

Educational Multiwavelength Atomic Emission Spectrometer

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ABSTRACT

A simple multiwavelength emission instrument utilizing a commercial grating monochromator, a fiber optic sensor to collect radiation from an acetylene-air flame, and a CCD detector, has been evaluated for pedagogical value in the undergraduate curriculum. Simultaneous determination of Na, Li, K, Rb at ppb level, and Ca, Sr, Ba at ppm level was achieved. The instrument is affordable, yet suitable for solving real analytical problems. High quality visualization makes the spectrometer a useful educational tool.

Key Words: Atomic emission spectroscopy; CCD detector; Fiber optics; Alkali metals; Alkaline earth metals; Flame spectroscopy; Chemical education.

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INTRODUCTION

Atomic emission spectroscopy (AES) is one of the most important techniques of elemental analysis.^[1] One of its advantages over atomic absorption is the capability for simultaneous multielement analysis. It can be used for the analysis of major components of the sample as well as for trace analysis, because calibration curves are linear over several orders of magnitude. As a result of these advantages AES and especially the inductively coupled plasma (ICP) technique are popular in analytical laboratories. Unfortunately, the high cost of the ICP systems prevents their widespread use in undergraduate laboratories.

Most 4-year colleges had acquired atomic absorption instruments by the year 1990.^[2] In contrast, atomic emission spectrometers in the undergraduate laboratory are often limited to simple flame instruments for Na, K, Ca analysis, some of them being homemade devices.^[3] Although very helpful for teaching freshman through junior chemistry classes, these instruments do not provide senior students with the necessary skills and they give them an incorrect impression of the advantages of AES. It is possible to use the existing atomic absorption instrument in an emission mode. Unfortunately, this approach does not offer our students additional proficiency because of absence of the multielement advantage of AES and a lack of visualization of the atomic spectra.

Over the past decade, a new generation of spectrometer configurations based on charge coupled device (CCD) detectors has appeared.^[1,4] Some of them are simple and low-cost. As an example, a multielement atomic absorption instrument has been proposed^[5] and a design of a Raman spectrometer has been described.^[6] In this paper, we suggest the use of a CCD-based spectrometer in combination with the acetylene-air flame source taken from an existing atomic absorption instrument. Two spectrometer units with different resolutions (FWHM of 1.4 and 0.4 nm) were tested.

EXPERIMENTAL

We employed a Smith-Hieftje 11 atomic absorption instrument (Thermo Jarrell Ash Inc.) as a source of the acetylene-air flame and for the sample introduction. No modifications of the atomic absorption spectrometer were made. It was possible to use the instrument in its usual atomic absorption mode as well as in an atomic emission mode during the same class period.

The CCD spectrometer units were models numbers PC2000 (200–850 nm, 25 μm slit, 600 lines mm^{-1}) and HR2000 (500–950 nm, 5 μm slit, 600 lines mm^{-1}), both from Ocean Optics Inc. An optical fiber with a field of view of about 25° was placed at a safe distance from the flame (around 5 cm) in order to collect and transfer light to the spectrometer unit. The integration



time was adjusted in an interval from 20–500 ms. The results of at least five readings were averaged. The Ocean Optics data acquisition software, OOIBase 32, was employed for preliminary viewing and real time assessment of the raw data. No correction of the CCD sensitivity was made. The data files obtained were saved in ASCII format and processed using Microsoft Excel® and/or Origin 6.1 (Microcal Software, Inc.). Double deionized water ($>15\text{ M}\Omega$, Barnstead EASYpure LF) was used for the preparation of all solutions. Standard solutions of LiCl, NaCl, KCl, RbCl, CsCl, CaCl_2 , SrCl_2 , and BaCl_2 (1 g L^{-1}) were prepared from reagent grade chemicals. As a result of the high intensity of the appropriate emission lines, the Na and K impurities were clearly visible in the atomic spectra of Sr and Ba salts. More dilute solutions were prepared daily. The calibration solutions as well as the samples were made in 50-mL volumetric flasks and aspirated at a rate of 5 mL min^{-1} .

RESULTS AND DISCUSSION

Alkali Metals Determination with CCD Spectrometer

Lithium showed a line at 671 nm. The intensity was enough for its determination at $\mu\text{g L}^{-1}$ level, but still too low for direct lithium assay in natural water. At times, we have used the lithium line as an internal standard to familiarize students with this element.

