Oxalic Acid

Method number: PV2115

Target concentration:
OSHA PEL: 1 mg/m^3
ACGIH TLV: 1 mg/m^3 TWA, 2 mg/m^3 STEL

Procedure: Samples are collected by drawing workplace air through glass fiber filters. Samples are extracted with 10-mL 0.028 M NaOH and analyzed by IC using a conductivity detector.

Recommended sampling
time and sampling rate: 100 min at 1.0 L/min (100 L)

Reliable quantitation limit: 3.94 µg/sample

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

          Since OSHA did not have a procedure for oxalic acid and a method needed to be developed, this project was undertaken to fill its void.

    1.1.2   Toxic effects[1] (This section is for information only and should not be taken as the basis of OSHA policy.)

          The toxicity of dicarboxylic acids varies considerably due to its acidity, the spacing of the carboxyl groups, and solubility of the diacids.

          "Oxalic acid is a hazardous chemical because it is a strong acid and a precipitant of blood calcium. Prolonged skin exposure can cause dermatitis and contact with the dust or vapor severely irritates the eyes and respiratory tract. Severe exposure or ingestion causes such symptoms as vomiting, coughing, pain, and even death."

          Oxalic acid removes calcium in the blood to form calcium oxalate which in turn damages the kidney because of the insoluble oxalate salt.

          Oxalic acid is a severe eye irritant causing redness, pain, and damage to the cornea. Consult its MSDS before sampling.

          Oxalic acid is toxic and corrosive, neither its crystals nor its solution should be discarded to the environment without proper treatment. The common treatment methods are acidification, neutralization, and incineration.

    1.1.3   Workplace exposure[2]

          The following industrial processes are used worldwide for the manufacture of oxalic acid. They are: the oxidation of carbohydrates, the ethylene glycol process, the propylene process, the dialkyl oxalate process, and the sodium formate process. Nitric acid oxidation is used where carbohydrates, ethylene glycol, and propylene are the starting materials.

          The North American continent (United States, Canada, and Mexico) in 1992 had no production of oxalic acid. The United States imported and consumed 8,000 tons of this acid in 1992.

          Oxalic acid is used in various industrial areas, such as textile manufacture and processing, metal surface treatments, leather tanning, cobalt production, and separation and recovery of rare-earth elements. Substantial quantities of oxalic acid are also consumed in the production of agrochemicals, pharmaceuticals, and other chemical derivatives."[3] No data was found regarding the size of the worker population potentially exposed to oxalic acid.

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[1] *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.; [CD-Rom]; Grayson, M Ed.; The Dialog Corporation: Cary, NC 2000 Vol. 17.*

[2] Paul, M., *Occupational and Environmental Reproductive Hazards: A Guide for Clinicians,* Williams & Wilkins: Baltimore, MD, 1993, p290.

[3] *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.; [CD-Rom]; Grayson, M Ed.; The Dialog Corporation: Cary, NC 2000 Vol. 17.*

1.1.4 Physical properties and other descriptive information[4]

Oxalic acid comes as an anhydrous oxalic acid or in a dihydrate form.

Anhydrous Oxalic Acid, $C_2H_2O_4$

CAS #:   144-62-7
IMIS #:   1970
Molecular weight: 90.04
Melting point: Simultaneously melts and decomposes at 187 °C
Sublimes: Sublimation begins at 100 °C
Appearance: Although colorless, and odorless both forms may appear to be white.
                  The forms are rhombic (α-form) and monoclinic (β-form). The rhombic
                  form at room temperature is stable, but the monoclinic form is
                  metastable (slightly stable). The main difference between the forms are
                  the melting points which are 189.5 and 182°C, respectively.
Vapor pressure: <0.001 torr
Synonyms: ethanedioic acid, ethanedionic acid
Solubility: Very soluble in polar solvents
Structure:
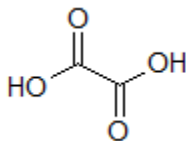
Oxalic Acid Dihydrate, $C_2H_2O_4 \cdot 2H_2O$

CAS #:   6153-56-6
IMIS #:   1970
Molecular weight: 126.07
Melting point: 101.5°C
Sublimes: 157°C
Appearance: Although colorless, and odorless both forms may appear to be white
                  and consists of monoclinic granules
Vapor pressure: <0.001 torr
Synonyms: ethanedioic acid, ethanedionic acid
Solubility: One gram dissolves in about 7 mL water; 2.5 mL alcohol; 100 mL ether.
                  Insoluble in benzene, chloroform, and petroleum ether.

