Constructing an Electronic Calorimeter That Students Can Use to Make Thermochemical and Analytical Determinations during Laboratory Experiments

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Abstract

In this article we describe the construction of a low-cost electronic device to adapt the widespread traditional approach of Analytical Chemistry teaching into laboratory experimentation based on the guided research model. To this aim we construct a portable electronic instrument based on the Arduino micro-controller and use it to develop various experiments. This instrument has been used, but is not limited to, determine thermochemical and analytical values of various enthalpies of neutralization, to measure the stoichiometry of neutralization and to determine the concentration of an acid of unknown concentration.

Keywords

Calorimetry / Thermochemistry, Electrochemistry, Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Hands-On Learning / Manip-

ulatives, Inquiry-Based / Discovery Learning, Laboratory Equipment / Apparatus

Introduction

In the scenario of new cooperative and dynamic student-centered teaching-learning models, one of the most important challenges turns out to be the adaptation of laboratory practices to competency-based learning. This teaching methodology aims to make students become the protagonists of their own learning by promoting a new learning process through active methodologies and cooperation among students, a model in which teachers act as facilitators of learning.

As stated in the bibliography, laboratory practices can be classified based on their complexity and didactic suitability in four large groups[1] : (i) experiences (mere realization of a practical essay); (ii) illustrative experiments (experiences accompanied with some kind of explanation by the teacher); (iii) practical activities (usual recipe-practices); and (iv) guided inquiry laboratory experiments (GILEs, see Figure 1). In this sense, laboratory experiments based on guided research are a tool that is gaining increasing attention among teaching experts. GILEs allow students to experience first-hand the usual challenges that analysts encounter in an analytical chemistry research laboratory[2] . From the didactic point of view, it is the guided research, and not the usual recipe practices, that allow a complete and effective learning of the procedural, attitudinal and conceptual contents of Chemistry[3,4] . Laboratory experiments based on guided research, also called GILEs, are a crucial tool for giving students the opportunity to experience the usual challenges that analysts encounter in a research laboratory. This process contrasts sharply with other anachronistic teaching methods based on erratic passivity (laissez faire model) or coercive imposition absent from dialogue (authoritarian model).

Guided research has shown that it significantly improves students' ability to face real problems[5,6] , as well as stimulating critical thinking, so that they offer numerous advantages

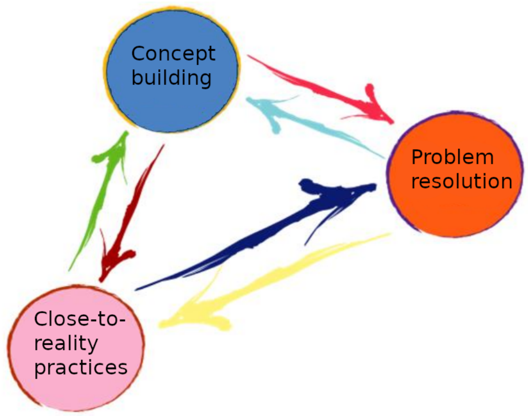


Figure 1: Guided research combines the acquisition and construction of concepts, the resolution of real problems and practical work.

over traditional laboratory practices (called, recipe-practices). Recipe-practices are based primarily on the strict follow-up of a detailed script with all the details regarding the different experiments that will be carried out in the laboratory[7]. From the didactic point of view, it is the guided research, and not the usual recipe-practices, that allow a complete and effective learning of the procedural, attitudinal and conceptual contents of Science.

In order to facilitate experimentation, in the recent past the interest in developing creative and low-cost tools for teaching Chemistry has popularized, not only at university, but also at college or high school[8–10]. The teaching-learning of Analytical Chemistry makes no sense without the practical use of the laboratory. In that sense, guided research is based on the approach of an initial problem in which information is lacking. This is an important aspect, usually absent in recipe-practices because the student does not know if he or she is following the appropriate strategy, a common fact in true research investigations.

