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ELECTROCHEMISTRY

Experiments for College/University Introductory and General Chemistry Laboratory courses.

About this Experiment Series:

Electrochemistry is somewhat of a step-child in the general chemistry curriculum. Often left for quick treatment at the end of the semester, "hands-on" electrochemistry labs are thought to be difficult and expensive.

This need not be true. Here are some new tools and ideas that will make electrochemistry understandable, affordable, and easy and fun to teach – and learn! They are designed to help students visualize and understand rather than just memorize chemical concepts.

MicroLab's team are all practicing or recently-retired college/university faculty. Recognizing that the best experiments are those the instructor "tunes" for their course goals and the background of their students, the experiments presented here are in Word format, our fellow faculty are encouraged to freely use these ideas, text, or photographs as they develop lab materials for their students.

Except for the first experiment, Conductivity / Electroplating, all experiments in this Electrochemistry suite use transparent MicroLab software to organize and to quickly graph experimental data. This creates a quick visual and conceptual link between the experiment and the student. Software may be freely downloaded from the MicroLab web site ***www.microlabinfo.com.***

Voltage measurements may be read directly into this software by MicroLab instruments, or hand-entered if observations are made with a digital voltmeter.

Typical student results are included within this experiment text so that faculty may evaluate the experiment. If desired, these results may be removed during edit for student use.

THE ELECTROCHEMICAL SERIES AND MATERIAL SCIENCE

Overview :

This experiment is an extension of the Citrus Battery experiment, which introduced the idea of the electrochemical series and the arbitrary but essential nature of reference electrodes.

The Citrus battery experiment used only three elements – Cu, Fe, and Zn, and very low-cost materials to introduce several important basic electrochemical concepts.

This experiment uses MicroLab's Mult-EChem Half-cell module to extend the number of elements tested. This module can simultaneously manage up to eight metal-ion half-cells of different elements, concentrations, or temperatures. All access a common aqueous potassium nitrate salt bridge through a porous polyethylene cylinder. Required sample volume is 3 mL; the aqueous salt bridge produces stable readings ± 1 mV for more than an hour.

The Mult-EChem Half-cell module can also incorporate an Ag/AgCl reference electrode, maintaining the reference electrode's concentration and temperature when sample cell concentrations or temperatures are changed.

The experiment concludes by correlating the industrial uses and measured electrochemical properties of a dozen elements of industrial importance.

The experiment also introduces the MicroLab Model 252 Electronic Half-cell module, which provides instant access to 194 accurate, stable electrochemical half-cells of variable concentration and temperature, for both demonstration and laboratory.

Concepts:

- Students can experimentally add to the list of elements used to build the electrochemical series.
- An element's industrial value is related to its position in the electrochemical series.
- Industrially-important elements that occupy the middle of the electrochemical series – iron, for example, may be protected from environmental oxidation with a "sacrificial anode" of an element of lower reduction potential such as -zinc or magnesium.
- Hydrogen and Ag/AgCl reference electrodes are international standards because they are stable and can be reproduced anywhere in the world. The Ag/AgCl reference electrode is used world-wide in pH electrodes because of its stability and its ease of manufacture. A pH electrode will fit into one of the sample wells in the Mult-EChem Half-cell module, providing access to a stable, repeatable reference electrode for electrochemical series and Nernst experiments.
- The Model 252 Electronic Half-cell module expands safe electrochemical series measurements to expensive and dangerous elements such as gold and sodium. It also provides both stable Standard Hydrogen and Ag/AgCl reference electrodes for electrochemical measurements.

Materials:

- MicroLab Model 152 Mult-EChem Half-cell module. The 152 Mult-EChem Half-cell module requires 3 mL samples of each ion solution, and about 5 mL of 1 M KNO_3 solution to fill the salt bridge. It is important to soak the porous polyethylene salt bridge cylinder overnight with KNO_3 solution to saturate its pores before use. The module may be stored in a 1-quart zip-lock freezer lab to keep the porous cylinder moist between lab sections. Allow it to dry out between semesters to avoid growth of mold.
- A voltage measuring device – A MicroLab 238 USB voltmeter, a MicroLab 252 Electronic Half-cell Module, a MicroLab FS-522 or FS-528 lab measurement system, or a digital voltmeter.
- A computer with MicroLab *Electrochem Series* software loaded.

Resource Materials:

- Check the MicroLab web site www.microlabinfo.com under "Help" for short video clips.

