Article

Camping Burner-Based Flame Emission Spectrometer for Classroom Demonstrations

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Ⓢ Supporting Information

ABSTRACT: A flame emission spectrometer was built in-house for the purpose of introducing this analytical technique to students at the high school level. The aqueous sample is sprayed through a homemade nebulizer into the air inlet of a consumer-grade propane camping burner. The resulting flame is analyzed by a commercial array spectrometer for the visible spectrum in the range of 350−1000 nm. The cost of the instrument is mainly given by that of the spectrometer and computer/projector. The obtained emission spectrum is characteristic of each individual atom, such as sodium (589 nm) and potassium (766 nm), or molecule, such as calcium hydroxide (554 and 622 nm). The readout signal (either peak height or peak area) is shown to be proportional to the sample concentration. Both qualitative and quantitative analyses may be performed with this robust and low-cost device. Samples can be rapidly changed, giving a 95% response time of under 3 s. The analytical figures of merit were characterized for calcium, potassium, and sodium in different water samples, and the resulting precision (standard deviation) for a 1 s acquisition time was typically on the order of 2%. Observed calcium levels were lower than expected because of the presence of refractory compounds, such as calcium phosphate or sulfate, that are difficult to fully atomize with the simple flame used here. Lanthanum(III) chloride was successfully used to increase the calcium response. The lower limit of detection for sodium was approximately 3 ppb and comparable to that of conventional commercial emission spectrometers.
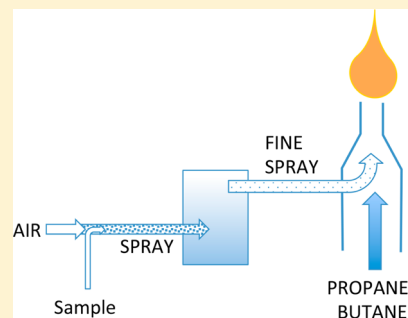
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INTRODUCTION

Flame emission spectroscopy (FES) has been a widespread analytical tool for research and education for years, and its comparatively simple design and attractive sensitivity for many elements have resulted in a broader adoption of emission methods compared to atomic absorption spectrometry in recent years.[1] FES is based on the principle of energy transfer between atoms and an external heat source. A free atom, in the gas phase, reaches a higher state of energy when thermally excited. Following the Boltzmann equation, the ratio between the population of atoms at a higher energy level and the population at the ground state increases with temperature:

$$\frac{n_1}{n_0} = \frac{g(n_1)}{g(n_0)} \exp\left(\frac{-(\varepsilon_1 - \varepsilon_0)}{kT}\right) \tag{1}$$

where n_0 and n_1 are the number of atoms in the ground state and excited state, respectively, with ε_0 and ε_1 the associated respective energy levels, and $g(n_0)$ and $g(n_1)$ the degeneracy of these energy levels; k is the Boltzmann constant, and T is the temperature in Kelvin. The lifetime of this excited state is typically 10^{-8} s, and the return to the ground state is accompanied by light emission (see Figure S5 in the Supporting Information), the intensity of which is ideally proportional to the concentration in solution. The spectrum of this light emission is discrete and characteristic for an element, and this spectral signature is used to identify the element.

A typical FES instrument is composed of a nebulizer, which transforms a liquid sample into a thin spray of droplets. This spray is then directed toward a burner fed by a mixture of acetylene and air or oxygen, or a plasma as in ICP-OES (Inductively Coupled Plasma−Optical Emission Spectroscopy). There, it undergoes solvent evaporation, then bond breaking of molecules, atomization and excitation to higher levels of energy. A fine spray is necessary since large droplets will not allow for the complete atomization of the sample. The emitted light from the excited species then passes through a monochromator and is detected/amplified by a suitable detector. A computer finally analyzes the resulting signal, which can optionally be projected live onto a screen. The peak height of the light emitted at a wavelength characteristic of the analyte will indirectly be proportional to the concentration in the initial solution. Since a commercial device usually combines AAS (Atomic Absorption Spectroscopy) and AES (Atomic Emission Spectroscopy), its price is typically between 15,000 and 30,000 US$ and requires connections for gas supplies and a fume exhaust, which is not always an option in teaching laboratories or in demonstration scenarios to students at the high school level.