In the present communication, we describe the construction of an electronic device that enables laboratory practices based on guided research, instead of the traditional recipe-practices. Among the main advantages of the present approach for Analytical Chemistry education, we remark teamwork activities, the acquisition of true critical thinking and the ability to find solutions to the problems posed. The supplementary material provided along this article and the inherent low-cost prices of components used for the development of the device also try to reduce the impact of the limitations of GILE practices for teachers, which are mainly the time consumption and cost that must be faced in the transition period. Despite possible limitations, GILEs are crucial for giving students the opportunity to experience the usual challenges that analysts encounter in a research laboratory.

Low-cost microprocessor usage in education

The usual activity of the scientist is experimentation, therefore, experimentation must be the main tool for teaching Science. The teaching-learning of Science does not make sense without the practical use of the laboratory, thus, laboratory experiments based on guided research are configured as an excellent proposal for the curricular development of university teaching or Secondary Education. During experimentation, students continuously use various electronic tools and gadgets and are familiar with the use of video games, computers and smartphones[11] .

One of the most interesting and useful areas in General Chemistry is the development of electronic instruments, especially taking into account the impact that electronics have on current students. In recent years (2013-2019) various Arduino-based projects have been appearing in a timely manner, that are continuously increasing, including different proposals for the teaching of Chemistry[12–15] (See Figure 2). These works perform experiments in a creative and economic way both at university level and in Secondary Education. Programmable integrated circuits, known as micro-controllers, offer many and varied possibilities for laboratory automation and their use deserves to be studied in the Chemistry curriculum[16] . In that sense, Arduino microprocessors are increasingly used in the teaching of Chemistry in general[7] , but there is also an interesting niche in the teaching of Analytical Chemistry.

Part of the interest devoted into developing Arduino based devices is related to the fact that these low-cost microprocessors enable the building of creative and economic tools for teaching Chemistry. In the state-of-the-art, there are different and diverse projects related

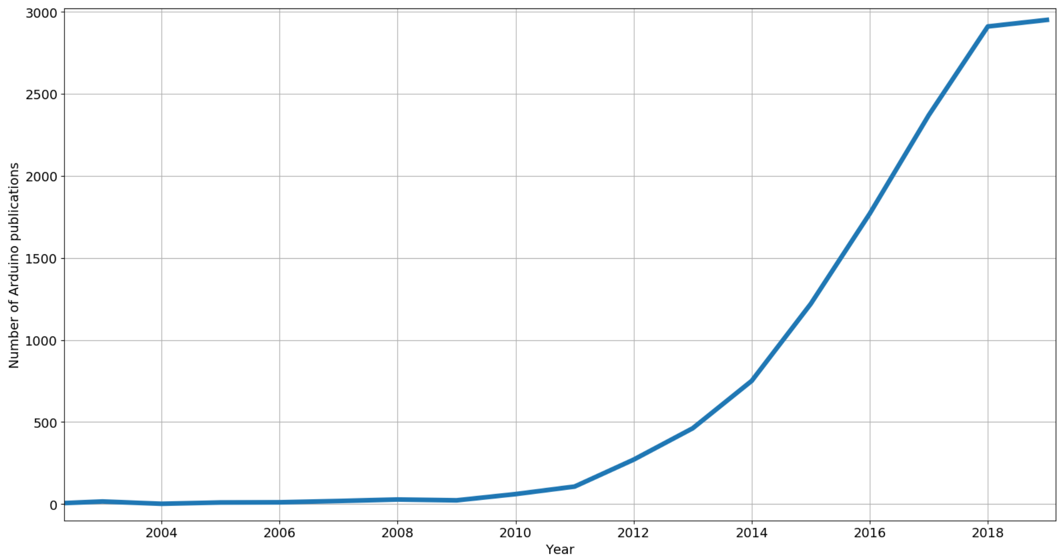
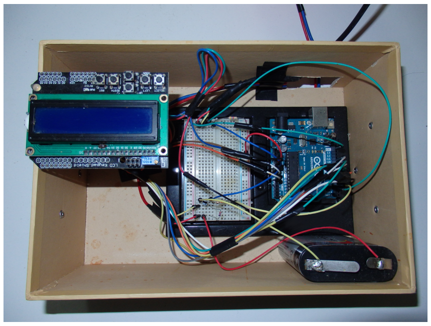


