



Method number: PV2119

Target concentration: 10 ppm (25 mg/m³)

Procedure: Samples are collected by drawing a known volume of air through glass sampling tubes containing coconut shell charcoal (SKC Anasorb CSC, lot 2000). Samples are extracted with 0.01 N NaOH and analyzed by IC using a conductivity detector.

Recommended sampling time and sampling rate: 240 min at 0.2 L/min (48 L)

Reliable quantitation limit: 2.9 ppb

Status of method: Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History

The previous partially validated method for acetic acid, ID-186SG, called for collection on charcoal tubes and extraction with 1.5 mM sodium borate.¹ An extraction study of acetic acid using coconut shell charcoal (SKC Anasorb CSC, lot 2000) using 1.5 mM sodium borate had non-linear extraction efficiencies, which ranged from 99.3% for a 2.098 mg loading to 66.8% for a 0.105 mg loading. Extraction studies using 0.01 N NaOH had an average recovery of 98.6 over the range of 0.15 to 2.31 mg loading. Retention studies showed no loss of acetic acid when 48 L of humid air (~80% RH) was drawn through spiked tubes at 0.2 L/min. Storage studies showed little loss when stored for 14 days at either refrigerated or ambient temperatures.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)²

Acetic acid is a severe skin, eye and mucous membrane irritant. As an eye irritant it can cause burns, lachrymation, and conjunctivitis. Skin exposure can cause burns. Mucous membrane exposure results in burns and bleeding from ulcerations, along with nausea, vomiting and diarrhea.

1.1.3 Workplace exposure^{3,4}

Acetic acid is used as a feedstock in the production of acetates, acetyls, cellulose acetate, acetate rayon, and plastics. It is used as a laundry sour, in tanning, and printing and dyeing. It is used as an acidulant and preservative in foods and pharmaceuticals. It is used as a solvent for gums, resins, volatile oils, and other organic compounds. In 2002 4.8 billion pounds of acetic acid were produced in the US.

1.1.4 Physical properties and other descriptive information^{5,6}

CAS number:	64-19-7	IMIS:	0020 ⁷
synonyms:	glacial acetic acid; methane carboxylic acid; ethanoic acid; vinegar acid		
RTECS number:	AF1225000	molecular weight:	60.05
melting point:	16.7 °C	boiling point:	118 °C
appearance:	clear liquid	molecular formula:	C ₂ H ₄ O ₂
odor:	vinegar	flash point:	39 °C (103 °F)(cc)
autoignition		vapor	11.52 kPa or
temperature:	465 °C (869 °F)	pressure:	11.4 mm Hg @ 20 °C

¹ OSHA Sampling and Analytical Methods. <http://www.osha.gov> (accessed 6/21/02).

² Lewis, R., *Sax's Dangerous Properties of Industrial Materials*, Tenth Ed., Vol. 2, Van Nostrand Reinhold: New York, 2000, p15.

³ O'Neil, M.J., Ed, *The Merck index*, Merck & Co. Inc. Whitehouse Station, NJ, 2001, p 56.

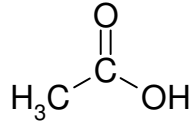
⁴ ChemExpo Chemical Profiles. <http://www.english.cornell.edu> (accessed 6/21/02).

⁵ O'Neil, M.J., Ed, *The Merck index*, Merck & Co. Inc. Whitehouse Station, NJ, 2001, p 56.

⁶ Lewis, R., *Sax's Dangerous Properties of Industrial Materials*, Tenth Ed., Vol. 2, Van Nostrand Reinhold: New York, 2000, p15.

⁷ OSHA Chemical Sampling Information. <http://www.osha.gov> (accessed 6/21/02).

solubility: water, alcohol, ether density: 1.049
 structural formula:



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"⁸. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the lowest sampler loading was 1.02 µg of acetic acid. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response for a sample blank. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and slope) for the calculation of the DLOP. The slope was 2.29×10^4 and the SEE was 783.3. The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The DLOP and RQL were 0.103 µg and 0.342 µg respectively.