To simplify the instrument for educational purposes, some simplifications have already been reported in the literature, but still required either a commercial air/acetylene burner[1,2] or were limited to the analysis of only one element.[3] To build the most complete yet low-cost FES, three key aspects were here combined:

(i) A commercial propane-based camping stove was used to replace the regular acetylene burner by a readily available, inexpensive stand-alone flame source. Such flames exhibit a temperature of ca. 2250 K,[4] sufficient for the atomization of alkali metals (see below for details).

(ii) Furthermore, an efficient custom-made 3D printed nebulizer was designed.

(iii) An educational grade miniature grating spectrometer was used to analyze the entire visible spectrum for subsequent quantification at multiple wavelengths. This array spectrometer is the only part of this setup that is of appreciable cost (ca. 1500 US$). Note, however, that such a spectrometer can find many other uses, as in the observation of the spectra of different light sources (sun, tungsten bulbs or metallic or halide lamps) or the establishment of Beer's law with visible-absorbing solutions and therefore may be a worthwhile purchase.

The number of emission events per second is directly proportional to the number of atoms in the excited state. Thus, from Figure 1 one understands why acetylene burners[5] are used
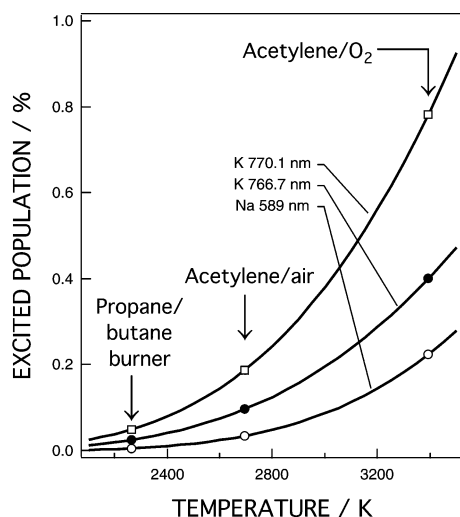
Figure 1. Calculated percentage of the total population of sodium in the excited state for different temperatures according to the Boltzmann equation and calculated percentage of the population in the excited state in both peaks of the potassium doublet for different temperatures according to the Boltzmann equation. The points correspond to the behavior at the typical temperatures of acetylene/air or O_2 burners and a simple propane stove. The signal for sodium is in reality a doublet, but it cannot be resolved by the setup introduced here.

in commercial FES applications. However, despite the lower yield of the propane/butane burner with respect to acetylene burners, it gives already a better signal than the Bunsen burners (ca. 1400 K) used in previous reports.[3]

■ EXPERIMENTAL SECTION

Chemicals

Sodium chloride, calcium chloride, and potassium chloride (analytical grade, 99.9%) and lanthanum(III) chloride (ACS reagent, 65−70%) were obtained from Sigma-Aldrich. The

solutions were prepared from their respective salts using Milli-Q water (Millipore, 18.2 MΩ·cm). Commercial standard solutions of sodium, calcium, and potassium (standards for AAS, 1000 ± 4 mg/L, Fluka) were used for the calibrations. Commercial waters were purchased (Evian, Valser, and Alpina), and the tap water was obtained from the municipal water network of the city of Geneva.

Commercial Atomic Spectrometer

The reference method for the ion analysis was the commercial atomic spectrometer Varian AA240FS equipped with an Al/Ca/Mg lamp and a Na lamp and an air/acetylene flame. Potassium was analyzed in emission mode (at 766.5 nm), and sodium and calcium were analyzed in absorption mode (respectively, at 589.0 and 422.7 nm).

Figure 2 presents a photograph and a scheme of the actual setup used to carry on the experiments. The role of each component is further explained as follows.