The sodium doublet (589.0 and 589.6 nm), known in spectroscopy as Fraunhofer's D-line, was clearly visible as an absorption line in a solar spectrum (see Fig. 1). As the doublet nature of the sodium line is discussed in numerous textbooks such as Ref.^[7], p. 193, it was helpful to resolve this line in an emission spectrum. The 1.4 nm FWHM of the model PC2000 was not enough for this task, but the HR2000 easily provided the necessary resolution (Fig. 2). It was possible to resolve the asymmetric peak with the data from PC2000 using a gaussian two-peak fit method. Both instruments, of higher and of lower resolution, provided high sensitivity for sodium. The detection limit was at $0.5\text{ }\mu\text{g L}^{-1}$ in our experiments.

The two-peaks of the potassium doublet line at 767 and 769 nm was clearly visible with the both monochromators tested (Fig. 3). The high abundance of sodium and potassium in laboratory air, and glassware, is the limiting factor for their determination in the students' laboratory. Nevertheless, a detection limit of $4\text{ }\mu\text{g L}^{-1}$ was achieved.

Lines of cesium and rubidium are well separated and the instruments are sensitive enough to detect $5\text{--}10\text{ }\mu\text{g L}^{-1}$ quantities, despite the relatively low intensities. There is practically no rubidium or cesium contamination of the laboratory environment. Therefore, higher sensitivity can be easily achieved



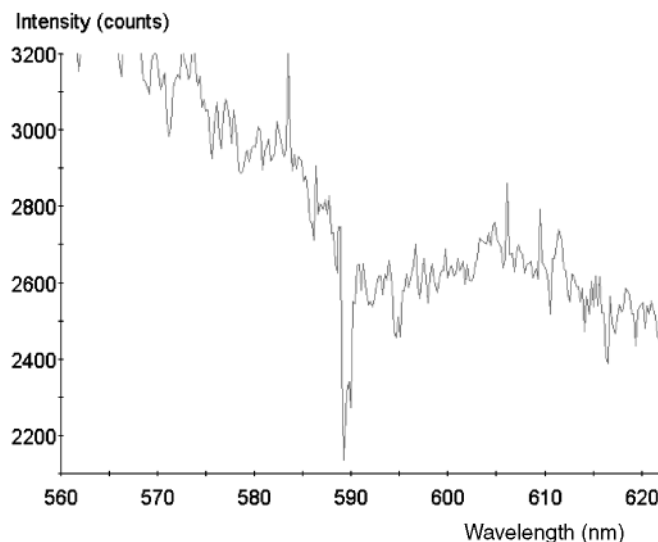


Figure 1. A snapshot of the computer display with the Fraunhofer D-line in the solar spectrum. (View this art in color at www.dekker.com.)

using longer integration times. We have also used cesium chloride as an example of an ionization buffer.

Alkali Earth Metals Determination with CCD Spectrometer

Both atomic emission lines and molecular emission bands were observed in the flame spectra of Ca, Sr, and Ba. Determinations of Ca, Sr, and Ba are possible with detection limits of 0.05, 0.1, and 4 mg L⁻¹, respectively. The sensitivity of these determinations in the acetylene-air flame was significantly lower than for the alkali metals. These spectra are helpful to demonstrate the nature of spectral interference. For example, the flame emission spectra of Ba and Ca show the overlap of the CaOH molecular emission band with the Ba resonance line at 553.6 nm (see Ref.^[7]).

UNDERGRADUATE LABORATORY EXPERIMENTS

Several undergraduate laboratory experiments and demonstrations were designed. They included a demonstration of a sodium absorption line in sunlight, for a general chemistry course, a laboratory experiment for the qualitative



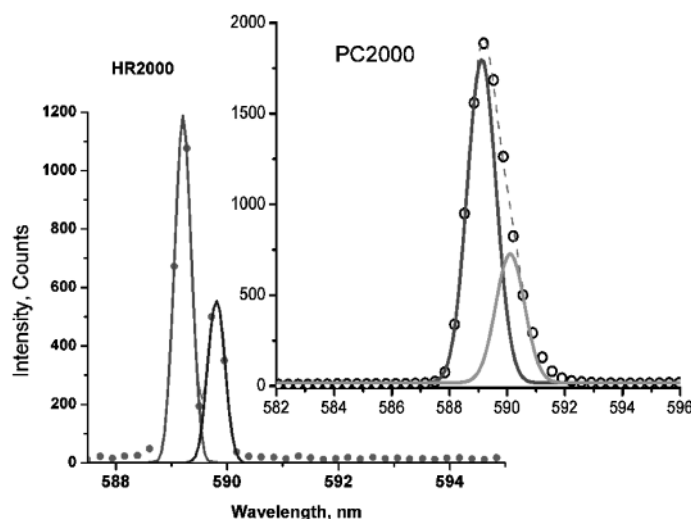


Figure 2. The sodium D-line. Experimental points and a gaussian two-peak fit are shown for both the spectrometers used in the experiments. (*View this art in color at www.dekker.com.*)