Figure 2: Arduino keyword appearances over time in Google Scholar database. We search for all publications making use of Arduino keyword in the title. The keyword for the search is the following: *« intitle : arduino »* and we also removed the count patents and cites parameters from the search database interface. We also used the database interface to specify the time periods for the search.

to Chemistry of recent publication. For instance, with regard to Analytical Chemistry the construction of instruments to measure analytical parameters such as absorbance is described in McClain 2014 [11] . In addition, the construction of instruments to measure air quality or electronic burettes is also described in the literature[12,13] . The ascending trend of Arduino keyword appearances in conference and indexed journal manuscript titles over time (See Figure 2) suggests that the number of publications related to Arduino technology will gradually increase, given the multiple educational benefits that these projects bring.

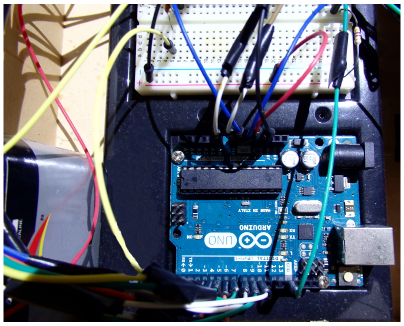
Construction of the calorimeter

In this section we describe the process of building a portable electronic instrument based on the Arduino micro-controller. The resulting instrument has the utility of mixing liquids and measuring the temperature of the mixture over time. So, the device can be used in a wide variety of multipurpose thermochemical experiments for General Chemistry (see Figure 3).

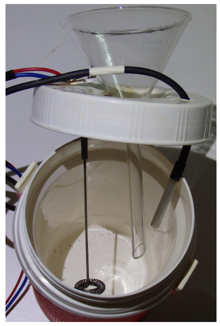


Whole electronic components

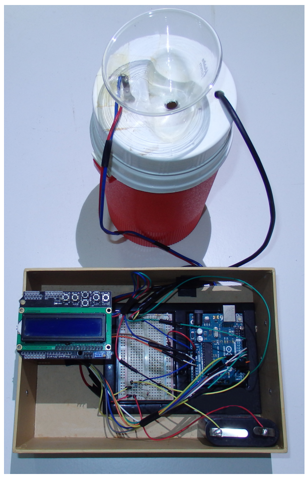
Thermal container



Arduino Uno board



Thermal container insights



Final build of the device

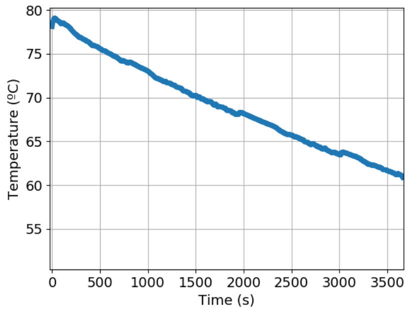
Figure 3: Top left figure shows the electronics of the instructional calorimeter based on the Arduino microprocessor and middle left figure zooms in the Arduino Uno board. Top right figure shows the thermal container and middle right figure zooms in the insights of the thermal container, showing from left to right: the motor stirrer, the funnel and the submersible temperature sensor. Bottom figure shows the final build of the electronic calorimeter where the electronic parts are shown along the Arduino Uno microprocessor, the LCD screen and the prototyping board. The bottom figure also shows the thermally insulated test container. These parts are further analyzed in Section **Construction of the calorimeter**

The project is based on a set of Arduino modules, such as: (i) a submersible temperature sensor (which allows to read the temperature with decimal precision), (ii) a 4.5 volt motor (extracted from a milk vaporizer) that allows the correct agitation of liquids inside a thermally insulated vessel and (iii) a liquid crystal display (LCD), used as user interface to easily collect the results of the experiments and to control the activation of the engine. It should be noted that all parts of the built instrument were easily obtained for under 25 €.

The detailed final build can be observed in Figure 3. The specific build procedure is described in the supporting material (See Section ***Supporting Information Available***) The electronic components of the calorimeter and the submersible temperature sensor, the motor used to agitate liquids, the thermally insulated vessel can be observed in Figure 3 (left) and Figure 3 (right) respectively. Depending on the criteria of the teacher or professor, students are expected to participate in wiring up and programming the microcontroller as well as using it in calorimetry experiments, or just use the calorimeter as an instrument in making measurements in the laboratory.