Equipment:

(A) Setting up the Mult-EChem Half-cell Module

The **Model 152** Multi-EChem Half Cell Module has space for eight half-cells, each equally accessing a central aqueous potassium nitrate salt bridge through a porous cylinder. A milled "overflow" area prevents spills and mixing of solutions. The post in the center simply reduces the volume of KNO_3 required for the salt bridge.

The Multi-EChem design provides three advantages:

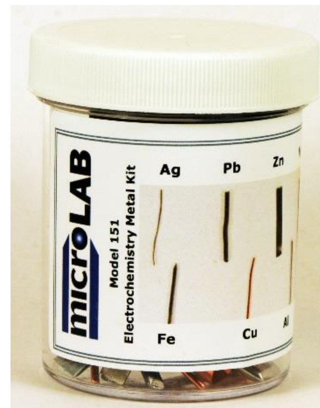
(1) Connection of half-cell pairs is easily implemented and clearly visualized.
These may be different metal/ion pairs to develop the electrochemical series, or different concentrations of the same metal/ion pair to create concentration cells.

(2) The salt bridge does not dry out and electrochemical cell voltages are extremely stable for long periods of time.

(3) The polypropylene body of the module is rugged and chemically resistant. Its non-skid feet keep it securely in place on the lab bench. It will have a long service lifetime

To prepare the Multl-EChem Half-cell module for use, immerse it for a few hours (or overnight) in potassium nitrate solution – concentration not important. 1M KNO3 can be prepared by dissolving 101 g of granular KNO3 in 1 liter of distilled water. This will saturate the pores in the porous polyethylene cylinder. Rinse the module before use with DI water. If the pores in the polyethylene cylinder are saturated with KNO3 solution before the sample cylinders are filled, little sample solution will diffuse into the porous salt bridge, but ions will be able to move. The module may be stored and kept damp between lab sessions by zipping it into a 1-quart zip-lock freezer bag.

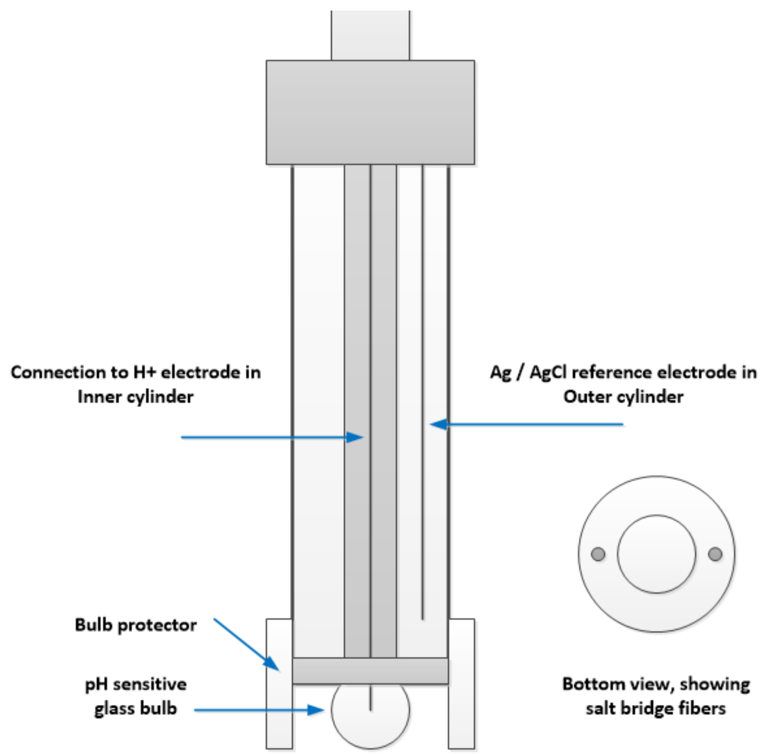
(B) Using the Model 151 Electrochemistry Metal Kit



The metal kit contains two each 5 cm lengths of wire representing seven elements: Cu, Ni, Fe, Pb, Zn, Al, and Ag (one wire) Sandpaper is provided to clean the metal samples before each measurement. Some elements will oxidize when simply exposed to air, particularly moist air.

(C) Using a silver/silver chloride reference electrode.

