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#12 Using Bottled Water as a Problem Solving Exercise in Chemical Identification

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Introduction

Description

In this exercise, students are divided into groups of two or three. The groups are given four unidentified bottled waters in unmarked containers and the chemical characteristics taken from the labels on the bottled waters. The students must devise and carry out a plan to match the water in the unmarked containers with the appropriate labels. This lab is appropriate after a discussion on water quality so that students have a basic knowledge of hardness, alkalinity, pH, metals, and nutrients found in unprocessed water. A typed proposal outlining the methods, chemicals, equipment, and instruments needed for analysis, with references, must be approved by the instructor before students analyze the samples. Students are coached on the appropriate methods without dictating exact procedures.

Based on their preliminary research, discussion, and the methods available to them, students conclude that potassium, nitrate, and sodium cannot be used to differentiate the bottled waters. Furthermore, the imprecise values listed for several metals are typically below the detection limits of available instrumentation, therefore Cu, Pb, Zn, and As analyses are also ruled out. Through a process of elimination and researching the chemicals on the labels, students discover calcium and magnesium ions combined as hardness can be used to differentiate several of the bottled waters. Alkalinity (bicarbonate) can also be used to help identify the waters because HCO_3^- is also included on the labels and has a high variability among bottled waters.

Student Audience

This activity is appropriate for high school or first-year college students and may be modified for general non-science majors in college. Students should be familiar with titration, water chemistry, solutions, and basic experimental techniques.

Goals for the Activity

The goals for this activity are for students to:

- develop their critical-thinking skills by conducting an open-ended investigation;
- become familiar with standard methods for water analysis, particularly determination of alkalinity, pH, and hardness;
- understand the analytical techniques that are major tools for the identification of unknowns; and
- develop good experimental techniques to achieve intended results.

Recommended Placement in the Curriculum

This activity should be used in the second term after students have developed some laboratory and experimentation skills and following a basic discussion of water quality.

STUDENT HANDOUT

Using Bottled Water as a Problem Solving Exercise in Chemical Identification

Scenario

Chemistry has many applied applications in the field of environmental science. Oil spills, toxic spills, waste discharges, and air emissions that exceed acceptable discharge limits to the environment occur regularly, and the guilty party usually reports this to the proper authorities as required by law. In such cases, clean-up costs and penalties may be assessed appropriately. However, spills occur where the culprit is not readily identified, as when an oil slick is observed at sea or oil washes up on shore. The offender may be miles away by the time the problem is discovered, or may be one of numerous vessels that could be responsible for the pollution. In this case, chemical detective work is needed to find the guilty party. Fuel oil carried aboard a ship has a distinct chemical fingerprint, which depends on the source of the fuel, impurities, and trace chemical constituents. This fingerprint can be used to identify the source of the fuel, and possibly the ship or ships that spilled the fuel. Similarly, source receptor modeling is a technique that can be used to help track air emissions back to their source of origin. This is particularly useful in distinguishing between natural and anthropogenic sources of pollutants.

Purpose

In this lab you will use the tools of chemical analysis to identify the sources of different waters. Each water corresponds to one of the labels, and your job is to find which label matches each unknown water. By identifying each water, you will have identified the source of the water.

Answer the following questions before proceeding.

Questions

1. What common chemical characteristics are listed on the bottled water labels?
2. Which characteristics have high variability between the different bottled waters? What characteristics have little variability between the bottled waters? Why is this important in identifying which chemical characteristic to use to identify different waters?
3. What are the sources of the different waters?
4. Where does your drinking water come from? If possible, call the supplier of your water source and find out what chemical characteristics are available for your local water.
5. What characteristics of crude oil might be beneficial in helping someone identify the source of spilled crude oil? (Check a reference book to help answer this question.)
6. Propose a plan for identifying the different bottled waters using materials available to you in lab. Explain the rationale of the method you propose.

Safety, Handling, and Disposal

Wear safety glasses at all times in the lab. Acids and bases should be handled with caution. Dispose of used reagents according to local ordinances.

Materials Needed

The materials needed will depend on the procedures you choose to identify your unknown water.

Procedure

Determine what chemical characteristics of the bottled waters you will use for identification. A number of books are available that discuss standard methods for measuring chemical properties of the water. Your instructor should have several available reference books for you to consult once you have determined which properties you wish to measure.

