

Chemicals needed for the following procedures:

Kaolin: Obtained from the University of Missouri Clay Repository. Product KGa-1b. The origin of the clay, chemical composition, cation exchange capacity, surface area are given at <http://web.missouri.edu/~geoscjy/SourceClay/chem.html>. Ordering information is also available at this web site.

Data from the web site is given below:

Kaolin KGa-1(KGa-1b), (low-defect)

ORIGIN: Tuscaloosa formation? (Cretaceous?) (stratigraphy uncertain)

County of Washington, State of Georgia, USA

LOCATION: 32o58' N-82o53' W approximately, topographic map Tabernacle, Georgia N 3252.5-W 8252.5/7.5, Collected from face of Coss-Hodges pit,

October 3, 1972.

CHEMICAL COMPOSITION (%): SiO₂: 44.2, Al₂O₃: 39.7, TiO₂: 1.39, Fe₂O₃: 0.13, FeO: 0.08, MnO: 0.002, MgO: 0.03, CaO: n.d., Na₂O: 0.013, K₂O: 0.05, F:0.013, P₂O₅: 0.034, Loss on heating: -550oC: 12.6; 550-1000oC: 1.18.

CATION EXCHANGE CAPACITY (CEC): 2.0 meq/100g

SURFACE AREA: N₂ area: 10.05 +/- 0.02 m²/g

THERMAL ANALYSIS: DTA: endotherm at 630oC, exotherm at 1015oC, TG: dehydroxylation weight loss 13.11% (theory 14%) indicating less than 7% impurities.

INFRARED SPECTROSCOPY: Typical spectrum for well crystallized kaolinite, however not as well crystallized as a typical China clay from Cornwall, as judged from the intensity of the 3669 cm⁻¹ band. Splitting of the 1100 cm⁻¹ band is due to the presence of coarse crystals.

STRUCTURE:(Mg.02 Ca.01 Na.01 K.01)[Al_{3.86} Fe(III).02 Mntr Ti.11][Si_{3.83} Al.17]O₁₀(OH)₈,

Octahedral charge:.11, Tetrahedral charge:-.17, Interlayer charge:-.06, Unbalanced charge:0.00

Montmorillonite: Obtained from the University of Missouri Clay Repository. Product STx-1. The origin of the clay, chemical composition, cation exchange capacity, and surface area are given at <http://web.missouri.edu/~geoscjy/SourceClay/chem.html>. Ordering information is also available at this web site. 0.100 +/-0.001 g per vial

Data from the web site is given below:

Texas Montmorillonite STx-1

ORIGIN: Manning formation, Jackson group (eocene)

County of Gonzales, State of Texas, USA

LOCATION: 29o30' N, 97o22' W approximately, topographic map: Hamon, Texas, N 2922.5-W 9715/7.5,

Collected from face of pit, October 17, 1972.

CHEMICAL COMPOSITION (%): SiO₂: 70.1, Al₂O₃: 16.0, TiO₂: 0.22, Fe₂O₃: 0.65, FeO: 0.15, MnO: 0.009, MgO: 3.69, CaO: 1.59, Na₂O: 0.27, K₂O:

0.078, F: 0.084, P₂O₅: 0.026, S: 0.04, Loss on heating: -550oC: 3.32; 550-1000oC: 3.22, CO₂: 0.16.

CATION EXCHANGE CAPACITY (CEC): 84.4 meq/100g, major exchange cation Ca.

SURFACE AREA: N₂ area: 83.79 +/- 0.22 m²/g

THERMAL ANALYSIS: DTA: endotherms at 185oC (shoulder at 235oC), desorption of water: 725oC, dehydroxylation; shoulder at 920oC, exotherms at 1055oC, 1065oC, 1135oC. TG: Loss in dehydroxylation range: 3.88% (theory: 5%).

INFRARED SPECTROSCOPY: The spectrum indicates a low iron content. Quartz (697 cm⁻¹), a silica phase (797 cm⁻¹), and a trace of carbonate (1400 cm⁻¹) are detectable.

STRUCTURE:(Ca.27 Na.04 K.01)[Al₂.41 Fe(III).09 Mntr Mg.71 Ti..03][Si₈.00]O₂₀(OH)₄, Octahedral charge:-.68, Tetrahedral charge:0.00, Interlayer charge:-.68, Unbalanced charge:-.08, Extra Si:.59

Stock Copper Solution: CAS Number 1344-67-8. The stock Cu solution (1000 mg/L) was made from Cu(NO₃)₂ in 1 % nitric acid. Dissolve 0.268 g of CuCl₂·2H₂O (GMW 170.34) in 100.0 mL deionized

water (volumetric flask) to make a 1000 mg/L solution. Make a 1:100 dilution of this solution to obtain a 10.0 mg/L solution of Cu^{2+} .