If you wish to use a silver/silver chloride reaction for a reference electrode, one is integrated into pH electrodes. This reaction is stable, non-toxic, and easy to manufacture. The pH electrode consists of two concentric tubes. The center tube is closed at its end by a thin pH-sensitive glass bulb. A silver wire extends into this bulb and is connected to the center electrode of the BNC plug.



The outer concentric tube is filled with KCl solution and contains a silver wire coated with solid AgCl. A very small amount of AgCl is dissolved in the KCl filling solution. Because the solubility of AgCl is so small (about 1.3 x 10-5 moles/liter), the Ag+ ion concentration remains very constant if any solid AgCl is present, producing a stable reference voltage.

Ions can move from this KCl solution through a saturated fiber plug at the bottom of the pH electrode. If you look into the bottom of the pH electrode, you will see the pH-sensitive glass bulb and on either side of it small fibers which serve as a salt bridge between the Ag/AgCl/KCl reference reaction and the solution.

The wire connecting to the silver wire in the reference electrode is brought out through the cable to the outer metallic case of the BNC connector. You can clip your black voltage lead to this case to connect to the Ag/AgCl reference electrode.

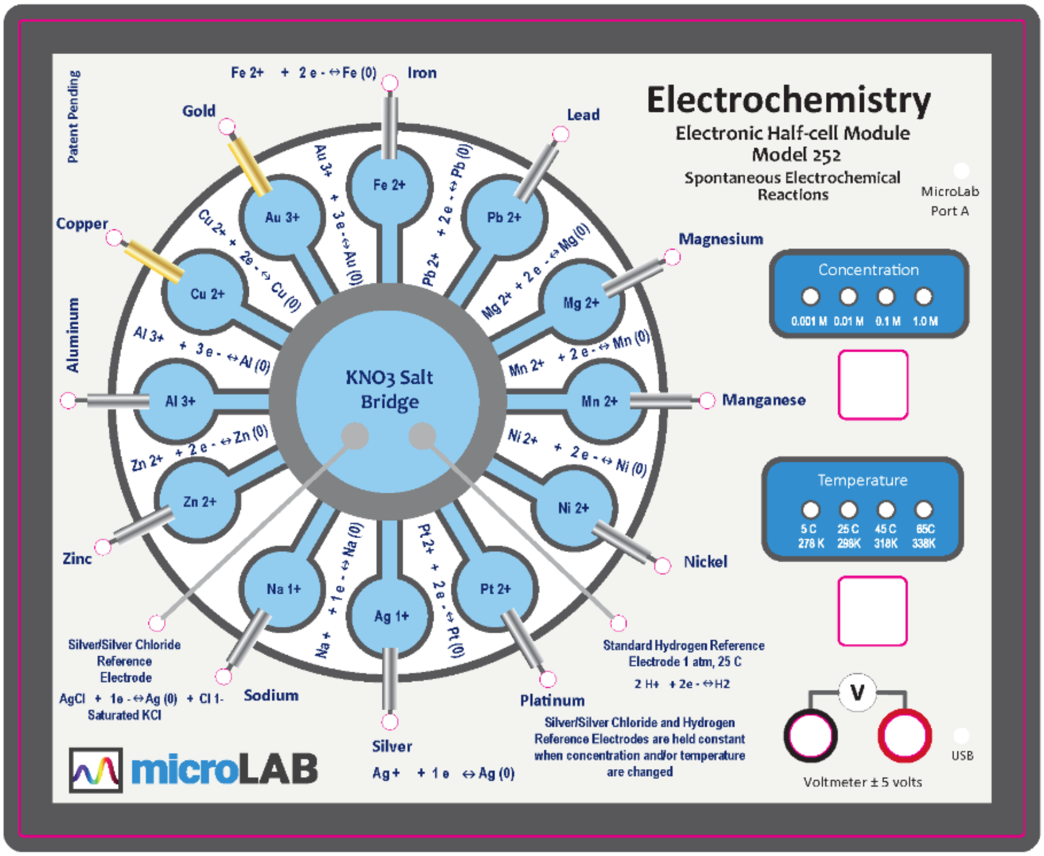
The pH electrode will fit into one of the outer wells in the Multi-EChem Half-cell module. Put about 2 mL of KNO3 salt bridge solution into the well, then insert the pH electrode.

Do not place the pH electrode in a well with silver nitrate solution. The KCl solution that will slowly leak from the reference electrode will react with silver ion to form insoluble silver chloride and will plug the salt bridge fibers in the pH electrode.