Table 1.2
 Detection Limit of the Overall Procedure
 for Acetic acid

mass per sample (µg)	area counts (µV-s)
0.00	0
0.102	1449
0.204	3508
0.306	5138
0.408	7505
0.510	9314
0.612	11963
0.714	15314
0.816	17662
0.918	20064
1.02	23125

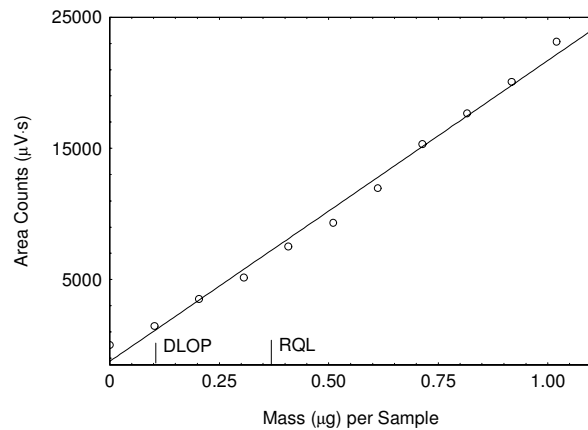


Figure 1.2.1. Plot of data to determine the DLOP/RQL for acetic acid. ($Y = 2.29 \times 10^4 X - 1240$; SEE = 783.3)

Below is a chromatogram of the RQL level.

⁸ Burrig, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

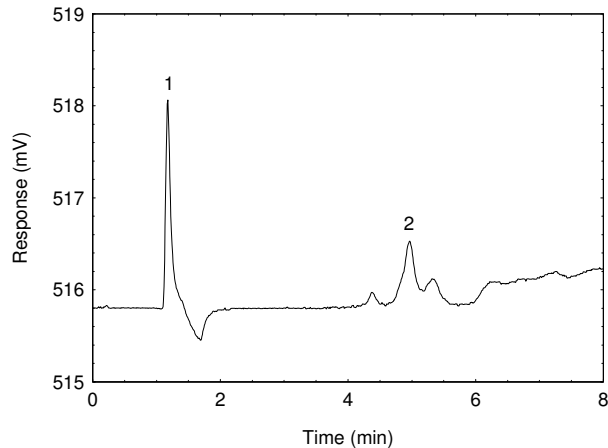


Figure 1.2.2. Chromatogram of the acetic acid standard, as the acetate ion, near the RQL. (Key: (1) water; (2) acetate ion)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

- 2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within $\pm 5\%$ of the recommended flow rate.
- 2.1.2 Samples are collected with 7-cm \times 4-mm i.d. \times 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of coconut shell charcoal, Anasorb CSC, lot 2000. The sections are held in place and separated with a glass wool plug and two urethane foam plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-01).

2.2 Reagents

None required.

2.3 Technique

- 2.3.1 Immediately before sampling, break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking ends. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.
- 2.3.2 The smaller section of the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder and tubing so they do not impede work performance or safety.
- 2.3.3 Draw the air to be sampled directly into the inlet of the tube holder. The air being sampled is not to be passed through any hose or tubing before entering the sampling tube.

- 2.3.4 After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form as soon as possible.
- 2.3.5 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.
- 2.3.6 Record sample air volumes (liters), sampling time (minutes) and sampling rate (mL/min) for each sample, along with any potential interferences on the OSHA-91A form.
- 2.3.7 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator. Ship any bulk samples separate from the air samples.

2.4 Extraction efficiency

The extraction efficiency was determined by liquid-spiking charcoal tubes, lot 2000, with acetic acid at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted for 30 minutes on the shaker, then spun down on the centrifuge at 2800 rpm for 5 minutes, and analyzed. The mean extraction efficiency over the studied range was 98.6%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the acetic acid onto charcoal tubes which had 10-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them immediately before spiking. The mean recovery for the wet samples was 99.0%.