Nebulization. Sample nebulization is an ongoing challenge to improve the devices that analyze a spray of liquid, like FES or ICP-OES. This may be the key to a more sensitive device.[6] Here, the nebulization is performed with a custom-made 3D-printed (Mojo, Stratasys) nebulizer fitted with three standard tubings: 2 rigid PEEK tubings (o.d. = 1/8 in.; i.d. = 1/16 in., Supelco) and a soft PTFE tubing (o.d. = 1/16 in.; i.d. = 1/32 in., Bohlender). Owing to the imprecision of the printer, holes of the printed nebulizer were re-drilled at the external diameter of each tubing for a best fit. Several prototypes of nebulizers, all based on the Venturi effect, were designed before the final version (blown and glued glass, glued plastic and metal and glued parts of plastic before it was finally 3D printed), and it was observed that a more reliable nebulizer gave rise to a higher signal intensity. All instructions for the assembly of the nebulizer are made available in the Supporting Information (Figures S1−S4), along with a link to download the STL file for direct 3D printing.

The soft tubing connecting the sample vial to the nebulizer can be as long as 50 cm, the length of which defines the latency of color change of the flame owing to the time required to aspirate the sample. As shown in Figure 2, the nebulizer is placed 2 cm up from the bottom of the nebulization chamber (a 250 mL commercial polypropylene bottle), and the spray outlet (1 cm i.d.) is placed 2 cm below the top of the bottle and rotated by 90° from the inlet for best performance. Assembly instructions of this second part of the nebulizer are also available in the Supporting Information. With this config-uration, approximately 10% of the sample is effectively sprayed from the outlet while the rest is directed to waste, located below the nebulizing chamber.

Flame generation. The outlet of the nebulizer was guided to the air inlet of a portable camping burner stove (Butagaz with propane/butane cartridge) as shown in Figure 2. The compressed air nebulizing the sample was adjusted to the highest possible velocity before resulting in a dimming of the flame (ca. 1 bar for an opening of 0.8 mm). The used air was from the University of Geneva's compressed air system but can easily be substituted with a compressed air bottle if needed.

Flame analysis. The analysis was carried out in a dark room, but comparable results can be obtained by broad daylight, provided the blinds are closed and a black matt panel is placed behind the flame in the axis of the optical fiber to avoid stray light from reaching the detector. An optical fiber (400 μm diameter, flame resistant) was directed to the widest

Atomic Emission Spectrometry Instrument
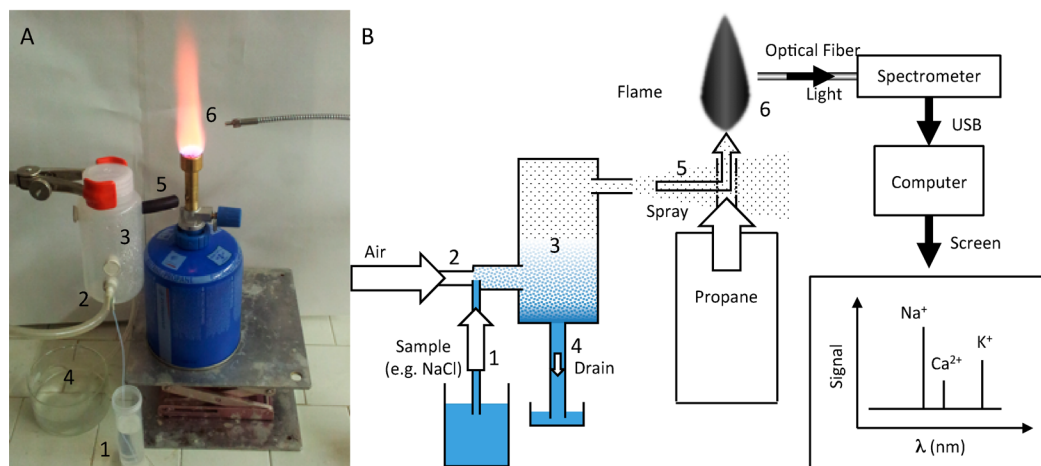
Figure 2. Photo (A) and scheme (B) of the FES setup. From left to right, a flow of air pumps the sample from a vial (1) to the nebulizer (2). The vertical spray chamber (3) guides only the smallest droplets to the camping burner (5); the heavier droplets are collected to waste (4) through a tube. The sample is atomized and excited in the flame, which is observed by an optical fiber (6) linked to a spectrometer and a computer.