Suggested Reading

1. Hedden, C. R. *Am. Demographics* **1996**, 18, 46-54.

2. Lambert, V. *FDA Cons.* **1993**, 27, 9-11.

3. *Fed. Regist.* 1996, 21,103.35, 1996.

INSTRUCTOR NOTES

Using Bottled Water as a Problem Solving Exercise in Chemical Identification

Time Required

The time required for this activity depends on how much guidance you give the students. You may want to structure the activity so the students test specifically for hardness and alkalinity. In this case, the research and discovery time is greatly reduced. The time for the actual analysis can be as little as an hour if the students used kits, e.g., Hach, LaMotte. If the students do not use kits, the time for analysis should be 1 hour and 50 minutes when you prepare reagents.

Materials Needed

Burette, pH meter, beakers, 1000-mL volumetric flask, concentrated HCl, reagents for hardness determination: EDTA solution, NH_4OH, NH_4Cl, $MgCl_2$•$6H_20$, ascorbic acid, Calmagite indicator. Alternatively, hardness and alkalinity kits can be used.

Safety, Handling, and Disposal

Concentrated acids and bases are used to determine alkalinity and hardness. You may want to mix the acids and bases. Dispose of used reagents according to local ordinances. Warn students about the potential hazard of using concentrated reagents. Since bottled waters are being used, caution students not to treat the samples as drinking water, but as chemical samples requiring analysis.

Points to Cover in Pre-Lab Discussion

Students should have a good understanding of basic water chemistry before they start this activity. Students should be familiar with hardness, bicarbonate, calcium, magnesium, lead, nitrates, and pH; how these are measured; and what values to expect in unprocessed waters.

Procedural Tips and Suggestions

You may have to tailor this lab for different brands of bottled water, depending on what is available in your area.

Students should discover that the only characteristics useful for identifying the bottled waters are hardness and bicarbonate. Select bottled waters that ensure students can use hardness and bicarbonate (HCO_3^-), i.e. there should be enough variability in chemical characteristics to differentiate the waters. Other characteristics such as nitrate and lead are eliminated from use either because there is little difference between the waters or the concentrations are below the limits of detection using methods available in an introductory chemistry course.

Total hardness is defined as the sum of Ca^{2+} and Mg^{2+} ion concentrations. For the waters listed in Table 1, the hardness values are 102 ppm (Evian), 16 ppm (Volvic), 60 ppm (NAYA), and 109 ppm (Avalon). The range of hardness values for this sample of bottled waters allows students to differentiate between all of them except Evian and Avalon. Bicarbonate alkalinity can be used to distinguish between Evian and Avalon.

Students use titrametric procedures for determining total hardness and alkalinity based on *Standard Methods* (3). You will want to cover these procedures with students before they perform the lab. Hardness is determined by EDTA titration using Calmagite indicator. The

EDTA is standardized against a known sample of $CaCO_3$. Although doing titrations is probably best, a commercial test kit (HACH, LaMotte, CHEMetrics) can be used as an alternative for determining hardness.

At the pH of bottled water (~7.0), almost all of the alkalinity is in the form of bicarbonate. Therefore the measurement of HCO_3^- is used to determine alkalinity. Alkalinity is found by titrating 100 mL of the sample to a pH of 4.3 with 0.012 N HCl. *Standard Methods* (3) suggests titrating with 0.01N or 0.02N HCl. Using stock HCl and diluting 1:1,000 in a volumetric flask gives an acceptable concentration (~0.012 N) for alkalinity determinations. Since the HCO_3^-: H^+ ratio is 1:1, the amount of HCO_3^- present is determined from the volume of acid required to reach the 4.3 end-point and converting to mg/L. Alkalinity can also be found using methyl orange indicator to determine the end-point.

Procedure for Hardness

Values obtained by this procedure should approximate the sum of calcium and magnesium concentrations on the bottle.

1. Place 4.0 grams disodium EDTA and 100 mL distilled water into a 500-mL Erlenmeyer flask. Add 10 mL of concentrated ammonium hydroxide. Warm the container slightly if necessary to dissolve all the EDTA.

2. When the EDTA has completely dissolved, add 0.1 g of $MgCl_2 \bullet 6H_20$. Swirl to dissolve and transfer solution to a 1000-mL graduated cylinder or volumetric flask. Add enough distilled water to reach the 1000-mL mark. Transfer the EDTA to a polyethylene bottle.