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[5]. 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) is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with descending increments of analyte, such that the highest sampler loading was 4.437 μg/sample for oxalic 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 (Section 3.5), and the

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[4] *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.; [CD-Rom]; Grayson, M Ed.; The Dialog Corporation: Cary, NC 2000 Vol. 17.*

[5] Burright, 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.

data obtained was used to calculate the standard error of estimate and the slope of the calibration curve for the calculation of the DLOP. The slope of the curve is 2191.7 and the SEE is 862.6. 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 are 1.18 ug/sample and 3.94 ug/sample, respectively.

Table 1.2.
Detection Limit of the Overall Procedure for Oxalic Acid

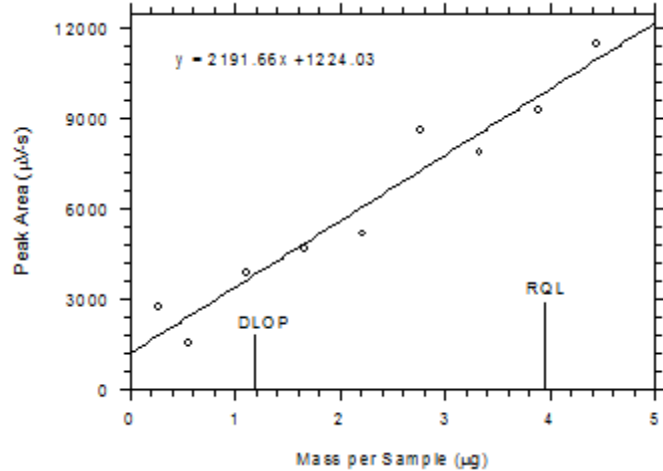| mass per sample (µg)	area counts (µV-s)
0.277	2749
0.555	1535
1.109	3916
1.664	4715
2.218	5190
2.773	8623
3.328	7888
3.882	9272
4.437	11494

Figure 1.2.1. Plot of data to determine DLOP/RQL for oxalic acid.

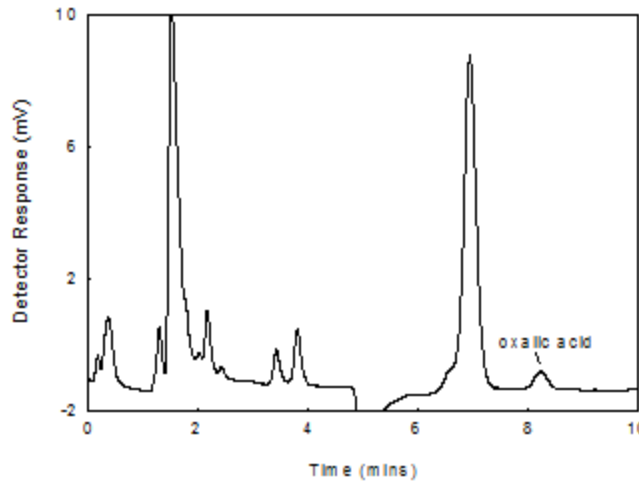Below is the chromatogram of the RQL level for the analyte.

Figure 1.2.2. Chromatogram of RQL for oxalic acid

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 ±5% of the recommended flow rate.

2.1.2   Samples are collected on 37-mm diameter binderless glass fiber filters, type A/B. Filters are placed into three-piece cassettes and sampled open face.

2.1.3   Glass Fiber Filter. Gelman Science, P/N 66208, Type A/B 37-mm extra thick and binder free.

2.2   Reagents

None required.

2.3   Technique

2.3.1   Immediately before sampling, remove the top piece and the end plug from the cassette.

2.3.2   Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing up during sampling. Position the sampling pump, cassette and tubing so it does not impede work performance or safety.

2.3.3   Air being sampled should not pass through any hose or tubing before entering the cassette.

2.3.4   After sampling for the appropriate time, remove the sample, and replace the top piece and the end plug. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.5   Submit at least one blank sample with each set of samples. Handle the blank cassette in the same manner as the other cassettes except do not draw air through it.

2.3.6   Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.3.7   Ship any bulk samples separate from the air samples.