determination of alkali metals in a natural gas flame, and more sophisticated experiments for senior students. OceanOptics *.sample files can be directly opened in Microsoft Excel. The nature of CCD detector is such that the readings corresponding to each wavelength always come from the same element of the detector and, therefore, appear in the same Excel cell. Thus, a small set of Excel formulas can be written to process the experimental data file. These formulas may include functions to read the emission intensities at any wavelength of interest, calculate background correction, and correction by an internal standard as appropriate.

These formulas can be easily prepared by the instructor, while advanced students may write their own set of Excel formulas for data analysis.

Sodium Doublet Line in Sunlight

The Fraunhofer D-line is clearly visible in the solar spectrum. The students can easily view the split absorption line in the spectrum when they direct the optical fiber of HR2000 towards the laboratory window. It is helpful to compare the results of observation with the emission spectrum of sodium (see the next experiment). The demonstration takes 1–2 min and gives a powerful example of the abilities of spectral analysis; in this case, the possibility of sodium detection in the chromosphere of the sun.



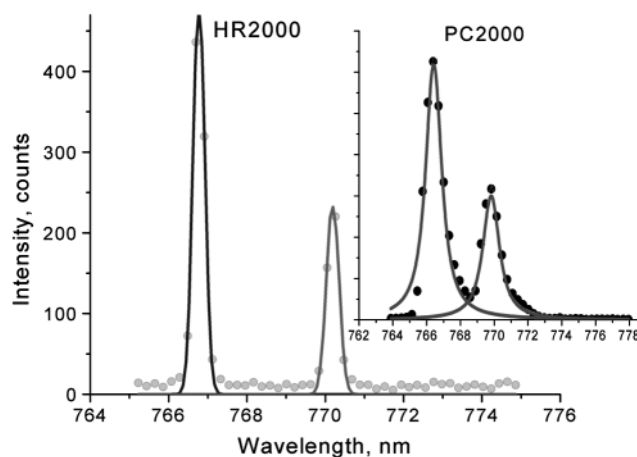


Figure 3. The potassium doublet at 767/769 nm. The experimental points and a gaussian two-peak fit are shown for both spectrometers used in the experiments. (View this art in color at www.dekker.com.)

Sodium and Potassium Detection in Aqueous Solution

This experiment is a part of general chemistry laboratory experiment on qualitative determination of K^+ , Na^+ , Ca^{2+} , Ba^{2+} , NH_4^+ , and Al^{3+} in solution. Na and K emission lines are visible in a natural gas flame. Here, we provide an example of the laboratory instructions for their detection.

Laboratory Instructions for Sodium Detection

Sodium atoms emit light at 589 nm that colors the flame yellow. Use a clamp to hold the fiber optic light input in place, and make sure that it is pointing directly at the flame. Dip a wire into the sodium chloride solution and hold it above the burner. The yellow color immediately appears resulting in a doublet peak at 589 nm visible on the computer display. Remember to save the resultant spectrum. Compare it with the solar spectrum in the vicinity of 590 nm.

Laboratory Instructions for Potassium Detection

Potassium atoms emit light at 404 nm which tints the flame violet. A much stronger emission line is at 767 nm, and it is easily detectable by the spectrometer. We cannot see this line because it is out of the spectral range



of human eyes. As before, dip a wire into the test solution and observe the spectrum on the computer display.

The appearance of the 589 and 767 nm doublet lines in the flame spectrum coming from the unknown solution shows the presence of the corresponding elements.

Sodium, Potassium, and Calcium Determination in Drinking Water

Water analysis is a typical application of AES. Here, we present a procedure we have been using for the simultaneous determination of K, Na, and Ca in drinking water in the instrumental analysis laboratory. Standard solutions of Na, K, and Ca (20 mg L^{-1}) were prepared by the instructor before the assay. In this protocol, the addition of ionic buffer (ion suppressant, 100 mg L^{-1} Cs and 40 mg L^{-1} Li) is not mandatory; nevertheless, it is helpful because it familiarizes the students with Li and Cs spectral lines.