$\text{Ca}(\text{NO}_3)_2$, 0.500 M: CAS Number 13477-34-4. Dissolve 11.808 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (GMW 236.16 g/mol) in 100.0 mL deionized water to make a 0.500 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution.

HEPES (N-2-hydroxyethylpiperazine-N -2-ethanesulfonic acid), CAS Number 7365-45-9. 0.80 M: Dissolve 47.66 g of N-2-hydroxyethylpiperazine-N -2-ethane sulfonic acid (HEPES, GMW 238.30 g/mol) in ~200 mL deionized water in a beaker. Adjust the pH of this solution to approximately 7.5 using 1.0 M NaOH. Quantitatively transfer this solution to a 250.0 mL volumetric flask and fill to the mark.

NaOH, CAS Number 1310-73-2. 1M for pH adjustment of buffer solutions.

HCl, CAS Number 7647-01-0. 1M for pH adjustment of buffer solutions.

Equipment:

50-mL centrifuge tubes with caps: Blue Max Disposable Centrifuge Tubes, Polystyrene, Conical-Bottom, Sterile, Falcon, VWR Scientific Products Number 21008-939.

25-mm diameter polycarbonate filter cartridge, Polycarbonate Filter Holder, 25 mm filter, 12 per pack, VWR Scientific Product Number 22001-800.

25-mm Gelman type A/E glass fiber filter, Glass Fiber Filters, Type A/E, Pall Gelman, VWR Scientific Products Number 28150-178.

Spartan-13 0.2 μm membrane filter or similar brand (Agilent Technologies, HP-5061-3366.)

Any 25-mL disposable plastic/polycarbonate syringes

Test tube rotator, Glas-Col Mini-Rotator, 120V, VWR Scientific Products Number 33725-042.
(Test tube rockers will probably work just as well.)

A flame atomic absorption spectrophotometer (AAS) unit capable of analyzing aqueous copper solutions is needed.

Student procedures and handouts (^WSupplemental Material, JCE online)

Lab Documentation

Procedure for the Determination of a Distribution Coefficient as a Function of Pollutant Concentration

First Week:

Select a solid phase (either KGa-1b Kaolin or STx-1 Montmorillinite).

Preparation of Stock Copper Solution

Dissolve 0.268 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (GMW 170.34) in 100.0 mL deionized water (volumetric flask) to make a 1000 mg/L solution. Make a 1:100 dilution of this solution to obtain a 10.0 mg/L solution of Cu^{2+} .

Preparation of Calcium Nitrate Solution (ionic strength adjustor)

Dissolve 11.808 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (GMW 236.16 g/mol) in 100.0 mL deionized water to make a 0.500 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution.

Preparation of 0.80 M HEPES Solution (pH buffer solution)

Dissolve 47.66 g of N-2-hydroxyethylpiperazine-N -2-ethane sulfonic acid (HEPES, GMW 238.30 g/mol) in ~200 mL deionized water in a beaker. Adjust the pH of this solution to approximately 7.5 using 1.0 M NaOH. Quantitatively transfer this solution to a 250.0 mL volumetric flask and fill to the mark.

Preparation of Polycarbonate Vials

Place approximately 0.100 g (be as precise as possible) into each of 14 polycarbonate vials. Add 2.00 mL of the calcium nitrate solution, 2.00 mL of the HEPES solution, and the appropriate amount of copper solution from Table 1 (below) to a 100. mL graduated cylinder. Dilute to 40.0 mL with deionized water. Quantitatively transfer this solution to a polycarbonate vial, label it, cap it, and mix by shaking. Repeat this procedure to make two suspensions for each copper concentration shown in Table 1.

Preparation of Blanks (for determination of total Cu concentration)

Add 2.00 mL of the calcium nitrate solution, 2.00 mL of the HEPES solution, and the appropriate amount of copper solution from Table 1 (below) to a 100. ML graduate cylinder. Fill the

graduated cylinder to 40.0 mL with deionized water and add this solution to a polycarbonate vial.

Repeat to make two blanks for each final copper concentration.

