

USEPA¹ Reactor Digestion Method²

Method 8000

0.7 to 40.0³ mg/L COD (ULR); 3 to 150 mg/L COD (LR); 20 to 1500 mg/L COD (HR); 200 to 15,000 mg/L COD (HR Plus)

Scope and application: For water and wastewater. Digestion is required.

¹ Ranges 3 to 150 mg/L COD and 20 to 1500 mg/L COD are USEPA approved for wastewater analyses (Standard Method 5220 D), Federal Register, April 21, 1980, 45(78), 26811-26812.

² Jirka, A.M.; Carter, M.J., Analytical Chemistry, 1975, 47(8), 1397.

³ The ULR is only available with spectrophotometers that can measure at a wavelength of 350 nm.



Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows adapter and light shield requirements for the instruments that use them.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for test tubes

| Instrument | Adapters | Light shield |
|---------------------------|---------------------------|------------------------------------|
| DR 6000, DR 5000 | — | — |
| DR 3900 | — | LZV849 |
| DR 3800, DR 2800, DR 2700 | — | LZV646 |
| DR 1900 | 9609900 (D ¹) | — |
| DR 900 | 4846400 | Cover supplied with the instrument |

¹ The D adapter is not available with all instrument versions.

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.

DR 3900, DR 3800, DR 2800 and DR 2700: Install the light shield in Cell Compartment #2 before this test is started.

The reagent that is used in this test is corrosive and toxic. Use protection for eyes and skin and be prepared to flush any spills with running water.

The reagents that are used in this test contain mercury. Collect the reacted samples for proper disposal.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Run one blank with each set of samples. Run all tests (the samples and the blank) with the same lot of vials. The lot number is on the container label. Refer to [Blanks for colorimetric determination](#) on page 4.

Store unused (light sensitive) vials in a closed box.

If the samples contain high concentrations of chloride, refer to the Alternate reagents section.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

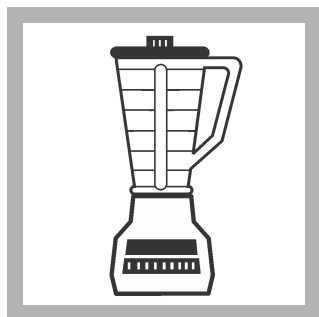
| Description | Quantity |
|--|----------|
| Beaker, 250-mL | 1 |
| Blender | 1 |
| COD Digestion Reagent vials | varies |
| DRB200 Reactor | 1 |
| Light shield or adapter (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.) | 1 |
| Magnetic stirrer and stir bar | 1 |
| Opaque shipping container for storage of unused, light-sensitive reagent vials | varies |
| Pipet, TenSette, 0.1- to 1.0-mL, with pipet tips (for use with the 200–15,000 mg/L range) | 1 |
| Pipet, volumetric, 2.00-mL | 2 |
| Pipet filler safety bulb | 1 |
| Test tube rack | 2 |

Refer to [Consumables and replacement items](#) on page 7 for order information.

Sample collection and storage

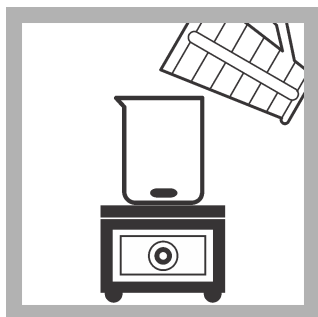
- Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination.
- Test biologically active samples as soon as possible.
- Homogenize samples that contain solids to get a representative sample.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated sulfuric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at 2–6 °C (36–43 °F) for a maximum of 28 days.
- Correct the test result for the dilution caused by the volume additions.

Reactor digestion procedure

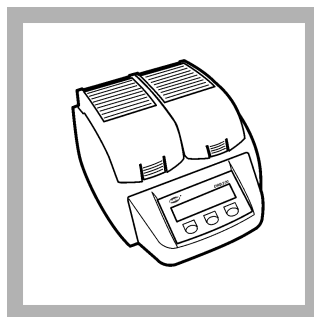


1. Put 100 mL of sample in a blender. Blend for 30 seconds or until homogenized.

For samples with large amounts of solids, increase the homogenization time. If the sample does not contain suspended solids, go to step 3.



2. For the 200–15,000 mg/L range or to improve accuracy and reproducibility of the other ranges, pour the homogenized sample into a 250-mL beaker and gently stir with a magnetic stir plate.



3. Set the DRB200 Reactor power to on. Preheat to 150 °C.

Refer to the DRB200 User Manual for selecting pre-programmed temperature applications.



