ACETIC AND FORMIC ACIDS IN WORKPLACE ATMOSPHERES

Method No:	ID-186SG
Matrix:	Air
OSHA Standard:	5.0 ppm for Formic Acid, HCOOH 10.0 ppm for Acetic Acid, CH_3COOH
Collection Procedure:	A known volume of air is drawn through a charcoal tube. Acetic and Formic acids are collected on the charcoal tube.
Recommended Air Volume:	48 liters maximum
Recommended Sampling Rate:	0.2 liters per minute
Analytical Procedure:	The charcoal is desorbed in 0.0015 M borate eluent and is analyzed by Ion Chromatography (IC).
Quantitative Detection Limit:	0.0016 ppm for HCOOH 0.006 ppm for CH_3COOH
Precision and Accuracy:	CV_1 = 0.018 for HCOOH 0.016 for CH_3COOH
Method Classification:	P

This method was last revised on April 8, 1993

1. Introduction

This method describes the collection by charcoal tube and analysis using Ion Chromatography of acetic and formic acids. The method measures the total concentration of the airborne anions. The corresponding acids may be collected on a single charcoal tube and determined simultaneously.

1.1. History

Prior to the use of this method, acetic acid was collected on charcoal tubes, desorbed in 0.1 N NaOH and analyzed by gas chromatography. Before that, acetic and formic acids were collected in 0.01 N NaOH, and were analyzed by ion chromatography.

1.2. Uses (9.1., 9.2.)

Acetic acid is mainly used in the manufacture of cellulose acetate fibers and plastics, ester solvents, dyes, metal salts, and many other chemicals. Acetic acid is one of the most important industrial organic acids. It is most widely known in the form of vinegar, which is a dilute aqueous solution of acetic acid.

Formic acid is important in textile souring, leather preparation, and cattle-fodder preservation. It is also used in the textile industry, and as an intermediate in the production of many

chemicals. It is also used as a coagulant for rubber latex. Formic acid is used in nickel plating baths, and in the production of wire-stripping compounds needed for soldering bare wire.

1.3. Physical Properties (9.1., 9.2.)

Acetic acid, CH_3COOH, is a colorless, water-like liquid that has a sharp, vinegary odor and a burning taste. Commercial grades of acetic acid are approximately 99.5% pure. Acetic acid is soluble in alcohol and water. Acetic acid is highly caustic to the skin.

Formic acid, HCOOH, is a colorless, odorous acid. It is the first and strongest of the unsubstituted series of carboxylic acids. Formic acid decomposes readily to water and carbon monoxide. Formic acid or its aqueous solutions dissolve many of the more active, main group metals and their oxides to give corresponding formates. The anhydrous acid must be handled with the same care as concentrated sulfuric acid. It is a powerful dehydrating agent and serious burns can result from its action on the skin. Formic acid burns when ignited. Commercial grades of formic acid are approximately 90% pure. Formic acid is soluble in water, alcohol, ether, and glycerol.

Physical Constants:	HCOOH	CH_3COOH
Density, 20.0° C:	1.220 g/cm^3	1.049 g/mL
Melting Point:	8.4° C	16.6° C
Boiling Point:	100.7° C	117.9° C

Formula Weight:	46.03	60.06

2. Working Range and Detection Limit (9.3.)

2.1. The working range for a 48 liter air sample is 0.002 to 0.05 ppm for $HCOO^-$ and CH_3COO^-. This corresponds to 0.1 to 2.5 ug. The upper range can be extended by sample dilution.

2.2. The quantitative detection limits for acetic and formic acids were calculated using the IUPAC Method. The detection limits are as follows at a confidence level of 99.86%:

$HCOOH$ = 0.0016 ppm or 16 ng

CH_3COOH = 0.006 ppm or 60 ng

The detection limits were calculated based on a sample volume of 10 mL and an injection volume of 50 uL. The detection limits for each analyte were calculated in the presence of the other. The detection limits are for a 48 liter air volume at a 0.2 liters per minute sampling rate.

3. Stability of acetic and formic acids on charcoal tubes.

3.1. A recovery study of acetic and formic acids was done at the 0.5X, 1.0X, and 2.0X levels. Six samples at each of three levels were spiked, let sit for an hour and then desorbed with 0.0015 M borate eluent. The samples were analyzed by ion chromatography. The

results can be seen in Table III. Two problems were seen in the formic acid analysis. First the charcoal tubes contained an interference which had the same retention time as formic acid. The mean of this interference is 85.9 ug (n = 5, std. dev. = 12.2) for section A, and 48.7 ug (n = 5, std. dev. = 3.3) for section B. The second problem is that the formic acid is not stable unless refrigerated. See section 3.2. NIOSH found a CV_T of 0.058, with a CV_1 of 0.007 and a CV_2 of 0.030 for their recoveries when desorbed with formic acid and analyzed for acetic acid by gas chromatography (9.4.).