There are three ways to run this experiment:

(1) You can use the Model 152 Multi-EChem Half-cell module and up to eight metal/ion pairs, selecting one as a reference reaction.

(2) You can use the Model 252 Electronic Electrochemical Half-cell module. This module has twelve different metal/ion pairs, and silver/silver chloride and standard hydrogen reference electrodes. It also includes elements that are considered costly or dangerous but electrochemically important, such as gold and sodium.



(3) If you choose to use a silver/silver chloride reference electrode, you can do some of the experiments with "wet" samples in the 152 Multi-ECHem Half-cell module, and some with the 252 Electronic Electrochemical Half-cell module. Just transfer the black 252 voltmeter lead from outer metal case of the pH electrode BNC connector to the silver/silver chloride reference electrode pin on the Electronic Electrochemical Half-cell module.

The same voltage measurement system and MicroLab software (Electrochem Series) is used for all of these different approaches.

Part I: Expanding on the Citrus Battery Electrochemical Series

Experiment II of this series developed three general ideas:

(1) There is a natural order among elements of ability to attract electrons.
(2) This order is the same regardless of the element/reaction used as a "zero" reference for the measurements.
(3) This order is the same regardless of the identity of the salt bridge that moves positive and negative ions between the oxidation and reduction reactions to maintain a neutral charge balance.

Experiment II used just three elements – Zn, Fe, and Cu – to develop these ideas. This experiment will simply extend these measurements to …

(1) Test the generalizations to see if they will hold for seven to twelve different elements.
(2) Consider the electrochemical properties of a dozen different elements of industrial importance and decide if reduction potential plays a role in the industrial use and value of each element.

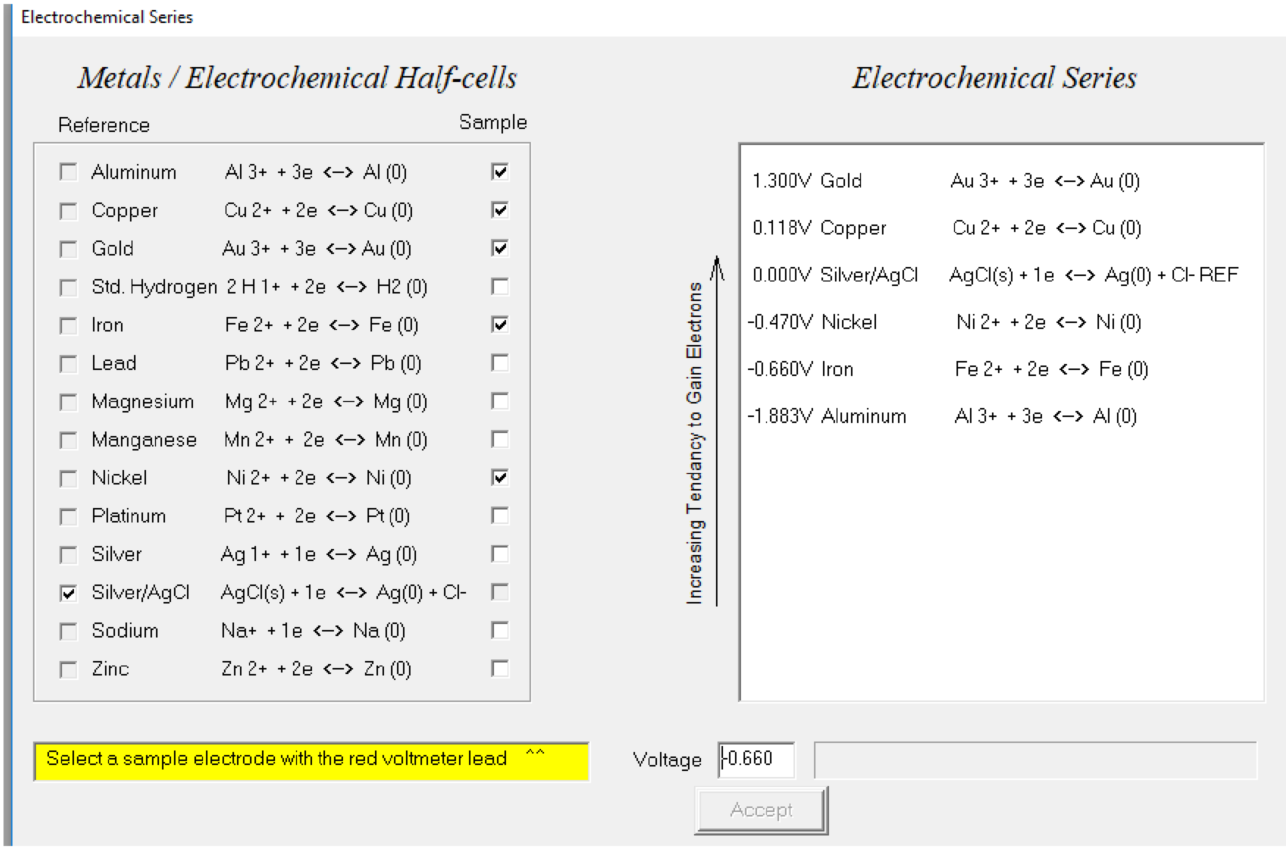
Experimental:

(1) Set up your experimental half-cells – either wet, electronic, or a combination of both. Select a reference electrode. If you are using the Electronic Electrochemical Half-cell module, connect its USB connector to a PC, start the MicroLab Electrochem

Series software, and push the red buttons to select concentration at 1.0 M and temperature at 25 C, standard conditions for comparing electrochemical measurements.

(2) Measure each of your electrochemical half-cell voltages, using the same reference electrode. Create a table of increasing tendency to gain electrons.

Here is sample data for six different elements, using Ag/AgCl as a reference electrode. You can use any element/reaction as a reference. The voltage readings will change, but the order should remain the same regardless of the identity of the reference electrode/reaction. This natural order is called **"The Electrochemical Series".**



Part II: Industrial implications of the Electrochemical Series

The tables below list twelve industrially-important elements mined on Earth. You worked with most or all of these in your experimental work in this experiment. These elements are listed by …

(1) Their abundance on the earth, in parts per million (pp).
(2) The annual industrial production (mining) of the element, in tons.
(3) The reduction potential of the element.
(4) An alphabetical listing.

Use this information and the information gained from your experimental measurements to consider the following questions?

LISTING BY ABUNDANCE OF THE ELEMENT

	Element		Abundance Rank	Abundance ppm	Reduction Potential	Annual Production tons
1	Aluminum	3+	3	82000	-1.662	27,600,000
2	Iron	2+	4	41000	-0.44	1,150,000,000
3	Sodium	1+	6	23000	-2.71	255,000,000
4	Magnesium	2+	8	23000	-2.37	1,010,000
5	Manganese	2+	12	1000	-1.18	16,000,000
6	Nickel	2+	24	80	-0.25	2,250,000
7	Zinc	2+	25	79	-0.7618	11,900
8	Copper	2+	26	100	0.337	19,400,000
9	Lead	2+	37	14	-0.126	4,820,000
10	Silver	1+	65	0.07	0.799	27,000
11	Platinum	2+	71	0.003	1.188	172
12	Gold	3+	72	0.0011	1.52	3,100

There are two +3 elements — There are eight +2 elements — There are two +1 elements

LISTING BY ANNUAL PRODUCTION OF THE ELEMENT

	Element	Abundance Rank	Abundance ppm	Reduction Potential	Annual Production tons
1	Iron	4	41000	-0.44	1,150,000,000
2	Sodium	6	23000	-2.71	255,000,000
3	Aluminum	3	82000	-1.662	27,600,000
4	Copper	26	100	0.337	19,400,000
5	Manganese	12	1000	-1.18	16,000,000
6	Lead	37	14	-0.126	4,820,000
7	Nickel	24	80	-0.25	2,250,000
8	Magnesium	8	23000	-2.37	1,010,000
9	Silver	65	0.07	0.799	27,000
10	Zinc	25	79	-0.7618	11,900
11	Gold	72	0.0011	1.52	3,100
12	Platinum	71	0.003	1.188	172

LISTING BY REDUCTION POTENTIAL OF THE ELEMENT

	Element	Abundance Rank	Abundance ppm	Reduction Potential	Annual Production tons
1	Gold	72	0.0011	1.52	3,100
2	Platinum	71	0.003	1.188	172
3	Silver	65	0.07	0.799	27,000
4	Copper	26	100	0.337	19,400,000
5	Lead	37	14	-0.126	4,820,000
6	Nickel	24	80	-0.25	2,250,000
7	Iron	4	41000	-0.44	1,150,000,000
8	Zinc	25	79	-0.7618	11,900
9	Manganese	12	1000	-1.18	16,000,000
10	Aluminum	3	82000	-1.662	27,600,000
11	Magnesium	8	23000	-2.37	1,010,000
12	Sodium	6	23000	-2.71	255,000,000