3. Pipet a 50-mL aliquot of bottled water into a 250-mL Erlenmeyer flask. Add successively with mixing 10 mg of ascorbic acid, 10 mL of NH_3/NH_4OH buffer (35 g of NH_4Cl in 285 mL of concentrated NH_4OH diluted to 500 mL) with a pH of 10, and 3-4 drops of Calmagite indicator (0.10 g Calmagite in 100 mL distilled water).

4. Titrate the bottled water from step 3 with the EDTA solution using a 50-mL buret. The end-point is where the last tinge of red disappears and a purple color appears. Repeat the titration at least two more times.

5. Use the following equation to calculate the approximate hardness (Ca^{2+} + Mg^{2+}):

$$\text{Hardness} = \text{mL of EDTA used} \times 8.0$$

6. Repeat the titration at least two more times to determine the hardness of the bottled water.

Notes

Equation 1 is derived from titrating a standard 0.50 g sample of $CaCO_3$ with the EDTA solution: Weigh a 0.50 g sample of $CaCO_3$ into a 250-mL beaker. Using a pipet, slowly add 10 mL of 6 M HCl, being careful not to splatter the $CaCO_3$.

If necessary, add more HCl to insure all the $CaCO_3$ dissolves. Add 50 mL of distilled water and transfer to a 500-mL volumetric flask or graduated cylinder. Dilute to the 500-mL mark and mix thoroughly. Titrate with the EDTA solution following steps 3 and 4 above.

Following this procedure should produce a standard solution of 4.0×10^2 ppm of Ca (.01 mol Ca/L x 40 g/mol x 1000 mg/g). Assuming there is no magnesium present, titrating should require approximately 50 mL of EDTA solution. Hence, 50 mL of EDTA is required to reach the end-point for a hardness of 400 ppm. If a subsequent titration of an unknown requires Y mL, then the hardness of the unknown is (Y/50) x 400, or 8Y.

Procedure for Bicarbonate

At the pH of bottled water (~7.0), most of the alkalinity of the water is in the form of bicarbonate, HCO_3^-. Following a modified version of determining alkalinity will give the approximate bicarbonate concentration. The actual value determined by this procedure will be about 10% higher than the actual bicarbonate value due to the slight contribution of carbonate to alkalinity.

1. Dilute standard HCl stock solution by a thousand-fold, 1 mL of stock solution in a 1000-mL volumetric flask. This gives a concentration of approximately .012 M (.012 N).

2. Place a 100-mL sample of the bottled water into a 250-mL beaker.

3. Using a pH meter, titrate this with the 0.012 M acid until a pH of 4.3 is reached. (See notes below.)

4. The bicarbonate concentration is given by:

bicarbonate in mg/L = mL acid used in titration x 7.32

Notes

Equation 2 comes from the fact that H^+ combines with the bicarbonate to produce CO_2 and H_2O. There is a 1:1 ratio of carbonate to hydrogen ion. The bicarbonate concentration in mg/L can be calculated by taking:

$$(\text{concentration of acid used}) \times (\text{volume of acid in L}) \times (61\ \text{g/mol}) \times 1000\ \text{mg/g} \div 0.1\ \text{L}$$

Other concentrations of acid can be used. Standard Methods (2,3) suggests .01N or .02N. Diluting stock solution by a factor of 1000 gives 0.0121N solution.

Use a pH meter and titrate to 4.3 or use methyl orange indicator.

Throughout this exercise students must use problem solving and critical-thinking skills to identify the bottled waters. The instructor can decide how much information to give students, making the exercise more or less challenging. Students also become familiar with water quality testing, working with standards, understanding units of measurement, and data interpretation. Values obtained by students for both hardness and alkalinity are typically within 10% of the label values, and the collected data are sufficient to differentiate the waters.

After collecting their data and comparing it to the label values, students realize that the chemical values given on the bottle represent a statistical mean and not an absolute value. For this reason, results will vary. If calcium is listed as 78 ppm and magnesium as 24 ppm, students should not expect to measure 102 ppm when they test for hardness. Knowing the approximate range of unknown concentrations also serves as a quality control check on the students' procedures.

Sample Results

Four bottled waters and their characteristics used for this exercised are summarized in Table 1. One analysis of Evian and NAYA for hardness and alkalinity found a hardness of 116 mg/L for Evian and 70 mg/L for NAYA. For bicarbonate, values of 380 mg/L and 250 mg/L were found for Evian and NAYA, respectively. These values are close enough to values given in Table 1 to identify these bottled waters.