part of the flame transmitted the light to a USB powered spectrophotometer (Oceanoptics Red tide USB 650, 350−1000 nm range, 16 bits, 2 nm resolution, 3 ms to 65 s integration time). Its grating and diode array allow one to record the entire visible spectrum at the same time. The signal was sent through a USB port to a Windows computer with the appropriate software, Overture 1.01 (OceanOptics, Inc.), from where it can be projected live on screen. Spectra were exported to Igor Pro 6 software (Wavemetrics) for the off-line analysis of peak intensities.

■ RESULTS AND DISCUSSION

Identifying Individual Elements

With the aim of identifying different elements, several spectra of the light emitted by the flame for different types of samples containing pure water and dilute concentrations of either NaCl, KCl, or $CaCl_2$, and tap water were recorded, see Figure 3. The approximate colors associated with various regions of the visible spectrum are overlaid to the spectra for educational purposes.

In the flame, the products of the combustion of the gas produce a continuous background emission that corresponds to the baseline. Thus, emission signals that are less intense than this baseline will not be detected. As shown in Figure 3, pure water does not show a clear peak in the visible range, while sodium gives a peak at 589 nm, potassium a double peak at 766 nm, and calcium two maxima at 554 and 622 nm. While one should observe very defined lines of ca. 0.01 nm width, wider peaks for sodium and potassium are observed because of the limited resolution of the instrument of ca. 2 nm and the imperfect alignment of the optics. The peculiar emission spectrum of calcium is due to the emission of the molecular bands of CaOH in this low temperature flame.[7]

The spectrum for tap water indicates the presence of all three elements sodium, potassium and calcium (Figure 3). This is a simple qualitative demonstration of the presence of alkali and alkaline earth metals in aqueous samples without the need for quantitative concentration data. Such visualization can be used to give an appreciation of analytical instrumentation to young pupils and to people without an educational basis in chemistry or physics. As shown below, quantitative analysis of the data is
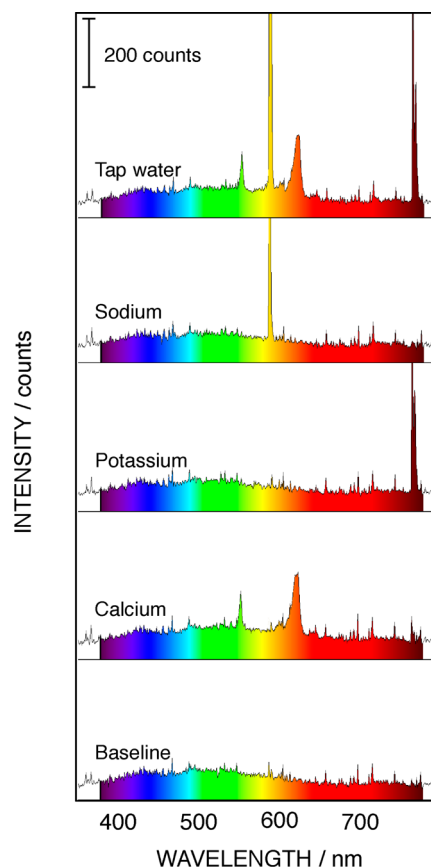

Figure 3. Overlay of screenshots of the software Overture for the indicated samples. The acquisition time was 1 s. From bottom to top: Milli-Q water, background signal; 50 ppm calcium, band maxima at 622 and 554 nm; 1 ppm potassium, peak maximum at 766 nm; 5 ppm sodium, peak at 589 nm; tap water.

conveniently possible as well, which is very useful for more advanced students at the precollege and undergraduate levels.