2.3.8   After sampling, submit the samples to the laboratory for analysis as soon as possible.

2.4   Extraction efficiency

The extraction efficiencies of oxalic acid were determined by liquid-spiking of glass fiber filters with the analyte at 0.2 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted and analyzed. The mean extraction efficiency over the studied range was 98.7% for oxalic acid.

The wet extraction efficiency was determined at 1 times the target concentration by liquid-spiking of glass fiber filters with the analyte. A 100-liter air volume of humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) was drawn through the glass fiber filters immediately before spiking. The mean recovery for the wet samples was 100% for oxalic acid.

Table 2.4
Extraction Efficiency (%) of Oxalic Acid

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.2	20.3	99.2	99.6	99.3	100.3	99.6
0.5	60.9	98.4	97.1	99.4	98.1	98.3
1.0	101.4	97.4	97.2	97.1	96.8	97.1
1.5	162.3	98.9	99.6	99.2	100.0	99.4
2.0	202.4	98.4	99.6	99.4	99.4	99.2
1.0 (wet)	101.4	100.7	100.7	99.6	99.0	100.0

2.5   Retention efficiency

Six glass fiber filters were spiked with the analyte, allowed to equilibrate for 6 hr, and then placed into a three-piece cassette with another glass fiber filter as a back-up, with a spacer between the filters. The amounts spiked on the filters was 202.86 µg (1.91 mg/m^3) of oxalic acid. The cassettes had 106 L of humid air (about 80% relative humidity at 22.2 °C) pulled through them at 1 L/min. The samples were extracted and analyzed. The mean retention efficiency was 96.7%.

Table 2.5
Retention Efficiency (%) of Oxalic Acid

section	sample number						
	1	2	3	4	5	6	mean
GFF	96.8	97.2	95.9	96.8	97.6	96.1	96.7
back-up GFF	4.0	3.8	3.5	3.6	2.9	3.5	3.6
total	100.8	101.0	99.4	100.4	100.5	99.6	100.3

2.6   Sample storage

Twelve glass fiber filters were each spiked with 101.43 µg (1.01 mg/m^3) of oxalic acid. They were allowed to equilibrate over night, then 100 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. They were sealed and stored at room temperature in a drawer. Three samples were analyzed immediately. Three more were analyzed after 9 days of storage and three other samples were analyzed after 21 days of storage. The remaining three samples were analyzed after 28 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 Oxalic Acid
(% Recovery)

time (days)	1	2	3	mean
0	99.2	97.2	99.3	98.6
9	96.9	91.7	101.3	96.6
21	95.0	92.7	91.0	92.9
28	97.6	96.0	95.4	96.3

2.7   Recommended air volume and sampling rate

The recommended air volume is 100-L of air at a sampling rate of 1.0 L/min.

2.8   Interferences (sampling)

2.8.1   It is not known if any compounds will severely interfere with the collection of oxalic acid on the glass fiber filter.

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[6]. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analysis.

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[6]   Occupational Exposure to Hazardous Chemicals in Laboratories. Code of Federal Regulations, Part 1910.1450 (f), Title 29.

3.1 Apparatus

    3.1.1   An ion chromatograph equipped with a conductivity detector. A Waters IC 600S controller and 626 pump, Waters 432 conductivity detector, and a 717 Plus autosampler coupled with a Dionex ASRS anion suppressor controller were used in this evaluation.

    3.1.2   An IC column and guard column capable of separating the analyte from any interferences. A 25-cm × 4-mm i.d. Dionex IonPac AS11 column with particle size of 5 µm and a 5-cm × 4-mm i.d. Dionex IonPac AG11 guard column were used in this evaluation.

    3.1.3   An electronic integrator or some suitable method of measuring peak areas. A Waters Millennium[32] data system was used in this evaluation.

    3.1.4   Water's 4-mL IC vials with caps and glass inserts.

    3.1.5   A 100-µL syringe or other convenient size for sample injection.

    3.1.6   Pipets for dispensing the extracting solvent.

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

3.2 Reagents

    3.2.1   Sodium hydroxide, A.C.S. reagent grade. Aldrich 97+%, lot 0971DQ was used in this evaluation.

    3.2.2   Eighteen megohm water. A Millipore Milli-Q water purification system was used for this evaluation.

    3.2.3   Oxalic acid. Eastman Kodak Co. 98%, was used in this evaluation.

    3.2.4   The IC mobile phase was 6.77 mM solution of sodium hydroxide in water.

    3.2.5   The extraction solvent is a solution of 0.028 M NaOH in water.

3.3 Standard preparation

    3.3.1   At least two separate stock standards were prepared by dissolving a known quantity of oxalic acid in eighteen megohm water. The concentrations of these stock standards were 2.029 µg/µL and 2.047 µg/µL. Micro-liter amount of stocks standards were spiked into 10-mL volumetric flasks containing a solution of 0.028 M NaOH.