4. **Prepare the sample:** Remove the cap from a vial for the selected range. Hold the vial at an angle of 45 degrees. Use a clean pipet to add 2.00 mL of sample to the vial.

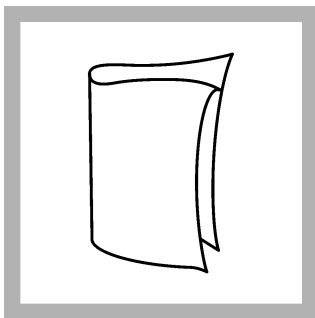
For 250–15,000 mg/L vials: Use a TenSette Pipet to add 0.20 mL of sample to the vial.



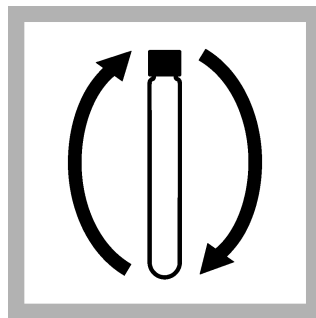
5. Prepare the blank:

Remove the cap from a second vial for the selected range. Hold the vial at an angle of 45 degrees. Use a clean pipet to add 2.00 mL of deionized water to the vial.

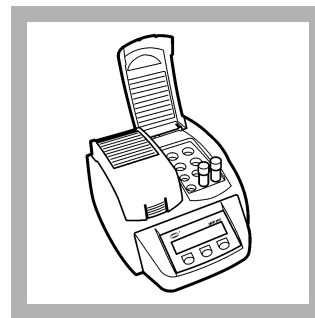
For 250–15,000 mg/L vials:
Use a TenSette Pipet to add 0.20 mL of deionized water to the vial.



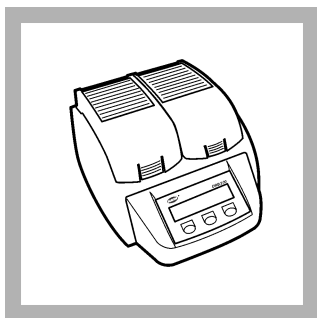
6. Close the vials tightly. Rinse the vials with water and wipe with a clean paper towel.



7. Hold the vials by the cap, over a sink. Invert gently several times to mix. **The vials get very hot during mixing.**



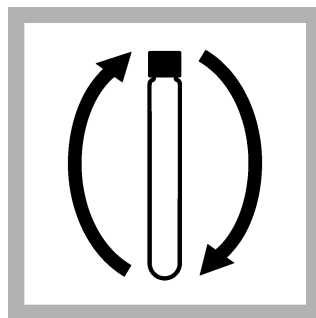
8. Put the vials in the preheated DRB200 reactor. Close the lid.



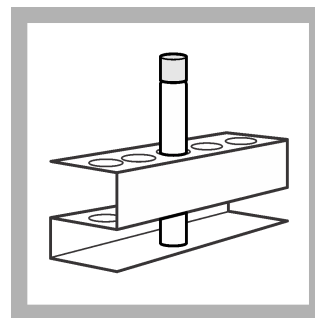
9. Heat the vials for 2 hours.



10. Set the reactor power to off. Let the vials cool in the reactor for approximately 20 minutes to 120 °C or less.

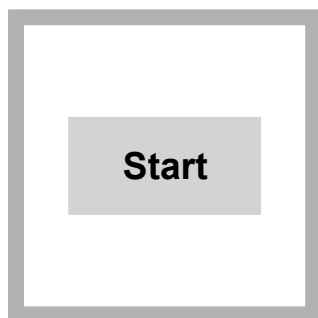


11. Invert each vial several times while it is still warm.



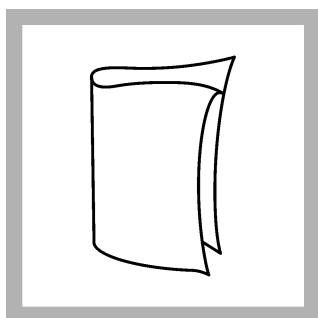
12. Put the vials in a tube rack to cool to room temperature.

Colorimetric procedure

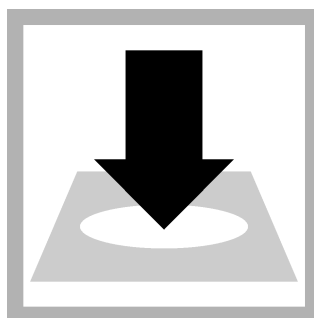


1. Start program **431 COD ULR**, **430 COD LR** or **435 COD HR**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.

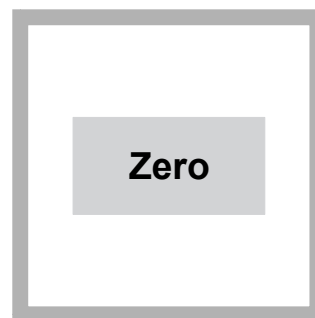
Note: Although the program name can be different between instruments, the program number does not change.