3.2. Acetic acid recovery from charcoal tubes after 2 weeks of storage is 93% when the samples are not refrigerated and 96% when refrigerated. Formic acid recovery is 18% for samples stored for two weeks when not refrigerated and 82% when refrigerated. Therefore, the samples must be kept refrigerated at $4^{o}C$ when analysis of formic acid is desired. See Table I.

3.3. Once the samples are desorbed in 0.0015 M borate eluent, they are stable for at least 2 weeks. Samples desorbed in the manner just described and kept unrefrigerated for 2 weeks showed a recovery of 94% for formic acid and 90% for acetic acid.

3.4. Acetate and formate standards in 0.0015 M borate eluent were determined to be stable for at least 2 weeks.

3.5. A breakthrough study was conducted under the following conditions.

Six charcoal tubes were spiked with acetic and formic acids at 2.0X the PEL and then exposed to 80% humidity air at 22°C at a flow of rate 0.2 liters/minute for four hours. No breakthrough was detected in the second portion of the charcoal tubes for either acetic or formic acid. The results of the breakthrough study can be seen in Table II. A typical chromatogram of a standard containing 1.0 ug acetate and formate is shown in Figure I.

4. Interferences

4.1. Butyric and propionic acids can cause an interference. If butyric acid is present, it can be separated from the formic acid peak by changing the flow rate to 1.0 mL/min. Propionic acid is difficult to separate from the acetic acid peak. The presence of butyric or propionic acids in the workplace must be reported to the laboratory.

5. Advantages and Disadvantages

5.1. The method is accurate and easily automated.

5.2. The sampling procedure uses charcoal tubes as opposed to older impinger sampling methods for these acids. Such a sampling procedure eliminates the inherent problems of spillage and release of a caustic solution or the potential contamination of the pump while using a impinger.

6. Sampling Procedure

6.1. Apparatus - Charcoal tubes, SKC Cat. No. 226-09 (or equivalent charcoal tubes which have been demonstrated to show low levels of the anions of interest), personal sampling pump which are calibrated at the recommended flow rate with a charcoal tube in line to an accuracy of ±10% at the 95% confidence limit.

6.2. The charcoal tube is attached to a calibrated personal sampling pump and the sampling tube is placed in the worker's breathing zone or in a area of the workplace. At least 10 liters of air should be drawn through the sampling tube.

6.3. After the desired sampling period is completed, the charcoal tube is removed from the pump. The charcoal tubes are then properly identified and official sealed with a OSHA Form 21, and shipped to the laboratory for analysis. Samples taken for formic acid must be shipped to the laboratory via overnight mail on ice. Proper planning should be undertaken to eliminate any possible delay in samples arriving at the laboratory before the ice is spent.

6.4. With each batch of up to 20 samples, a blank tube which has had no air drawn through it, is submitted for analysis. The blank tube should be from the same lot of tubes used for sampling.

6.5. It is very important that when particulate acids or salts of an

acid are known to be present in the workplace atmosphere each should be listed as interferences. It is important to note the presence of other low molecular weight carboxylic acids, particularly propionic acid.

7. Analytical Procedure

7.1. Apparatus - Ion exchange chromatograph and recorder, or integrator (an auto sampler helps automate the analysis), 10 mL pipette, 1 mL plastic syringe with male luer fitting, anion separator column with precolumn, anion membrane suppressor, and appropriate volumetric glassware for dilutions and standard preparation.

7.2. Reagents - All reagents used should be ACS analyzed reagent grade or better.

7.2.1. Deionized water with a specific conductance of 10 umho/cm or less for preparation of eluents and other solutions which will be used in the Ion Chromatograph.

7.2.2. Sodium Borate ($Na_2B_4O_7.10H_2O$).

7.2.3. Acetate Stock Standard (1000 ug/mL CH_3COO^-). Dissolve 0.6948 g of Sodium Acetate (CH_3COONa) or 1.1525 g of $CH_3COONa \cdot 3H_2O$ into 500 mL deionized water.