Table 1. Copper Dilutions for Equilibrations

Volume (mL)	of Cu Solution (mg/L)	Final Cu Conc. mg/L
2.00	1000.0	50.0
1.00	1000.0	25.0
4.00	100.0	10.0
2.00	100.0	5.00
4.00	10.0	1.00
2.00	10.0	0.50
1.00	10.0	0.25

Place the vials on the mixer for at least three days.

Second Week:

Turn on the FAAS and warm up the Cu lamp.

Preparation of Cu Calibration Standards

Dissolve 1.341 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (GMW 170.48) in a minimum amount of water and add 25.00 mL concentrated nitric acid. Quantitatively transfer this solution to a 500 mL volumetric flask and fill to the mark with deionized water. Follow Table 2 to prepare standards.

Table 2 Preparation of AAS Calibration Standards

For a Cu conc. of	dilute x mL	of x mg/L solution	in x mL volumetric
10.0	1.00	1000.	100
4.00	10.0	10.0	25
1.00	10.0	10.0	100
0.50	25.0	1.00	50
0.30	15.0	1.00	50
0.10	5.00	1.00	50
0.040	1.00	1.00	25

Filter the Equilibrated Solutions

Filter the solutions through a Gelman type A/E glass fiber filter first. Then filter again through a Spartan-13 0.20 μm nylon filter.

Analyze the filtered samples, standards, and blanks using the FAAS.

Compile the data in the sample spreadsheet and calculate K_a for each sample.

Procedure for the Determination of a Distribution Coefficient as a Function of Total Suspended Solids (TSS)

First Week:

Select a solid phase (either KGa-1b Kaolin or STx-1 Montmorillinite).

Preparation of Stock Copper Solution

Dissolve 0.268 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (GMW 170.34) in 100.0 mL deionized water (volumetric flask) to make a 1000 mg/L solution. Make a 1:100 dilution of this solution to obtain a 10.0 mg/L solution of Cu^{2+} .

Preparation of Calcium Nitrate Solution (ionic strength adjustor)

Dissolve 11.808 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (GMW 236.16 g/mol) in 100.0 mL deionized water to make a 0.500 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution.

Preparation of 0.80 M HEPES Solution (pH buffer solution)

Dissolve 47.66 g of N-2-hydroxyethylpiperazine-N -2-ethane sulfonic acid (HEPES, GMW 238.30 g/mol) in ~200 mL deionized water in a beaker. Adjust the pH of this solution to approximately 7.5 using 1.0 M NaOH. Quantitatively transfer this solution to a 250.0 mL volumetric flask and fill to the mark.

Preparation of Solutions with Low Solids Concentrations

Place 0.040 g of solid phase into a 100.0 mL volumetric flask and fill to the mark with deionized water to make a 400. mg/L clay solution. Add a stirring bean to the solution and place the solution on a stirring plate. Add 1.00 mL of this solution to each of two vials and 10.00 mL to two other vials. Add 4.00 mL of stock copper solution, 2.00 mL of calcium nitrate solution and 2.00 mL of HEPES solution to a 100. mL graduated cylinder. For the vials with 10.00 mL of solution in them, fill the graduated cylinder to only 30.0 mL. For the vials with 1.00 mL of solution in them, fill the graduated cylinder to 39.0 mL.

Preparation of Remaining Solids Concentrations

Place the following weights of solid phase into labeled polycarbonate vials: 0.020 g, 0.040 g, 0.100 g, 0.200 g, 0.400 g (two for each solid concentration). Add 4.00 mL of stock copper

solution, 2.00 mL of calcium nitrate solution and 2.00 mL of HEPES solution to a 100. mL graduated cylinder. Fill the graduated cylinder to 40.0 mL and add to the polycarbonate vials.

Preparation of Blanks

Place 4.00 mL of the stock copper solution, 2.00 mL of the calcium nitrate solution, and 2.00 mL of the HEPES solution into a 100. mL graduated cylinder. Fill the graduated cylinder to 40.0 mL with deionized water and add this solution to a polycarbonate vial. Repeat this procedure for the second vial.

Place the vials on the mixer for at least three days.

Second Week:

Turn on the FAAS and warm up the Cu lamp.

Preparation of Cu Calibration Standards

Dissolve 1.341 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (GMW 170.48) in a minimum amount of water and add 25.00 mL concentrated nitric acid. Quantitatively transfer this solution to a 500 mL volumetric flask and fill to the mark with deionized water. Follow Table 2 to prepare standards.