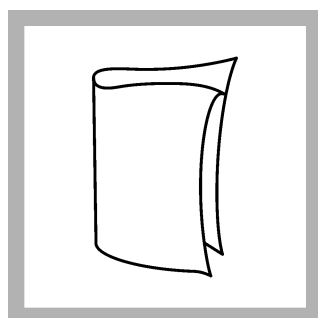
2. Clean the blank sample cell.



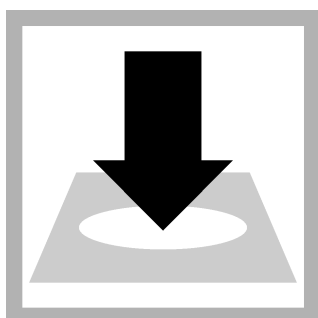
3. Insert the blank into the cell holder.



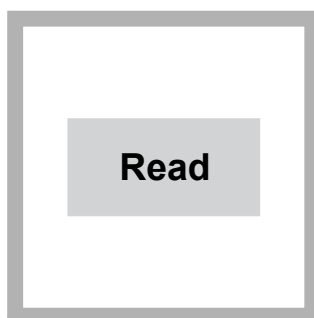
4. Push **ZERO**. The display shows 0 or 0.0 mg/L COD.



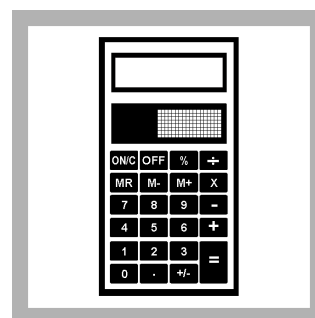
5. Clean the prepared sample cell.



6. Insert the prepared sample into the cell holder.



7. Push **READ**. Results show in mg/L COD.



8. If using High Range Plus COD digestion reagent vials, multiply the result by 10. For the most accurate results with samples near 1500 or 15,000 mg/L COD, repeat the analysis with a diluted sample.

Blanks for colorimetric determination

The blank vial can be used again and again for measurements that use the same lot of reagent vials. Measure the absorbance of the blank vial over time and prepare a new blank vial when the absorbance changes.

1. Put the instrument in the absorbance mode at the applicable wavelength. Refer to [Table 3](#) on page 7.
2. Add 5 mL of deionized water into an empty vial.
3. Put the vial in the instrument and zero the instrument.
4. Put the blank vial that is used in the test procedure into the instrument and record the absorbance value.
5. Keep the blank vial in the dark.
6. Prepare a new blank when the absorbance has changed by approximately 0.01 absorbance units.

Interferences

Chloride is the primary interference in this test procedure. Each COD vial contains mercuric sulfate that removes chloride interference to the level specified in Column 1 of Table 2. Dilute samples that have higher chloride concentrations to the level given in Column 2.

Note: For best results, use the low range and ultra-low range vials for samples that have high chloride concentrations (near maximum concentration) and low COD concentrations.

If sample dilution causes the COD concentration to be too low for accurate measurements, add 0.50 g of mercuric sulfate (HgSO_4) to each COD vial before the sample is added. The additional mercuric sulfate will increase the maximum chloride concentration to the level given in Column 3.

Note: Bromide interference is not removed with mercuric sulfate.

Table 2 Chloride concentration limits in the sample

| Vial range | Column 1 (maximum mg/L Cl^-) | Column 2 (mg/L Cl^- for diluted samples) | Column 3 (maximum mg/L Cl^- with mercuric sulfate) |
|----------------------------------|--|---|---|
| ULR ¹ (0.7–40.0 mg/L) | 2000 | 1000 | N/A |
| LR (3–150 mg/L) | 2000 | 1000 | 8000 |
| HR (20–1500 mg/L) | 2000 | 1000 | 4000 |
| HR Plus (200–15,000 mg/L) | 20,000 | 10,000 | 40,000 |

¹ The ULR is only available for spectrophotometers that can measure at a wavelength of 350 nm.