Optimization of the Experimental Conditions for Water Analysis

As seen in Figure 1, the temperature of the flame is a critical parameter for the efficiency of the emission. With such a burner, the hottest flame is of a blue color, while a yellow flame, containing more fuel, is colder. A blue flame is therefore more suitable for a flame emission spectrometry. To test this effect on this setup, the fuel content at a constant flow of air was increased, and the efficiency of the emission significantly decreased by 30% ± 2 for potassium and 33% ± 2 for sodium (see Supporting Information Figure S6).

A flame being inhomogeneous, one expects to find an optimum position in the flame at which the emission signal is at its maximum. For a similar experiment, Kékédy-Nagy et al.[8] achieved an optimum rubidium emission signal between 8 and 10 mm from the base of a methane/air flame. A similar result was obtained with this setup, as shown in Figure 4. The subsequent quantification measurements were then all taken approximately 10 mm above the base of the flame.
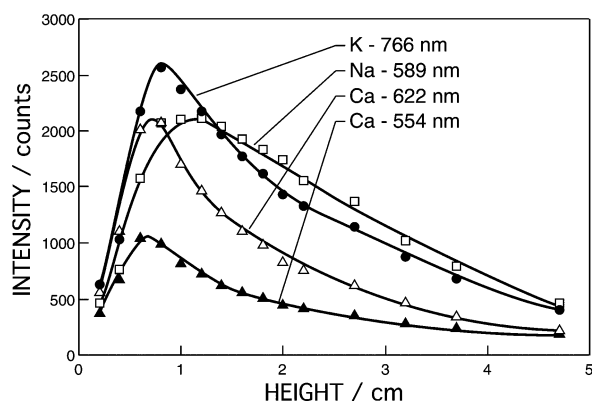
Figure 4. Influence of the vertical position of the optical fiber (label 6 in Figure 2) from the base of the flame on the intensity of the signal of a mixture composed of 10 ppm of sodium and additions of calcium and potassium such that the signals exhibit similar intensities. Errors bars (±1 standard deviation) are smaller than the size of the symbols.

Moreover, several parameters influence the quality of the measurement on this homemade apparatus, and some of them must be optimized for best results: (1) Increasing the air flow will yield a larger quantity of fine droplets and a higher signal, but too much air will extinguish the flame. (2) Orienting the air flow to the air inlet of the burner will introduce a variable amount of the spray droplets, and the optimum position has to be found. (3) The acquisition time should be evaluated for each calibration and measurement set.

Calcium tends to form strong bonds with sulfate and phosphate, which can be suppressed by the addition of lanthanum salt to the sample solution.[9] The response for calcium was indeed considerably improved by addition of lanthanum chloride. Successive additions of lanthanum chloride to the analyzed aqueous samples (see Table 1) show that the amount of lanthanum chloride necessary to reach the maximum signal at 622 nm depends on the concentration of calcium and other components in the water sample.

Quantification of Sodium, Potassium, and Calcium

Since sodium, potassium, and calcium are major components of bottled mineral water, these concentrations were measured from calibration curves realized with the FES apparatus and

Table 1. Composition of Three Mineral Waters and the Number of Calcium Equivalents of La^{3+} Needed To Reach the Maximum Signal at 622 nm

Mineral Water	Ca^{2+}/ (mg/L)[a]	SO_4^{2-}/ (mg/L)[b]	$H_2PO_4^-$/ (mg/L)[b]	La^{3+} (Ca^{2+} equivalents)[c]
Alpina	150 ± 2	463	NC	4
Valser	47 ± 1	8.5	<0.04	1.5
Evian	71.3 ± 0.9	12.6	NC	2.5
Tap water	42.9 ± 0.9	NC	NC	2