Experimentation

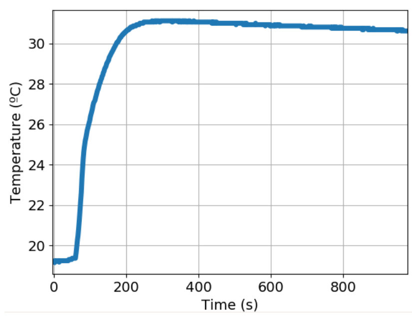
This section presents the experiments performed with the electronic calorimeter built according to Section ***Construction of the calorimeter***. The intention of these experiments is to update, evaluate and show the feasibility of self crafted instructional devices within the literature regarding the use of microprocessors in Analytical Chemistry. With this project we aim to give teachers and professors the chance to consider the feasibility of using microprocessors in their own fields of knowledge. Once the electronic instrument, which acts as a calorimeter, is built, it can be used to carry out various calorimetry related experiments, which consist of common practices in university and pre-university laboratories of General Chemistry. In our investigation, we demonstrate that the calorimeter can effectively be used to determine:



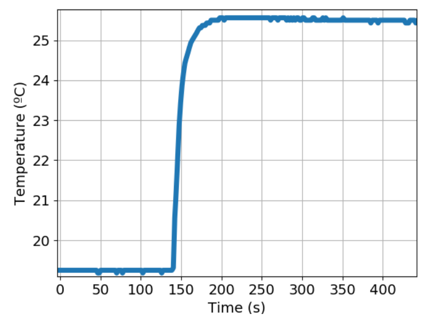
(1) Temperature cooling curve over time

$C_{CAL} = 117.8$ J/K ($m = 700$ g), given
$T_{Cold} = 20$ °C, and $T_{Hot} = 40$ °C.
$C_{CAL} = 270.93$ J/K ($m = 700$ g), given
$T_{Cold} = 20$ °C , and $T_{Hot} = 80$ °C.

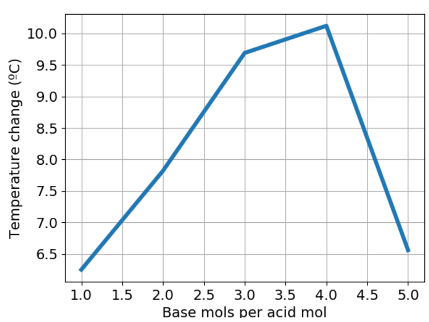
(2) Calorimeter constant calculation



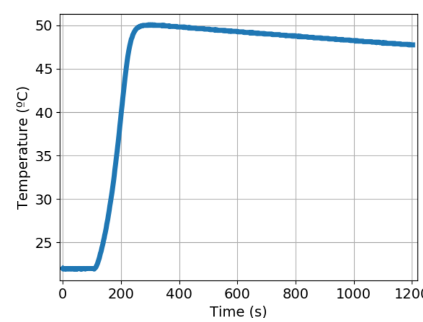
(3) Temperature over time during dissolution



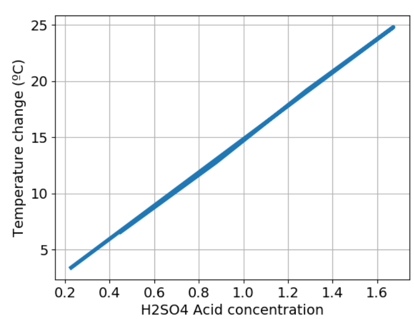
(4) Temperature over time during neutralization



(5) Stoichiometry of neutralization



(6) Temperature over time during decomposition



(7) Determination of concentration

Figure 4: Experiments performed with the electronic calorimeter. The following substances have been employed during experimentation: (part 3) 30 g NaOH + 600 mL water, (part 4) 300 mL NaOH 1 M + 300 mL HCl 1 M, (part 5) $NaOH$ 1 M + Citric acid 1 M, (part 6) 500 mL 4,9 % H_2O_2 + 50 mL $FeNO_3$ 1 M.