ELEMENTS LISTED ALPHABETICALLY

	Element	Abundance Rank	Abundance ppm	Reduction Potential	Annual Production tons
1	Aluminum	3	82000	-1.662	27,600,000
2	Copper	26	100	0.337	19,400,000
3	Gold	72	0.0011	1.52	3,100
4	Iron	4	41000	-0.44	1,150,000,000
5	Lead	37	14	-0.126	4,820,000
6	Magnesium	8	23000	-2.37	1,010,000
7	Manganese	12	1000	-1.18	16,000,000
8	Nickel	24	80	-0.25	2,250,000
9	Platinum	71	0.003	1.188	172
10	Silver	65	0.07	0.799	27,000
11	Sodium	6	23000	-2.71	255,000,000
12	Zinc	25	79	-0.7618	11,900

(1) Recognize that aluminum and sodium are difficult to separate from their ore, and based on their availability, which of the elements listed above would probably be the least expensive?

(2) Suppose that you wanted to manufacture jewelry that would stay bright when exposed to air or to moisture on human skin.

   a. Which elements might you choose?
   b. Would you expect them to be hard to find?
   c. Would you expect them to be expensive or inexpensive?

(3) Recognizing that corrosion (oxidation) is removal of electrons from a metal to form an oxide coat on the outside, do you think copper would make as good jewelry as platinum?

(4) Inexpensive jewelry often sold to tourists is lacquered copper. Why is it lacquered after assembly?

(5) Suppose you want to build a large metal-frame building or a ship using materials that would be reasonably inexpensive and reasonably resistant to corrosion, which metal would you choose and why?

(6) Starting in the 1980's steel (iron) car bodies were galvanized by dipping them in molten zinc before assembly. Steel garbage cans were treated similarly. When galvanized, and any of the zinc coating remained, the steel would not rust. Why do you think this is true?

(7) Movies often portray sailors as constantly painting their (steel) ships when at sea. Recognizing that oxygen in water has a reduction potential of about +0.40 volts. What will happen if sea water and air contact bare steel on a ship?

(8) Of the elements on this list, sodium is the second most important industrially in terms of amount of it produced. Sodium Is electrically-separated from saltwater. Almost all of it is immediately converted into sodium hydroxide which is used in multiple industrial processes.

Because there is so much sodium produced industrially, why is it not used as a building material?

(9) Gold is often found as nuggets or metallic flakes, as in "panning for gold". Why would you not expect to find nuggets of zinc or nuggets of sodium when you are out gold-panning?

(10) The wires on high-quality electronic circuit boards are often plated with a very thin layer of gold. This is one of the major industrial uses of gold. Why do you think this is so?

(11) Nickel and lead are about equal in abundance on the earth. Why do you think objects such as automobile hubcaps are often nickel-plated, but not zinc-plated?

(12) Expensive tableware is sometimes gold-plated. Silver-plated tableware is more common.

a. Based on elemental abundance, which do you think would be more expensive?
b. Based on electrochemical properties, which do you think would require the least polishing?

Conclusions

There are two parts to this experiment:

- Part I is an extension of the electrochemical series measurements started in Experiment II of this series, Citrus Batteries.

  Did you observe anything unusual when you added elements to your electrochemical series list? Do the generalizations you started in Experiment II still hold?

- Part II pointed out that the electrochemical properties (reduction potentials) of metals are a factor when considering their industrial use.

  Electrochemistry, however, is just part of the picture. If you were an engineer selecting materials for construction or perhaps jewelry or joint replacement in humans, what are some other factors you might consider that could affect its cost or suitability for your application. Here are a few to think about.

  For example:

  - How difficult it is to mine, as balanced by its industrial value. Gold mines, for example, often move a lot of dirt and rock to retrieve a small amount of gold.
  - How expensive is it to separate the metal from the ore?
  - Are there toxic by-products of the refining process?
  - Is the metal itself toxic to humans, animals, or the environment?
  - Can you think of other factors?

  Your instructor might wish to assign you a few metals to research on the web and to evaluate for specific purposes.