[a]Calcium concentrations measured by commercial FAAS. [b]Sulfate and phosphate concentrations given by the producer. [c]See Figure 5 and, in the Supporting Information, Figure S7.
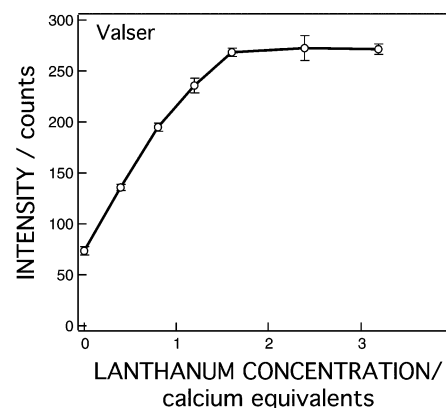
Figure 5. An example of calibration curve for the addition of lanthanum chloride in Valser water realized with our setup. The error bars represent ±1 standard deviation. The lanthanum effect on other water samples are found in the Supporting Information (Figure S7).

compared the values with the labels of the bottled water samples. A fixed wavelength was selected for analysis (for potassium and calcium, the wavelengths of the maxima were chosen), giving the calibration curves presented in the Supporting Information (Figure S8).

Owing to the consumer grade quality of the burner, the observed signal was still not found to be perfectly stable, even after the optimization steps outlined above. Air drafts will cause instability of the flame and the resulting signal, and the in-house airflow is also not perfectly stabilized. The relatively low flame temperature results in significant deviations of excited state population and hence in signal fluctuations with temperature changes.

Different commercial water samples and a tap water sample from the municipal water network of the city of Geneva were analyzed. Table 2 reports concentrations in ppm calculated from the calibration curves with ±1 standard deviation. A correspondence table for the methods used can be found in Table 3. The references to the graphs relative to each calibration are indicated beside the methods.

The first determinations of potassium, sodium, and calcium were performed with an external calibration. However, the values for potassium were the only ones within 5% of the value determined by the reference method; the values of sodium and calcium were randomly scattered around ±50% of the target value (data not shown). The standard addition method was then applied to the measurement of these two ions, which allowed the results presented in Table 2.

Table 2. Comparative Analysis of Different Mineral Waters and a Sample of Tap Water

Ion	Sample	Homemade Analysis/ppm	Reference Method/ppm	Bottle Indication/ppm
Sodium	Alpina	4.4 ± 0.3	4.59 ± 0.07	4.2
	Valser	0.34 ± 0.05	0.474 ± 0.006	0.3
	Evian	6.2 ± 0.4	6.4 ± 0.1	6.5
	Tap water	7 ± 1	8.3 ± 0.1	N/A
Calcium	Alpina	149 ± 13	150 ± 2	209
	Valser	63 ± 6	47 ± 1	51
	Evian	66 ± 3	71.3 ± 0.9	80
	Tap water	49 ± 7	42.9 ± 0.9	N/A
Potassium	Alpina	3.0 ± 0.2	3.26 ± 0.04	3.0
	Valser	0.2 ± 0.1	0.190 ± 0.002	0.2
	Evian	0.9 ± 0.1	1.05 ± 0.02	1
	Tap water	1.5 ± 0.1	1.8 ± 0.1	N/A

Table 3. Correspondence Table of the Methods Used for the Quantification of Sodium, Calcium, and Potassium for the Analysis with the Homemade Setup and the Reference Method

Ion	Homemade Analysis		Reference Method	
Sodium and calcium	Emission	Figures S9, S10	Absorption	Figure S11
	Standard additions		External calibration	
Potassium	Emission	Figure S8b	Emission	
	External calibration		External calibration	

These results show that despite its simple design, its low cost and its low spectral resolution, this device is capable of the accurate measurement of three major ions in water.

Response Times

To study the response time of the proposed FES, three different samples of sodium chloride with Na$^+$ concentrations of 1.1, 2.6, and 4.2 ppm were introduced to the instrument for 10 s, each segmented by a Milli-Q water plug of 5 s duration. The resulting time trace is shown in Figure 6.

From Figure 6, one can determine the t95% response time as 1 s from low to high concentration and 2.5 s for returning back to baseline. The decay of the signal to the baseline after each sample showed no memory effect. For instance, an acquisition time of three seconds and using three replicates allows one to measure two samples per minute.