Accuracy check

Standard solution method

Items to collect:

- 1000 mg/L COD standard solution
- 100-mL volumetric flask, Class A
- Volumetric pipets, Class A and pipet filler
- Deionized water
- Potassium acid phthalate (KHP), dried overnight at 120 °C (HR Plus only)

0.7 to 40.0 mg/L ULR

1. Prepare a 30-mg/L COD standard solution as follows:
 - a. Use a pipet to add 3.00 mL of the 1000 mg/L standard solution into a 100-mL volumetric flask.
 - b. Dilute to the mark with deionized water. Mix well.
2. Use the test procedure to measure the concentration of the standard solution.
3. Compare the expected result to the actual result.

Note: The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

3 to 150 mg/L LR

1. Prepare a 100-mg/L COD standard solution as follows:
 - a. Use a pipet to add 10 mL of the 1000 mg/L standard solution into a 100-mL volumetric flask.
 - b. Dilute to the mark with deionized water. Mix well.
2. Use the test procedure to measure the concentration of the standard solution.
3. Compare the expected result to the actual result.

Note: The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

20 to 1500 mg/L HR

1. Use the test procedure with a 300-mg/L, 800 mg/L or 1000 mg/L COD standard solution to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

Note: The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

200 to 15,000 mg/L HR Plus

1. Prepare a 10,000 mg/L COD standard solution as follows:
 - a. Dissolve 8.500 g of dried KHP in 1000-mL of organic-free deionized water.
2. Use the test procedure to measure the concentration of the standard solution.
3. Compare the expected result to the actual result.

Note: The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

Alternate reagents

Mercury-free COD2 Reagents are available as a mercury-free alternative. These reagents are fully compatible with test procedures and stored programs in the instruments. Chloride and ammonia determinations are recommended for accurate results.

NOTICE

COD2 reagents are not approved for USEPA reporting purposes. Because COD2 reagents do not contain mercury as a masking agent, they exhibit a positive interference from chloride. More information is available for use with specific applications.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

| Program | Standard | Precision (95% Confidence Interval) | Sensitivity Concentration change per 0.010 Abs change |
|---------------|---------------|-------------------------------------|--|
| 431 (ULR) | 30 mg/L COD | 28.8–31.2 mg/L COD | 0.5 mg/L COD |
| 430 (LR) | 80 mg/L COD | 77–83 mg/L COD | 3 mg/L COD |
| 435 (HR) | 800 mg/L COD | 785–815 mg/L COD | 23 mg/L COD |
| 435 (HR Plus) | 8000 mg/L COD | 7850–8150 mg/L COD | 230 mg/L COD |

Summary of method

The results in mg/L COD are defined as the milligrams of O₂ consumed per liter of sample under the conditions of this procedure. The sample is heated for 2 hours with sulfuric acid and a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion (Cr₂O₇²⁻) to green chromic ion (Cr³⁺). When the 0.7–40.0 or the 3–150 mg/L colorimetric method is used, the amount of Cr⁶⁺ that remains is measured. When the 20–1500 mg/L or 200–15,000 mg/L colorimetric method is used, the amount of Cr³⁺ that is produced is measured. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.

Test results are measured at the wavelengths that are specified in [Table 3](#).

Table 3 Range-specific test wavelengths

| Range in mg/L COD | Wavelength |
|-------------------|-------------------------------------|
| 0.7–40.0 mg/L | 350 nm (for applicable instruments) |
| 3–150 mg/L | 420 nm |
| 20–1500 | 620 nm (610 nm for colorimeters) |
| 200–15,000 mg/L | 620 nm (610 nm for colorimeters) |

Pollution prevention and waste management

Reacted samples contain mercury, silver and chromium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations. Users in the United States can use the ez COD Recycling Service for disposal of COD vials. Refer to [Consumables and replacement items](#) on page 7.

Consumables and replacement items

Required reagents

| Description | Quantity/test | Unit | Item no. |
|---------------------------------------|---------------|--------|----------|
| COD, Ultra Low Range, 0.7–40 mg/L | 1–2 vials | 25/pkg | 2415825 |
| COD, Low Range, 3–150 mg/L | 1–2 vials | 25/pkg | 2125825 |
| COD, High Range, 20–1500 mg/L | 1–2 vials | 25/pkg | 2125925 |
| COD, High Range Plus, 200–15,000 mg/L | 1–2 vials | 25/pkg | 2415925 |
| Water, deionized | varies | 4 L | 27256 |

