \frac{(24.45)(\mu\text{g/mL Iodide})(\text{Sample Volume, mL})(\text{Mole Ratio})}{(\text{MW})(\text{Air Volume, L})}$$

where:

Sample volume	25.0 mL
Mole ratio of I ₂ to Iodide	1.2
Molecular weight (MW) of I ₂	253.8

Therefore, for a 25 mL sample volume:

$$\text{ppm I}_2 = \frac{(2.89)(\mu\text{g/mL Iodide})}{(\text{Air Volume, L})}$$