Table 1: Bottled Water Chemical Characteristics

	Evian (France)	Volvic (France)	NAYA (Canada)	Avalon (Canada)
Ca^{2+}	78	10	38	73
Mg^{2+}	24	6	22	36
Si	14	nl	nl	nl
pH	7.2	7.0	nl	nl
HCO_3^-	357	65	243	260
SO_4^{2-}	10	nl	14	57
Cl^-	4	8	1	16
NO^{3-}	1	1	0.05	<0.05
K^+	nl	6	2	1
Na^+	nl	9	6	9
TDS	nl	109	nl	nl
Cu	nl	nl	<10 ppb	<10 ppb
Zn	nl	nl	<10 ppb	<10 ppb
Pb	nl	nl	<10 ppb	<10 ppb
As	nl	nl	<10 ppb	<10 ppb

Concentrations are in in ppm where units are not included.
nl= not listed

Plausible Answers to Student Questions

1. What common chemical characteristics are listed on the bottled water labels?

   The chemical characteristics of select bottled waters are given in Table 1 above. Many bottled waters do not give a comprehensive analysis on their labels. It is important to use bottled waters that give a fairly complete chemical analysis of their contents. The first two references listed at *the end of this section give a fairly comprehensive analysis of most of the bottled waters sold commercially.*

2. Which characteristics have high variability between the different bottled waters? What characteristics have little variability between the bottled waters? Why is this important in identifying which chemical characteristics to use to identify different waters?

   The characteristics that usually vary are the nitrate, bicarbonate, calcium, and magnesium. We use the sum of calcium and magnesium as a measure of hardness. The students should realize that they have to use characteristics that they can measure, and that will distinguish one water from another. More than one characteristic will have to be used. Several of the characteristics do not vary enough between waters to be of much use to identify the different waters. Several others are difficult to measure using simple analytical techniques.

5. What characteristics of crude oil might be beneficial in helping someone identify the source of spilled crude oil?

   Crude oil is a mixture of hydrocarbons and a number of other substances. These substances can help to give a fingerprint using modern techniques such as mass spectroscopy. Possible identifiers of crude oil include elements such as sulfur, iron, and boron. The percentage of different hydrocarbons can also be used to identify the oil.

6. Propose a plan for identifying the different bottled waters using materials available to you in lab. Explain the rationale of the method you propose.

   Student answers will vary.

Extensions and Variations

Many variations of this exercise may be used in the classroom. In addition to testing bottled water, the local drinking water can be tested. Then explore whether or not bottled water has an advantage over the local water source. In Anchorage, Alaska, the drinking water sources are either a pristine glacier-fed lake or a deep well. Other than the fact that Anchorage's water is chlorinated and fluoridated, it would seem that there wouldn't be any great demand for bottle water. Yet in Anchorage, bottled water seems just as popular as elsewhere in the country. It might be pointed out that public supplies are normally disinfected through chlorination, leaving a residual that can affect taste, while most bottled water is disinfected through ozonation. Blind taste tests can be used to determine if individuals can actually differentiate between bottled waters and tap water.

Another exercise might be to have students develop labels for bottled waters that do not have their chemical characteristics on the labels. Students might also be challenged to formulate their own water out of stock chemicals. Once students have formulated their own special blends, classmates can use their methods to try to determine the chemical characteristics of their classmates' water.

As a conclusion to this exercise, discuss what variables can be used to identify how pollution sources can be identified. Specific examples tracing pollution episodes back to their sources can be examined. This leads to an examination of more sensitive analytical techniques.

References

1. Wiesenberger, A.; The Pocket Guide to Bottled Water; Contemporary Books: Chicago, 1991.
2. Green, M., Green, T., Long, J.; The Good Water Guide; Rosendale Press: London, 1994.
3. *Standard Methods for the Examination of Water and Wastewater,* 19th ed.; Eaton, A. D., Clesceri, L. S., Greenberg, A. E., Eds.; American Public Health Service: Washington DC, 1995.
4. Baird, C.; Environmental Chemistry; W. H. Freeman: New York, 1995.
5. Sawyer, C. N., McCarty, P. L., Parkin, G. F. Chemistry for Environmental Engineering; McGraw-Hill: New York, 1994.