1. The cooling curve of a hot water mixture
2. The calorimeter constant
3. Enthalpies of dissolution of solid substances
4. Enthalpies of acid-base reactions
5. Stoichiometry of neutralization reactions
6. Enthalpy of decomposition of hydrogen peroxide
7. Sulfuric acid concentration of an unknown sample

(1) Cooling curve of a hot water mixture

As for the experiments performed with the electronic calorimeter, the cooling curve of the calorimeter was determined in a first exploration phase. For this, 700 g of water were added at 80 °C and a cooling of 0.30 °C/min was measured. The measured cooling curve can be observed in Figure 4 (1). The heat loss of the calorimeter was compared to other similar home-made calorimeters[17]. The rate of heat loss of the electronic calorimeter described here was considerably less than for other calorimeters.

(2) Calorimeter constant

Secondly, the calorimeter constant was obtained (C_{CAL}), which was used to compare the quality of the calorimeter with similar ones described in the literature. In our case, we report a calorimeter constant of $C_{CAL} = 117.80$ J/K ($m = 700$ g) in the case the cold temperature equals $T = 20$ °C and the hot temperature equals $T = 40$ °C and a calorimeter constant of $C_{CAL} = 270.93$ J/K ($m = 700$ g) in the case the cold temperature equals $T = 20$ °C and the hot temperature equals $T = 80$ °C. Calorimeter constant values described in the literature range, for example, from 5 J/K ($m = 60$ g)[18] to 29.4 J/K ($m = 100$ g)[17].

(3) Enthalpies of dissolution of solids

To continue with, we performed and experiment to determine the enthalpy of dissolution of solid substances. To this aim, we mixed 600 mL water and 30 g of a solid substance, NaOH, and measured the initial and final temperature. We obtained a temperature difference (ΔT) of 14.4 °C. Considering that $q_w + q_{cal} = -q_{reaction}$, we obtained a enthalpy of dissolution (ΔH) of -51.57 kJ/mol, close to the theorical value that was expected to be around -44.51 kJ/mol. Figure 4 (3) shoes the curve measured for the temperature rise. Based on the data obtained and the comparison of the experimental result with the theoretical values, the result was positively evaluated.

We also experimented with different enthalpies of dissolution of solids in which we mixed 600 mL of water and 30 g of different solids, such as sodium bicarbonate or calcium hydroxide.

(4) Enthalpies of acid-base reactions

We also elected to implement a new discovery thermochemical experiment that uses temperature change to study neutralization reactions. In the laboratory, we mixed 300 mL NaOH 1 M and 300 mL HCl 1 M in the calorimeter and temperature raise was calculated. The difference in temperature is that between the final temperature of the mixture and a weighted average of the initial temperature of the acid and base solutions. The curve of the obtained experimentation after dissolution of NaOH in water can be observed in Figure 4 (4), note that the heat capacity of the calorimeter was also considered to correct the results. From the temperature difference, and taking into account the calorimeter constant, the enthalpy of dissolution can be calculated. So, the parameters of the experimentation are resumed in the following equations:

$NaOH\ (aq) + HCl\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l)$

300 mL NaOH 1 M + 300 mL HCl 1 M

ΔH = -54.37 kJ/mol (Theoretical: -57.10 kJ/mol)

(5) Stoichiometry of neutralization reactions

Another plausible usage of the electronic calorimeter is to determine the stoichiometry of neutralization of different organic and inorganic acids. To this aim, we selected different volumes of an organic acid (e.g. citric acid) and a base (e.g. NaOH) and mixed them in the thermal container. From the measurement of the heat released we developed a graph that can be analyzed in Figure 4 (5), from which we can obtain the experimental value for the stoichiometry of neutralization. The figure shows the temperature change obtained after adding different proportions of acid and base. The maximum temperature change indicates neutralization stoichiometry. In this case, the reaction between NaOH and citric acid is observed. The maximum temperature change falls clearly at a 3:1 ratio, establishing the stoichiometry of the reaction, as expected.