Table 2 Preparation of AAS Calibration Standards

For a Cu conc. of	dilute x mL	of x mg/L solution	in x mL volumetric
10.0	1.00	1000.	100
4.00	10.0	10.0	25
1.00	10.0	10.0	100
0.50	25.0	1.00	50
0.30	15.0	1.00	50
0.10	5.00	1.00	50
0.040	1.00	1.00	25

Filter the Equilibrated Solutions

Filter the solutions through a Gelman type A/E glass fiber filter first. Then filter again through a Spartan-13 0.20 μm nylon filter.

Analyze the filter samples, standards, and blanks using the FAAS.

Compile the data in the sample spreadsheet and calculate K_d for each sample.

Procedure for the Determination of a Distribution Coefficient as a Function of Ionic Strength

First Week:

Select a solid phase (either KGa-1b Kaolin or STx-1 Montmorillinite).

Preparation of Stock Copper Solution

Dissolve 0.268 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (GMW 170.34) in 100.0 mL deionized water (volumetric flask) to make a 1000 mg/L solution. Make a 1:100 dilution of this solution to obtain a 10.0 mg/L solution of Cu^{2+} .

Preparation of Calcium Nitrate Solution (ionic strength adjustor)

Dissolve 11.808 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (GMW 236.16 g/mol) in 100.0 mL deionized water to make a 0.500 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution. Make 10:100 and 1:100 dilutions of this solution to obtain 0.08469 and 0.008469 M solutions, respectively.

Preparation of 0.80 M HEPES Solution (pH buffer solution)

Dissolve 47.66 g of N-2-hydroxyethylpiperazine-N -2-ethane sulfonic acid (HEPES, GMW 238.30 g/mol) in ~200 mL deionized water in a beaker. Adjust the pH of this solution to approximately 7.5 using 1.0 M NaOH. Quantitatively transfer this solution to a 250.0 mL volumetric flask and fill to the mark.

Preparation of Polycarbonate Vials

Place approximately 0.100 g (be as precise as possible) into each of 14 polycarbonate vials. Add 4.00 mL of the stock 10 mg/L copper solution, 2.00 mL of the HEPES solution, and the appropriate amount of calcium nitrate solution from Table 1 (below) to a 100. mL graduated cylinder. Dilute to 40.0 mL with deionized water. Quantitatively transfer this solution to a polycarbonate vial, label it, cap it, and mix by shaking. Repeat this procedure to make two suspensions for each calcium nitrate concentration shown in Table 1.

Preparation of Blanks (for determination of total Cu concentration)

Add 4.00 mL of the stock 10 mg/L copper solution, 2.00 mL of the HEPES solution, and the appropriate amount of calcium nitrate solution from Table 1 (below) to a 100. mL graduate cylinder. Fill the graduated cylinder to 40.0 mL with deionized water and add this solution to an

empty (no solid phase) polycarbonate vial. Repeat to make two blanks for each final ionic strength solution.

Table 1. Calcium Nitrate Dilutions

Volume (mL)	Of Ca(NO ₃) ₂ Solution (mg/L)	Final Ca(NO ₃) ₂ (mg/L)	Final Ionic Strength (mg/L)
2.00	0.008469	100	9600
1.00	0.08469	500	10900
2.00	0.08469	1000	12400
1.00	0.8469	5000	24400
2.00	0.8469	10000	39400
3.00	0.8469	15000	54400
4.00	0.8469	20000	69400

Place the vials on the mixer for at least three days.

Second Week:

Turn on the FAAS and warm up the Cu lamp.

Preparation of Cu Calibration Standards

Dissolve 1.341 g CuCl₂·2H₂O (GMW 170.48) in a minimum amount of water and add 25.00 mL concentrated nitric acid. Quantitatively transfer this solution to a 500 mL volumetric flask and fill to the mark with deionized water. Follow Table 2 to prepare standards.

Table 2 Preparation of AAS Calibration Standards

For a Cu conc. of	dilute x mL	of x mg/L solution	in x mL volumetric
10.0	1.00	1000.	100
4.00	10.0	10.0	25
1.00	10.0	10.0	100
0.50	25.0	1.00	50

0.30	15.0	1.00	50
0.10	5.00	1.00	50
0.040	1.00	1.00	25

Filter the Equilibrated Solutions

Filter the solutions through a Gelman type A/E glass fiber filter first. Then filter again through a Spartan-13 0.20 μm nylon filter.

Analyze the filter samples, standards, and blanks using the FAAS.

Compile the data in the sample spreadsheet and calculate K_d for each sample.