EXPERIMENT 4
Determination of Sodium by Flame Atomic-Emission Spectroscopy

Use Only *Deionized Water* (*Not* Distilled Water!) Throughout The Entire Experiment

Distilled water actually has too much sodium in it. Clean *all* glassware and rinse thoroughly with **deionized water** both before and after use. There is sufficient sodium in tap water and even in distilled water to invalidate your results. Remember also to rinse out your plastic wash bottle several times and then fill it with **deionized water.**

Safety Warning

Caution – Although the natural-gas/air flame is rather small, it has such a high temperature that contact of the flesh with even the outer edge of the flame will instantly produce a third-degree burn. Hands should be kept completely out of the "chimney" or burner housing whenever the flame is burning**.**
 Never put your hand above the burner housing.

Unknown

Submit a clean, labeled 100-mL volumetric flask to the instructor so that your unknown sodium solution can be issued. Your name, section number, and your locker number should be written legibly on this flask. The flask **does not need** to be dry on the inside, **but needs** to have been rinsed with **deionized** water thoroughly after it was washed. The flask must be turned in at least 1 lab period before you plan to do the experiment so that the Teaching Assistants will have time to prepare the unknown. Each student will have his or her own unknown to analyze even if working in pairs.

Background

Flame photometry, now more properly called **Flame Atomic Emission Spectrometry** or "**Flame Photometry**" is a relatively old instrumental analysis method. Its origins date back to Bunsen's flame-color tests for the **qualitative** identification of select metallic elements. Probably the most common example of the atomic emission effect is fireworks for 4th of July celebrations and other events. As an analytical method, atomic emission is a **fast, simple, and sensitive** method for the determination of trace metal ions in solution. Because of the very **narrow** (*ca.* 0.01 nm) *and characteristic* emission lines from the gas-phase atoms in the flame plasma, the method is relatively free of interferences from other elements. Typical precision and accuracy for analysis of dilute aqueous solutions with no major interferences present are about ±1-5% relative. Detection limits can be quite low. "Good" elements typically have detection limits between about (1–1000 ng/mL).

The method is suitable for many metallic elements, especially for those metals that are easily excited to higher energy levels at the relatively cool temperatures of some flames – Li, Na, K, Rb, Cs, Ca, Cu, Sr, and Ba. Metalloids and nonmetals generally **do not produce** isolated neutral atoms in a flame, but mostly as **polyatomic radicals and ions**. Therefore, nonmetallic elements are **not suitable** for determination by flame emission spectroscopy, **except** for a very few and under very specialized conditions.

Flame photometry is a highly empirical, rather than an absolute, method of analysis such as gravimetry. That is, you must calibrate the method carefully and frequently. Many different experimental variables affect the intensity of light emitted from the flame and that finding its way to the detector. Therefore, **careful and frequent calibration is required for good results.**

Instrumentation

JENWAY PFP7 Flame Photometer (FP) designed and manufactured in the UK by Bibby Scientific Ltd**,** it is a low-temperature (air/natural gas) flame atomic emission photometer designed for the routine **determination of sodium and potassium** in aqueous solutions, Additional filters are available for this instrument for **lithium, calcium, and barium.**

The low-temperature flame (about 1700°C as compared to oxygen/acetylene at 3100°C) generates strong emission only from the most easily excited elements. Wavelength isolation is by use of a simple narrow-band pass interference **filter** that is designed to transmit only the intense, characteristic **sodium**-doublet lines at about **589.0 and 589.6 nm**. [Separate filters must be used to transmit the **calcium** line at **442.7 nm** or the two **potassium** lines at **766.5 and 769.9 nm**.]

The detector is a relatively inexpensive, sturdy p-i-n photodiode. This solid-state device has an intrinsic (non-doped) layer sandwiched between the usual p- and n-doped layers that are in any diode – thus the origin of the appellation p-i-n. This arrangement gives the detector greater sensitivity and faster operating speed than standard photodiodes.

The instrument is called a "**single-channel**" photometer because it can determine **only one element at a time** and has a **single direct-reading output**. The filter must be changed and the instrument recalibrated for a different element. The instrument uses a capillary aspirator to inject the sample into a mixing chamber containing a PTFE spray-impact bead and several PTFE baffles that serve to mix the fuel, oxidant, and sample droplets. This combination generates a sample mist of only the smallest droplets to enter the burner; most of the sample aspirated goes down the drain. Sample solution consumption is 2-6 mL/min. The manufacturer claims the limits of

detection for the instrument are **0.2, 0.25, 15, and 30 µg/mL** for **Na, K, Li, Ca, and Ba,** respectively. The reproducibility is said to be better than 1% relative standard deviation for 20 consecutive samples using **10 ppm Na set to read 50.0** on the meter.