7.2.4. Formate Stock Standard (1000 ug/mL $HCOO^-$). Dissolve

0.7554 g of Sodium Formate (COONa) into 500 mL deionized water.

7.2.5. Borate Eluent and Desorption Solution (0.0015 M $B_4O_7^{=}$). Dissolve 1.25 g Sodium Borate ($Na_2B_4O_7.10H_2O$) in a 2 liter volumetric flask and dilute to volume with deionized water. Sonicate the solution under a vacuum for 5 minutes before use.

7.2.6. Regenerant Solution (0.025 N H_2SO_4). Add 2.8 mL of concentrated H_2SO_4 to 4 liters in deionized water. Sonicate the solution under a vacuum for 5 minutes before use.

7.3. Safety Precautions

7.3.1. When using the Ion Chromatograph, the column door should be kept closed during the analysis in case the columns burst. To avoid this danger the pressure should be checked at the beginning of the analysis and periodically during the analysis.

7.3.2. Care should be used when handling reagents, especially the regenerant solution (0.025 N H_2SO_4) to avoid chemical burns.

7.3.3. Care should be exercised when using laboratory glassware.

Chipped pipettes, volumetric flasks, beakers, or any glassware with sharp edges exposed should not be used to avoid the possibility of cuts, abrasions, and lost samples.

7.3.4. Pipetting should never be done by mouth - a bulb should always be used.

7.4. Standard Preparation

7.4.1. Working standards are prepared in the analytical range of 2 ug/mL to 50 ug/mL from dilutions of the 1000 ug/mL stock solutions. These standard solutions should be diluted to volume in 0.0015 M borate eluent and prepared fresh weekly.

7.4.2. If an auto sampler capable of variable volume injections is used, a combination 50 ug/mL acetate and formate standard is used. This intermediate working standard should be prepared fresh weekly. Injection volumes should always be 50 microliters or above for standards or samples.

7.5. Sample Preparation

7.5.1. The charcoal tube used to collect acetic and formic acids is separated into 2 parts. The first section (section A)

contains 100 mg charcoal. The backup section (section B) contains 50 mg charcoal and will collect any acid which passes through and is not collected by section A. Sections A and B are separated by a foam plug which is to be discarded.

7.5.2. Score the sampler with a file in front of the primary sorbant section (section A), then break the sampler at the score line. Transfer section A to a clean, labeled 20 mL vial. Place charcoal section B in a separate clean, labeled 20 mL vial.

7.5.3. If the air volume is greater than or equal to 10 liters pipette 10 mL of 0.1 N desorption solution into each sample vial and cap tightly. If the air volume is less than 10 liters use 5 mL desorption solution.

7.5.4. Let the samples sit overnight in the vials, or sonicate the samples for 10 minutes. Sample solutions must be filtered before analysis using LID/X syringe filters from Xydex Corporation, or equivalent, and the blank should be treated in a similar manner.

7.5.5. If using an auto sampler, transfer some of the sample into an appropriate sampling vial. If using the WISP autosampler, the vial should be at least half full. Label each vial with the appropriate laboratory identification

number. If using the Dionex autosampler, place an aliquot of 0.63 mL of each sample in separate polyvials. When using automatic injection use a 50 uL injection volume. The autosampler is less accurate below 50 uL.

7.5.6. For hand injection, use 1 mL of the eluent to flush the 0.1 mL injection loop thoroughly.

7.6. Analysis (9.4.)

7.6.1. For general instrument start up and operation, refer to Section 8 of the Ion Chromatography Standard Operating Procedure.

7.6.2. The normal instrument parameters are:

Sensitivity: 30 umho full scale
Eluent: 0.0015 M $B_4O_7^=$
Flow Rate: 2.0 mL/min
Run Time: Approximately 10 minutes.

7.6.3. If using the WISP autosampler, after the instrument is set up and stabilized, place the auto sampling vials into the sampling tray using tray positions one through five for standards.

7.6.4. If using the Dionex autosampler, refer to sections 8.1. to

8.3. of the Standard Operating Procedure.

7.6.5. Enter the proper parameters into the auto sampler (See the Ion Chromatography Standard Operating Procedure).

7.6.6. Start the auto sampler and observe the first few chromatograms to ensure proper operation. Periodically check the zero offset between samples to correct any baseline drift and to ensure proper sensitivity and retention time of the analytes.