The signal variations observed in Figure 6 may seem significant, but when averaged over 1 s or more or when the error on the mean is significantly reduced by the number of measurements, the variation of the measurements tends to decrease to within 5%.

Limit of Detection for Sodium

As a characteristic figure of merit of interest, the limit of detection of the proposed FES was evaluated for sodium because of its intense emission behavior. The resulting calibration curve is presented in Figure 7.
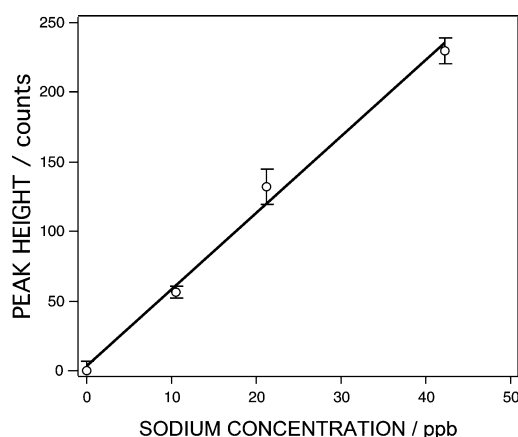
Figure 7. Trace level detection of sodium with a 3 s integration time with a calibration curve described by Signal = (5.50 ± 0.35) C(Na$^+$) (mg·L^{-1}) + (3.00 ± 8.42).

Figure 7 shows that the lowest measured concentration is at 11 ppb, while the limit of detection for an acquisition time of 3 s is around 3 ppb based on three times the standard deviation of the background signal. The calculation is available in the Supporting Information. If needed, this could be further improved by increasing the integration time, thus reducing the variability of the background.
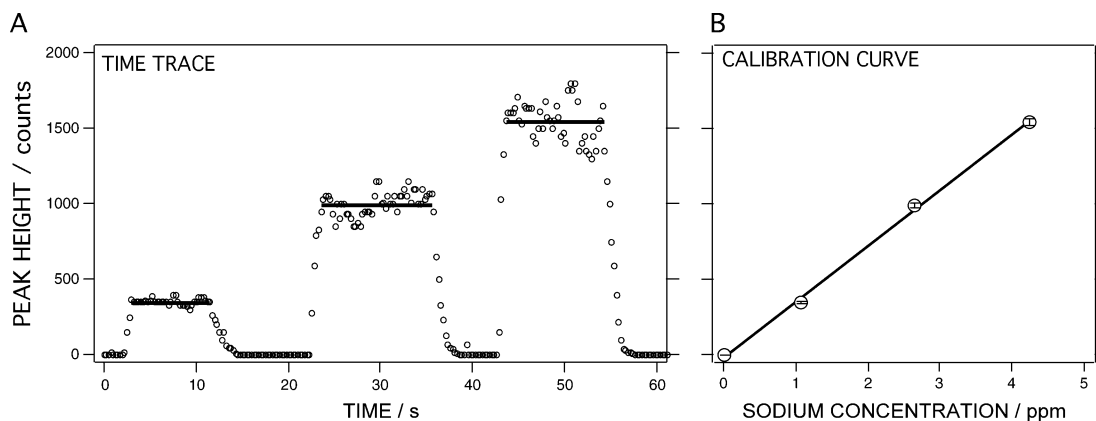
Figure 6. (A) Time trace of the raw signal for successive samples of sodium chloride (1.1, 2.6, and 4.2 ppm in sodium) separated by Milli-Q water. The solid lines represent the calculated average for each concentration. (B) Calibration curve obtained from the time trace. Each point represents the average of all the data points and the error bars are standard deviations of this average.

CONCLUSION

The simple and portable FES instrument introduced here can give qualitative and quantitative results that are adequate for experiments and demonstrations at the high school level and undergraduate university level. The quantitative analysis of calcium, sodium, and potassium were accurately performed, while being much less expensive, heavy, and bulky than comparable commercial instruments.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed description of the nebulizer, supporting figures and sets of calibration curves. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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