Laboratory Instructions for Na, K, and Ca Determination

Prepare the AAS instrument as described in the operating instructions. Set the fiber optic-based spectrometer to the wavelength range from 570 to 800 nm, integration time 20 ms, with averaging of 200 readings. These settings may vary with the instrument. Prepare 1 ppm solutions of Na, K, and Ca and measure their emission spectra. Assign appropriate wavelengths for the background and the analyte peak measurements.

Make up a series of six standards by measuring the appropriate volumes of 20 ppm standard solutions into 50-mL volumetric flasks. The resulting concentrations of Na, K, and Ca (in mg L^{-1}) should be the following: (1) blank (pure water); (2) 0.040, 0.040, 0.20; (3) 0.080, 0.080, 0.40; (4) 0.16, 0.16, 0.80; (5) 0.32, 0.32, 1.6; (6) 0.80, 0.80, 4.0.

Add 1 mL of ionic buffer solution into each of the calibration flasks and dilute to the mark. Measure the emission spectra of these six calibration solutions and process the emission intensities. Estimate the detection limits and the determination limits for Ca, Na, and K in water.

To analyze your tap water sample, transfer 2–5 mL of the sample solution into a 50-mL volumetric flask, add 1 mL of ionic buffer solution, and dilute to the mark. Measure the emission intensities and calculate the concentrations of Na, K, and Ca using the calibration plots.

Repeat your measurements using the standard addition procedure. To do that, transfer the same volume your sample as before, add 1 mL of ionic buffer solution and appropriate amounts of 20 mg L^{-1} standards (Na, K, Ca), and



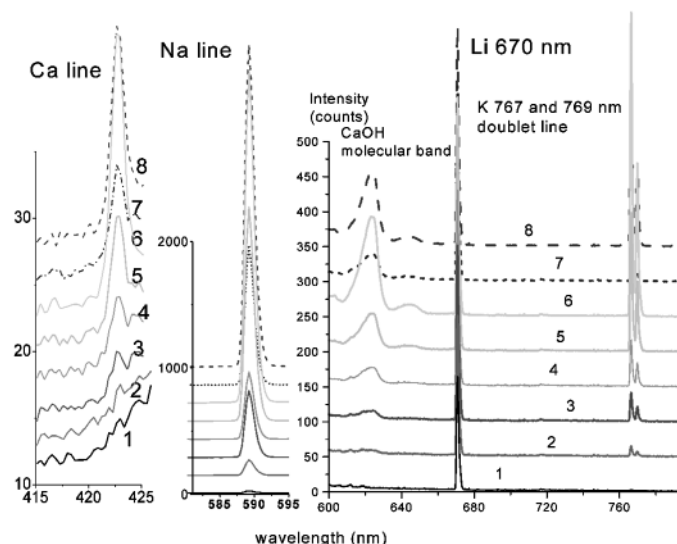


Figure 4. Emission spectra used in drinking water analysis. The spectra correspond to solutions 1–6 of the calibration (see text), diluted tap water solution (7), and diluted tap water solution with a standard addition (8). PC2000 spectrometer, 20 ms integration time. (View this art in color at www.dekker.com.)

dilute to the mark. Measure the emission intensities and calculate the amount of Na, K, and Ca in your sample using the standard addition formulas. Compare your results with those from the calibration plot.

A selection of spectra used for drinking water analysis is shown in Fig. 4. Additional experiments at the advanced undergraduate level may include the determination of alkali metals in reagent grade chemicals (for example, in barium chloride), rocks, and in sea water. Corresponding procedures can be easily developed through modification of known methods (see Ref. [8]). The same fiber optic-based spectrometer is a helpful tool for the demonstration of the emission spectrum of a hollow cathode lamp. While using just one resonance wavelength in an atomic absorption determination, students can see numerous additional lines emitted from the lamp using the CCD spectrometer. This simple demonstration results in a better understanding of the nature of an atomic absorption instrument.

CONCLUSION

We describe a simple multiwavelength emission device, which is affordable yet suitable for solving real analytical problems. Simultaneous

determination of Na, Li, K, Rb at $1-10 \mu\text{g L}^{-1}$ level, and Ca, Sr, Ba at mg L^{-1} level was achieved. High quality visualization makes the spectrometer a useful educational tool both for education in general chemistry and at the advanced analytical chemistry level.

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