7.6.7. Use the timer to stop the run if the auto sampler is to be left unattended.

7.6.8. Record the sample number onto the chromatogram. Keep a record of the sample identity and instrument conditions.

7.6.9. As the analysis proceeds, check the retention times of standards vs. samples to ensure uniformity.

7.6.10. If interfering substances are present, establish positive identity of the peaks by spiking known amounts of standard solution or try to obtain better separation by changing the eluent concentration or by reducing the flow rate.

7.7. Calculations

7.7.1. Peak areas or heights of the standards are used to construct a standard curve using the OSHA Auto Colorimetric Program. The samples results are obtained from a plot of peak height or peak area vs. concentration. The blank corrected sample values are then calculated using the Auto Colorimetric Program.

7.7.2. When using the OSHA Auto Colorimetric Program, sample numbers and volumes are entered into the calculator in the following manner:

Sample Number, Peak Area or Height, L Air Volume, mL Solution Volume, mL Aliquot Volume.

7.7.3. Air Concentration values are calculated by the following equation:

$$mg/m^3 = \frac{(\text{ug calculated})(\text{mL sample vol})(GF^*)(\text{dilution factor})}{(\text{liters of Air})(\text{mL Aliquot})}$$

GF* = Gravimetric Factor = 1.02 for HCOOH and CH_3COOH

7.7.4. Acetic and formic acids are reported in ppm. To convert the mg/m^3 values to ppm, the mg/m^3 value must be multiplied by the appropriate conversion factor.

Acid	Conversion Factor

HCOOH	0.532
CH_3COOH	0.407

8. Reporting Results for Compounds Determined by Ion Chromatography

8.1. Results are reported on the OSHA Form 91 in ppm for HCOOH and CH_3COOH, using two significant figures.

8.2. The estimated detection limit calculated by the Auto Colorimetric Program is reported on the OSHA Form 91 when no analyte is detected.

8.3. The presence of significant unidentifiable peaks is noted on the OSHA Form 91.

8.4. All data processor printouts and chart recorded chromatograms are filed in a central file according to laboratory sample identification.

8.5. Calculations are checked by a fellow chemist before the completed OSHA Form 91's are given to the supervisor.

9. References

9.1. Encyclopedia of Chemical Technology, Third Edition, 1978, Vol. 1 and 11.

9.2. Merck Index, Tenth Edition, 1983.

9.3. OSHA Ion Chromatography Standard Operating Procedure, Prepared by the Ion Chromatography Committee, Occupational Safety & Health Administration Analytical Laboratory, Inorganic Division.

9.4. Backup Data Report for Acetic Acid Method (by GC), NIOSH, Cincinnati, OH.

TABLE I

STABILITY STUDY

Refrigerated

Acetic Acid			Formic Acid		
Day 0	Day 7	Day 14	Day 0	Day 7	Day 14
1.034	1.051	0.964	1.149	0.999	0.821

Unrefrigerated

Acetic Acid			Formic Acid		
Day 0	Day 7	Day 14	Day 0	Day 7	Day 14
1.034	1.026	0.931	1.149	0.285	0.182

TABLE II
BREAKTHROUGH STUDY

Sample Number	Recovery Acetic Acid	Recovery Formic Acid
1	0.777	0.700
2	0.764	0.723
3	0.787	0.691
4	0.774	0.716
5	0.782	0.714
6	0.752	0.695
Mean	0.773	0.706
Std. Dev.	0.013	0.013

TABLE III
RECOVERY STUDY

Acetic Acid
Found/Theoretical

SAMPLE #	0.5X PEL	1.0X PEL	2.0X PEL
1	0.924	0.878	1.071
2	1.177	0.951	1.080
3	0.999	0.951	0.980
4	0.986	0.759	0.982
5	0.921	0.784	1.005
6	0.940	0.850	0.999
n =	6	6	6
Mean =	0.991	0.862	1.020
Std. Dev. =	0.097	0.081	0.045
CV_1 =	0.098	0.094	0.044
CV_1 (pooled)		0.0068	

Formic Acid
Found/Theoretical

SAMPLE #	0.5X PEL	1.0X PEL	2.0X PEL
1	1.108	0.966	1.069
2	1.338	1.032	0.982
3	1.159	0.994	0.920
4	1.272	0.792	0.931
5	1.032	0.855	1.009
6	1.334	0.920	0.972
n =	6	6	6
Mean =	1.207	0.926	0.980
Std. Dev. =	0.127	0.090	0.054
CV_1 =	0.105	0.097	0.055
CV_1 (pooled)		0.0078	