Equipment Needed
- Wash bottle(s) rinsed several times and then filled with deionized water
- One 50-mL volumetric flask, from your locker
- Assorted volumetric and/or graduated transfer pipets (provided for you in the locker) designated for this experiment.
- Five 25-mL volumetric flasks for the standards (experiment locker)

Preparation of Solutions

Standard Sodium Stock Solution, 100.0 ppm

1. Accurately (to 0.1 mg) weigh out by difference **0.1271 g** of reagent grade NaCl into a small plastic weighing boat (0.05g of Na). It is very difficult and time consuming to weigh out exactly this amount. Get it as close as you reasonably can, record the exact mass, and correct your concentrations accordingly. **Remember: NEVER transfer chemicals inside an analytical balance.**
2. Carefully transfer the salt quantitatively into a 500-mL volumetric flask. Use a few squirts of **deionized water** from your wash bottle on the weighing boat and the sides of the flask to wash all of it down into the flask. **[0.100 g Na/L = 100 mg/L = 100 µg/mL = 100 ppm Na].**
3. Add about 100 mL of deionized water to the flask, swirl several times, and dissolve all of the salt before diluting to volume with deionized water. **This is critical**.

Sodium Standard Calibration Solutions

1. Use **deionized water for the "blank".**
2. Pipet 0.20, 0.40, 0.60, 0.80, and 1.00 mL of the standard 100-ppm sodium solution into the first, second, third, fourth, and fifth 20-mL volumetric flasks, respectively.
3. Dilute carefully to the mark with deionized water and mix thoroughly.

Unknown Solution

Obtain the unknown from the instructor and carefully dilute to the 20-mL mark with deionized water. Mix thoroughly.

Procedure

Carefully follow the instructions provided you for use of the instrument and measure the emission intensity for the blank (deionized water), each standard, and the unknown (s).

1. When you are approaching the time to begin taking emission readings, **call the Teaching Assistant** to light the flame, stabilize the flame photometer, and instruct

you in its proper and safe use. The instrument should have been turned on and the flame lit **for 15 minutes [aspirating deionized water] to ensure stability**.

2. Thoroughly rinse all the equipment you will use in this experiment, **first with lots of distilled water, secondly with deionized water from a rinse bottle.**

3. Fill the tall, 25-mL, capped polyethylene vials with the Blank (deionized water), the five standards (1, 2, 3, 4, and 5 ppm Na) and the unknown solution (s) – in that order – and place them in the plastic holder designed for them. Because water droplets cling to the vials, their insides will need to be pre-rinsed with small amounts of their solutions first. Put a mL or two into a vial, cap it, shake it, then shake the contents into the sink. **Do this at least 3 times for each vial**.

4. Aspirate deionized water until the meter reading stabilizes, this may take 30-90 sec.

5. Use the blank knob to set the meter reading to 0.00.

6. Then aspirate the highest standard (5 ppm) until the meter reading has stabilized. Use the fine sensitivity knob to set the meter reading to 5.00. [The coarse sensitivity switch should be in the correct setting and not have to be switched.]

7. Repeat the two-step calibration procedure with deionized water and the 5 ppm standard as many times as it takes to get them both stabilized at 0.00 and 5.00, respectively.

8. Aspirate the blank, the 5 standards, and the unknown(s) in that order. Take three replicate readings of each solution once the meter reading has stabilized. There will be some "bounce" (noise) in the readings, especially at the higher concentrations.

9. For the second calibration run, place the unknown solution(s) between the two standards whose readings bracket that of unknown(s), so that the concentrations of the solutions aspirated **now all increase monotonically. Atomic emission instruments work best when going from low to high concentrations**.

10. Repeat the whole process of calibration and taking triplicate readings as before at least 1 or 2 more times. The more data you have to review, the better you will be able to detect and eliminate determinate error – inaccuracy in the final reported value.

11. **Instrument Alert**. The aspirator compartment does not drain properly sometimes. The symptom to watch for: You are aspirating some solution and the reading starts drifting around. You then aspirate deionized water, but there is still a drifting and significant signal for Na. If you open the little window on the flame chimney, you can see some of the yellowish emission of Na. This means that the aspirator compartment needs to be "flushed", that is, get it draining again. Usually this can be accomplished by gently wiggling the drain tygon tubing that is attached to the bottom of the aspirator-burner, just a little below where it is attached. If you have continuing trouble, ask the **Teaching Assistant** for assistance.

12. When completely done with the experiment, aspirate deionized water to clean out the aspirator/burner, clean the work areas up thoroughly, and notify a **Teaching Assistant** that the instrument is ready to be shut down.

13. Thoroughly rinse all the glass and plastic ware provided you for the experiment with deionized water. Drain the water out and put the equipment back in the drawer.

Hazardous Waste Disposal

NO hazardous materials are used or generated in this experiment. All we have are dilute solutions of ordinary table salt. Empty ALL the solutions down a sink drain with cold water running. Thoroughly rinse all glass or plastic ware you used with deionized water.

Data Treatment

Prepare a calibration curve by plotting the **emission intensities** as a function of **Na concentration**. Determine the concentration of sodium in the unknown sample by reading the concentration of the sample which corresponds to its emission intensity from the calibration curve. Depending on the drift in the instrument and other factors, it may be better to average all three values for each solution and obtain one final value for the unknown, or to get three separate values for the unknown, each using its "own" calibration curve, and average the three values. Try both to see if one approach seems to be better than the other. If the plot appears to be reasonably linear, or at least that portion of it that includes your unknown, use the **Excel LINEST** function to do a linear-least-squares fit to the data, which will also provide you some quality parameters for the fit. Report the "best estimate" for the average concentration of sodium in ppm (μg/mL) and the associated standard deviation of the value.

Text Reference

D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, Analytical Chemistry: An Introduction, 7th ed., Chapter 23, pp. 594-631.