Table 2.4
Extraction Efficiency (%) of Acetic acid

level		sample number						mean
× target concn	mg per sample	1	2	3	4	5	6	
0.1	0.115	97.4	97.6	99.5	97.3	99.4	99.8	98.5
0.25	0.288	98.4	99.0	98.6	99.2	99.0	98.7	98.8
0.5	0.577	98.9	99.2	99.3	99.2	99.1	99.6	99.2
1.0	1.15	98.0	99.7	99.2	98.5	98.8	99.1	98.9
1.5	1.73	98.8	98.1	99.1	98.5	98.9	98.4	98.6
2.0	2.31	96.8	97.6	98.1	97.6	97.8	98.7	97.8
1.0 (wet)	1.15	98.7	99.1	99.1	99.4	98.5	98.9	99.0

2.5 Retention efficiency

Six charcoal tubes, lot 2000 were spiked with 2.31 mg (19.6 ppm) of acetic acid and allowed to equilibrate for 6 h. The tubes had 48 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them at 0.2 L/min. The samples were extracted and analyzed. The mean recovery was 97.2%. There was no analyte found on the backup section of any of the tubes. Results are not corrected for extraction efficiency.

Table 2.5
Retention Efficiency (%) of Acetic acid

	sample number						mean
section	1	2	3	4	5	6	
front	96.4	98.5	97.4	96.2	97.6	97.1	97.2
rear	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	96.4	98.5	97.4	96.2	97.6	97.1	97.2

2.6 Sample storage

Fifteen charcoal tubes were each spiked with 1.15 mg (9.76 ppm) of acetic acid. They were allowed to equilibrate for 6 h, then 10 L of air, with an absolute humidity of 15.7 milligrams of water per liter

of air (about 80% relative humidity at 22.2 °C), was drawn through them. Three samples were analyzed immediately. Two groups of six samples were formed with the rest of the samples. One group was stored at room temperature and the other in a refrigerator. Three from each group were analyzed after 7 days of storage and the remaining three after 14 days of storage. The amounts recovered, which are not corrected for extraction efficiency, indicate good storage stability for the time period studied.

Table 2.6
Storage Test for Acetic acid

time (days)	ambient storage			refrigerated storage		
	recovery (%)			recovery (%)		
0	99.4	97.9	98.2	99.4	97.9	98.2
7	96.7	98.5	97.1	98.6	97.2	97.9
14	94.7	96.4	95.8	95.9	98.2	96.6

2.7 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 48-L air samples should be collected at a sampling rate of 0.2 L/min for 240 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of acetic acid.

2.8.2 Suspected interferences should be reported to the laboratory with submitted samples.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs.

3.1 Apparatus

3.1.1 Ion chromatograph with a conductivity detector. A Dionex DX500 ion chromatograph with a conductivity detector, and a ASRS anion suppressor was used in this evaluation.

3.1.2 IC column and guard column which can separate acetate from any potential interferences. A 250-mm × 4-mm i.d. Dionex IonPac AS4A column and 50-mm × 4-mm i.d. Dionex IonPac AG4A guard column were used in this evaluation. (Butyric acid is a potential interference on an AS4A column, to obtain a separation between acetate and butyrate use an AG14A guard column and AS14A column.)

3.1.3 A means to integrate the chromatograms. The Dionex AI450 software, and a Millennium³² data system were used in this evaluation.

3.1.4 Automatic sampler. A Dionex model AS40, and sample vials, 0.5-mL, with filter caps was used in this evaluation.

3.1.5 Volumetric flasks, pipets, and calibrated micropipets.

3.1.6 A pipettor capable of dispensing 10-mL of the extracting solvent to prepare standards and samples. If a dispenser is not available, a 10-mL volumetric pipet may be used.

3.1.7 Volumetric flasks - 10-mL and other convenient sizes for preparing standards.

- 3.1.8 Calibrated 10- μ L syringe for preparing standards if using acetic acid to make analytical standards.
- 3.1.9 Micro-analytical balance capable of weighing at least 0.01 mg.
- 3.1.10 Scintillation vials, glass, 20-mL.
- 3.1.11 Equipment for eluent degassing. A vacuum pump and ultrasonic bath were used for this evaluation.
- 3.1.12 Optional: Centrifuge for spinning down the precipitate in samples.