Alternate reagents and package sizes

| Description | Quantity/test | Unit | Item no. |
|---|---------------|---------|----------|
| COD2, Low Range, 0–150 mg/L COD | 1–2 vials | 25/pkg | 2565025 |
| COD2, High Range, 0–1500 mg/L COD | 1–2 vials | 25/pkg | 2565125 |
| COD2, High Range, 0–1500 mg/L COD | 1–2 vials | 150/pkg | 2565115 |
| COD2, High Range Plus, 0–15,000 mg/L COD | 1–2 vials | 25/pkg | 2834325 |
| COD Digestion Reagent Vials, 3–150 mg/L COD | 1–2 vials | 150/pkg | 2125815 |
| COD Digestion Reagent Vials, 200–1500 mg/L COD | 1–2 vials | 150/pkg | 2125915 |
| COD Digestion Reagent Vials, ULR 0.7–40.0 mg/L | 1–2 vials | 150/pkg | 2415815 |
| COD Digestion Reagent Vials, HR plus, 200–25,000 mg/L | 1–2 vials | 150/pkg | 2415915 |

Required apparatus

| Description | Quantity/test | Unit | Item no. |
|---|---------------|------|-----------------|
| Blender, 2-speed, 120 VAC option | 1 | each | 2616100 |
| OR | | | |
| Blender, 2-speed, 240 VAC option | 1 | each | 2616102 |
| DRB 200 Reactor, 110 VAC option, 15 x 16-mm wells | 1 | each | LTV082.53.40001 |
| OR | | | |
| DRB 200 Reactor, 220 VAC option, 15 x 16-mm wells | 1 | each | LTV082.52.40001 |
| Pipet filler, safety bulb | 1 | each | 1465100 |
| Pipet, volumetric, Class A, 2.00-mL | 1 | each | 1451536 |

Recommended standards and apparatus

| Description | Unit | Item no. |
|---|----------|----------|
| Beaker, 250-mL | each | 50046H |
| COD Standard Solution, 300-mg/L | 200 mL | 1218629 |
| COD Standard Solution, 300-mg/L | 500mL | 1218649 |
| COD Standard Solution, 800-mg/L | 200 mL | 2672629 |
| COD Standard Solution, 1000-mg/L | 200 mL | 2253929 |
| Oxygen Demand Standard (BOD, COD, TOC), 10-mL ampules | 16/pkg | 2833510 |
| Pipet, TenSette [®] , 0.1–1.0 mL | each | 1970001 |
| Pipet tips for TenSette [®] Pipet, 0.1–1.0 mL | 50/pkg | 2185696 |
| Pipet tips for TenSette [®] Pipet, 0.1–1.0 mL | 1000/pkg | 2185628 |
| Potassium Acid Phthalate (KHP), ACS | 500 g | 31534 |
| Stir bar, octagonal | each | 2095352 |
| Stirrer, electromagnetic, 120 VAC, with electrode stand | each | 4530001 |
| Stirrer, electromagnetic, 230 VAC, with electrode stand | each | 4530002 |
| Test tube rack, stainless steel | each | 1864100 |
| Wipes, disposable | 70/pkg | 2096900 |

Optional reagents and apparatus

| Description | Unit | Item no. |
|--|--------|----------|
| Balance, analytical, 80 g x 0.1 mg 100–240 VAC | each | 2936701 |
| Flask, volumetric, Class A, 1000-mL glass | each | 1457453 |
| Flask, volumetric, Class A, 100-mL glass | each | 1457442 |
| Mercuric Sulfate | 28 g | 191520 |
| Pipet, volumetric, Class A, 3-mL | each | 1451503 |
| Pipet, volumetric, Class A, 10-mL | each | 1451538 |
| Sulfuric Acid, ACS | 500 mL | 97949 |
| Wastewater Influent Standard Solution, Mixed Parameter, for NH ₃ -N, NO ₃ -N, PO ₄ , COD, SO ₄ , TOC | 500 mL | 2833149 |

Optional reagents and apparatus (continued)

| Description | Unit | Item no. |
|--|---------|----------------------|
| EZ COD™ Recycling Service with 5-gal bucket-mail back option (For US customers only. 20 and 55 gallon sizes are also available.) | each | 2895405 |
| EZ COD™ Recycling Service with 5-gal bucket- pick up option. (For US customers only. 20 and 55 gallon sizes are also available.) | each | 2895405P |
| Finger cots | 2/pkg | 1464702 |
| Gloves, chemical resistant, size 9–9.5 | pair | 2410104 ¹ |
| Paper, for weighing, 100 x 100 mm | 500/pkg | 1473885 |
| Safety goggles, vented | each | 2550700 |
| Wastewater Effluent Standard Solution, Mixed Parameter, for NH ₃ -N, NO ₃ -N, PO ₄ ³⁻ , COD, SO ₄ ²⁻ , TOC | 500 mL | 2833249 |

¹ Other sizes available



FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – Call toll-free **800-227-4224**
Outside the U.S.A. – Contact the **HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932