(6) Enthalpy of decomposition of hydrogen peroxide

Thermochemistry is an important topic in chemistry courses, but, these experiments usually involve measurements of heat of acid-base neutralizations or dissolution experiments, as also seen here before. However, the current experiment analyses the enthalpy of decomposition of hydrogen peroxide catalyzed by iron(III) nitrate. For this, 500 mL of 4.9% hydrogen peroxide was added to the calorimeter. At the 5-minute mark, 50 mL of 1 M iron (III) nitrate were added and mixed, producing the reaction described in the following equation and plotted over time in Figure 4 (6):

$$2\ H_2O_2\ (aq) \rightarrow O_2\ (g) + 2\ H_2O\ (l)$$

Once the decomposition reaction occurred, the enthalpy of decomposition was determined with a relative error of 6.35%. The temperature change is described in the following equation:

$$\Delta H = qn = \text{-100.61 kJ/mol (Theoretical: -94.6 kJ/mol)}$$

This value agrees well with the literature value of -94.6 kJ/mol[18] .

(7) Concentration of an unknown sulfuric acid sample

Finally, we used the microprocessor to determine the concentration of an unknown sulfuric acid sample, which is no doubt a concern of major interest in Analytical Chemistry education. This last experiment demonstrates that the electronic calorimeter can be used to carry out analytical determinations of unknown concentrations. To this end, different volumes of sulfuric acid (H_2SO_4) of known concentration were added and mixed in water, measuring the temperature raise (ΔT) for each mixture. Subsequently, the temperature change was plotted against the acid concentration, obtaining the calibration line shown in Figure 4 (7) and described in the following equation:

$$Y = 14.897X - 0.0989$$

Since Y is the estimation for the temperature change and X is the concentration of sulfuric acid employed. The calibration line corresponds to the temperature change versus the concentration of sulfuric acid in each mixture, which makes it easy to determine and efficiently guess future mixture's concentration. The obtained R^2 for the equation was 0.9998, showing an acceptable calibration curve.

Finally, the acid concentration of a test sample was determined accurately from the curve obtained, following usual practices in Analytical Chemistry laboratories. For this investigation we prepared a 1.042 M H_2SO_4 solution, so the theoretical expected value was 1.042 M. When this sample (considered of "unknown" concentration) was mixed with water the temperature change was measured to be $\Delta T = 15.38$ °C. By using the calibration curve we obtained a concentration of 1.039 M. The sulfuric acid was prepared to be 1.042 M, so, the experimental relative error was 0.3 %

Conclusion and future work

The process of adapting the traditional practices of the Analytical Chemistry laboratory to the guided research model is described in this article, for this aim, the construction of an electronic calorimeter based on the Arduino microprocessor is proposed. The instrumentation is then employed to develop various multipurpose thermochemical experiments, such as: to determine thermodynamic and analytical values of various enthalpies of neutralization, stoichiometry of neutralization and the concentration of an acid of unknown concentration, among others.

As it has been reviewed, the usage of Arduino microprocessors offers multiple innovative lines in the teaching of Chemistry and Science in general. One of its key points is the promotion of practical laboratory work through guided research and not through usual recipe practices. Through this practices laboratory instruments cease to be “black boxes” for students and, as a consequence, the relevance of understanding the experimental work is highlighted. Thus, from the interpretation, reflection and improvement of the results obtained, students can build solid scientific knowledge.

This project is a clear example of how to build an electronic instrument using relatively cheap and accessible tools, as the portable calorimeter can be used to quantify chemical parameters of interest, as well as for teaching-learning chemical concepts of a certain complexity. In the future, we intend to continue with the described research line of teaching research by expanding the use of the developed instrument and posing new challenges for chemistry students at university and pre-university level. It is also interesting to note that through this type of projects students can have an additional first contact with the development of electronic equipment. Future work includes real testing of the application of the project and evaluation of the results.

Acknowledgement

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Supporting Information Available

All the Arduino sketches required to build the project described in this article are accessible at `https://github.com/lgazpio/Electronic_Calorimeter/` along the electronic parts needed, build documentation, software related UML diagrams and schematics of circuits. The estimation to build the circuit using the provided supplementary material has been measured in under 2.5 hours, for newbie Arduino users. We suggest that for training purposes students previously complete the activities proposed in the instructional kit of the Arduino Uno, which includes all the parts and explanations needed to build a series of interesting hands-on circuits.

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