3.2 Reagents

- 3.2.1 Acetic acid, glacial, Reagent grade. Fisher 99.9% (lot 971803) was used in this evaluation. Alternately, sodium acetate may be used to make analytical standards.
- 3.2.2 Sodium acetate, Reagent grade. Aldrich 99%+ (lot 16530HS) was used for this evaluation.
- 3.2.3 Sodium hydroxide, Reagent grade. Aldrich 97% (lot 09701DQ) was used in this evaluation.
- 3.2.4 Sodium borate decahydrate, Reagent grade. Mallinckrodt 99% (lot KJEZ) was used in this evaluation.
- 3.2.5 Deionized water, 18 megaohm. A Barnstead NANOpure Diamond water deionizer was used in this evaluation.
- 3.2.6 Eluent was prepared by dissolving 1.25 g sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in 2 liters of deionized water, resulting in a 1.5 mM solution.
- 3.2.7 Extraction solvent is prepared by dissolving 0.4 g NaOH in 1 liter of deionized water, resulting in a 0.01 N NaOH solution.
- 3.2.8 A 1000 ppm or 1000 $\mu\text{g}/\text{mL}$ acetate ion stock solution is prepared by dissolving 0.6947 g sodium acetate in 500 mL deionized water.

3.3 Standard preparation

- 3.3.1 Prepare stock analytical standards by injecting microliter amounts of acetic acid into volumetric flasks containing 0.01 N NaOH. An analytical standard at a concentration of 1 $\mu\text{L}/10\text{ mL}$ (104.7 ppm solution or 104.7 $\mu\text{g}/\text{mL}$) is equivalent to 8.88 ppm based on a 48-L air volume. Alternately, a stock solution of sodium acetate (1000 ppm solution acetate ion or 1000 $\mu\text{g}/\text{mL}$ acetate ion) may be prepared by placing 0.6947 g sodium acetate in 500 mL deionized water.
- 3.3.2 Bracket sample concentrations with working standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, either analyze higher standards, or dilute the sample. The higher standards should be at least as high in concentration as the highest sample. Diluted samples should be prepared with extracting solvent to obtain a concentration within the existing standard range. Prepare dilutions of the stock standards in the concentration range of 0.1 to 200 $\mu\text{g}/\text{mL}$ for analysis with the 0.01 N NaOH solution used for extracting the samples. The same reagent solution should be used to prepare samples and standards, matrix matching, as the retention time of the acetate peak is affected by the matrix concentration.

3.4 Sample preparation

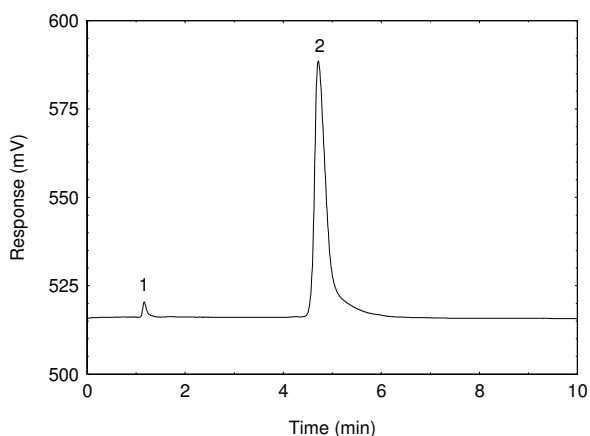
- 3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer the adsorbent sections to separate 20-mL vials. Discard the glass tube, urethane foam plug and glass wool plug.
- 3.4.2 Add 10 mL of 0.01 N NaOH to each vial using a pipettor or volumetric pipet.
- 3.4.3 Immediately seal the vials with caps.
- 3.4.4 Shake the vials on shaker for 30 minutes. Spin down the charcoal on a centrifuge for 5 min at about 2800 rpm, or allow to settle for at least two hours.
- 3.4.5 Transfer supernatant to autosampler vials for analysis, being careful not to transfer any particles of charcoal, as the particles may clog the autosampler or instrument.