    3.3.2   Dilutions of these stock standards were prepared to bracket sample concentrations. The standards in this study ranged from approximately 0.1 to 260 µg/sample.

3.4 Sample preparation

    3.4.1   Sample cassettes were opened and each glass fiber filter is placed in a scintillation vial.

    3.4.2   Each filter was extracted with 10 mL of 0.028 M NaOH.

    3.4.3   The vials were sealed immediately and the filters extracted for 30 to 45 minutes with occasional shaking of the vials by hand, but not to the extent of breaking apart the glass fiber filter.

3.5   Analysis

3.5.1   Ion chromatograph conditions.

Column: Dionex IonPac AG11guard column, 5-cm × 4-mm i.d. + AS11,
                           5-µm particle, 25-cm × 4.6-mm i.d.
Mobile phase: 6.77 mM sodium hydroxide
Flow rate: 1.2 mL/min
Injection size: 15 µL
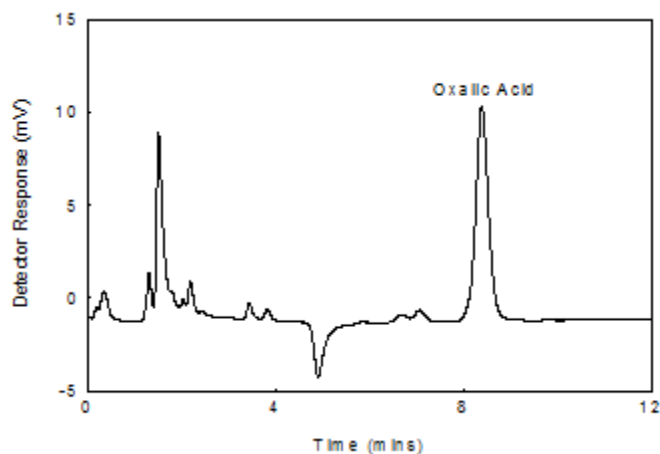Conductivity dectector

Figure 3.5.1. Chromatogram obtained at the target
concentration with the recommended conditions

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

3.5.3   An external standard calibration method was used. A calibration curve was constructed
         by plotting the response of the injections versus micrograms of analyte per standard.
         Bracket the samples with freshly prepared analytical standards over the range of
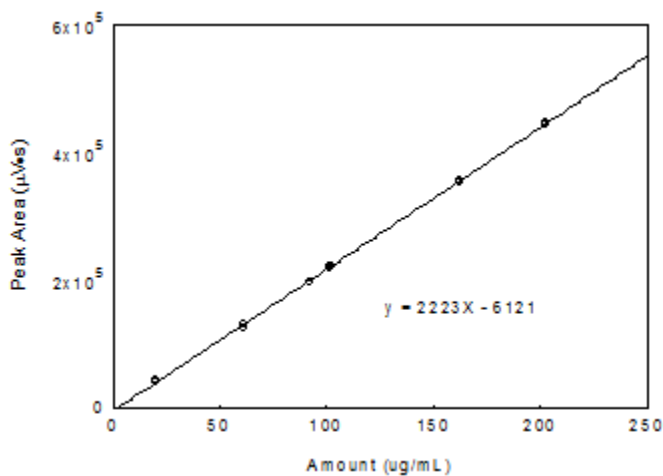   concentrations.

Figure 3.5.3. Calibration curve of oxalic acid.

3.6   Interferences (analytical)

3.6.1   Any compound that produces an 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.

    3.6.2   When necessary, the identity of oxalic acid may be confirmed by capillary electrophoresis or by another analytical procedure.[7]

3.7   Calculations

The amount of each analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. 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 formula.

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

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample (µg/sample corrected for the blank)
V is liters of air sampled
E_E is extraction efficiency, in decimal form

4. Recommendations for further study

Collection and reproducibility studies need to be performed to make this a validated method.

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[7] Suga, Hewlett Packard Application Note, Publication Number 12 - 5965 -7185E, 1996.