3.5 Analysis

3.5.1 Ion chromatograph conditions.

IC conditions

columns: IonPac AS4A column 250-mm × 4-mm i.d. and IonPac AG-4A guard column 50-mm × 4-mm i.d. at 30 °C
 flow rate: 1.4 mL/min
 eluent: 1.5 mM Na₂B₄O₇
 pump pressure: 1200 psi
 injection size: 50 µL
 retention time: 4.8 min acetate ion



3.5.2 Peak areas are measured by an integrator or other suitable means.

Figure 3.5.1. A chromatogram of 203 µg/mL acetic acid (200 µg/mL acetate ion) in 0.01 N NaOH. (Key: (1) water; (2) acetate ion.)

3.5.3 An external standard (ESTD) calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus milligrams of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

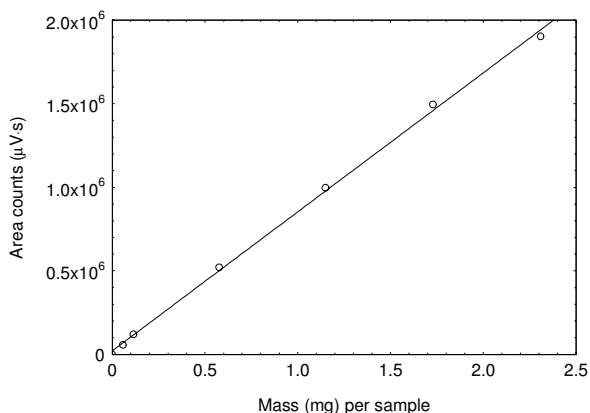


Figure 3.5.3. Calibration curve of acetic acid. (Y = $8.32 \times 10^5 x + 2.20 \times 10^4$).

3.6 Interferences (analytical)

- 3.6.1 Any compound that produces a IC response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte. Butyric acid, as the butyrate ion, is an interference on the AS4A analytical column, therefore an AS14A analytical column should be used to analyze samples from workplaces where butyric acid is present.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by mass spectrometry or by another analytical procedure. The sample must be acidified with sulfuric acid or phosphoric acid to a pH of 3 or less, to reform the acetic acid from the acetate ion, before it can be confirmed by GC mass spec. The mass spectrum in Figure 3.6.2. Confirmation of the acetate ion is also possible by analysis by capillary electrophoresis or by a second column on IC.

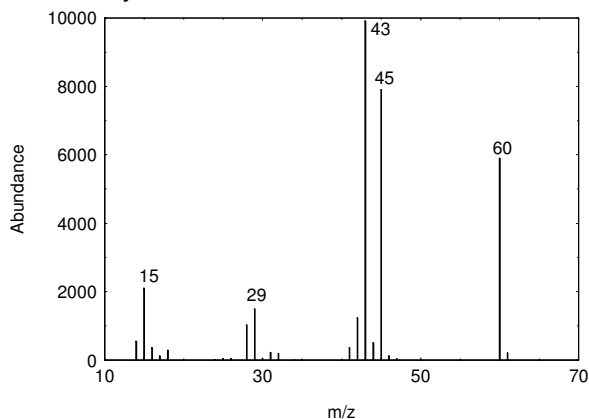


Figure 3.6.2. The mass spectrum of acetic acid.

3.7 Calculations

The amount of analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. If the instrument was calibrated on the concentration of the acetate ion, the results need to be converted to acetic acid concentration by multiplying the acetate ion concentration by a ratio of their molecular weights (60.05/59.04). This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m³)
 M is micrograms per sample
 V is liters of air sampled
 E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
 V_M is molar volume at 25 °C and 1 atm = 24.46
 C_M is concentration by weight
 M_r is molecular weight = 60.05

4. Recommendations for Further Study

Collection, reproducibility, and other detection limit studies need to be performed to make this a validated method.