

# Black boxes in analytical chemistry: University students misconceptions of instrumental analysis\*

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**Abstract:** Misconceptions of chemistry and chemical engineering university students concerning instrumental analysis have been established from coordinated tests, tutorial interviews and laboratory lessons. Misconceptions can be divided into: (1) formal, involving specific concepts and formulations within the general frame of chemistry; (2) operational/topical, dealing with specific capabilities, problems and operations in chemistry; (3) methodological, associated to peculiar methods of analytical chemistry and data treatment; and (4) social, regarding the relation of analytical data with the social frame. Such misconceptions define a non-structured view of analytical methods, procedures and protocols related with analytical instrumentation. Instruments are frequently viewed as an autonomous, error-free black box providing non-structured data with no need of calibration or control, whereas weak relationships are established between data and aims along the analytical process.

**Key word:** instrumental analysis; misconceptions; metaconceptions; spectroscopy

## 1. Introduction

Analytical chemistry can be considered as one of the essential branches of chemistry. As far as this branch possesses an obvious relationship with a variety of social demands, teaching of analytical chemistry at the university level should be devoted to provide fundamental “chemical” concepts and operative skills for its normalized application via chemical analysis.

During the last decades, teaching analytical chemistry has claimed considerable attention (Murray, 1989), so that different curricula have been proposed. Roughly, many of these approaches are focused on the study of fundamentals on “classical” analytical chemistry, namely, chemical equilibrium, ionic equilibria in aqueous solution, titrimetric and gravimetric methods; and those on “instrumental” analytical chemistry, namely, optical, electrochemical, magneto-optical methods, etc. (Braun, 1986; Laitinen, 1989; Sommer, 1993; Kellner, 1994). Proposed educational approaches recognize the importance of instrumental analysis for analytical chemistry teaching. Proposals range from complementary use for theory and experimentation (Wright, 1996) and laboratory-based approaches (Fitch, et al., 1996; Clark & Rest, 1996) to investigative (Wenzel, 1995), technological-based (Murray, 1989; Smith & Stovall, 1996) and problem-based (Mabrouk, 1998) ones, among

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others (Wilson, et al., 1999).

During the last decades, considerable research in science education has been devoted to characterize misconceptions, spontaneous conceptions or alternative conceptions influencing learning (Driver, 1981; Gilbert & Watts, 1983). Strategies for determining students' misconceptions can be considered of interest not only for understanding fundamental mechanisms governing learning, but also for leading instructional approaches. Reported studies are concentrated in students' misconceptions in chemical equilibrium (Gussarsky & Gorodetsky, 1990; Voska & Heikkinen, 2000; Wheeler & Katz, 2006), acidity (Ross & Munby, 1991; Schmidt, 1991, 1995) and fundamentals of electrochemistry (Garnett & Treagust, 1992a, 1992b; Sanger, et al., 1997; Ozkaya, 2002). However, studies dealing with misconceptions specifically related with instrumental analysis are limited to an analysis of errors (Tomlinson, et al., 2001) and near-infrared spectroscopy (DiFoggo, 1995).

In this context, elucidation of students' misconceptions in instrumental analysis can be considered of interest as a convenient tool for promoting an efficient teaching/learning of this branch of analytical chemistry. The current report is devoted to present a set of data on misconceptions concerning instrumental analytical chemistry revealed by university students on chemistry and chemical engineering graduations. For this purpose, a field study was performed with a sample of 45 chemistry students and 32 chemical engineering students from the University of Valencia, based on structured interviews during ordinary laboratory sessions along the 2007-2008 period. All students received, however, similar instruction in analytical chemistry during their regular lessons.

## **2. Concepts and methods on instrumental analysis**

Analysis of students' misconceptions in instrumental analysis has to take into account that this is an aspect to be integrated within the general frame of analytical chemistry and chemical analysis. With this regard, it should be emphasized that a hierarchical relationship exists between analytical chemistry, chemical analysis and analytical processes, as emphasized by Pardue and Woo (1984), and Valcárcel and Luque de Castro (1995). Analytical chemistry can be taken as the fundamental scientific discipline providing the fundamentals for determining the chemical composition of selected systems, whereas chemical analysis provides the systematic study of methods, techniques and procedures structuring concrete analysis. Apart from fundamental concepts, conventions and operations, there are a series of concepts, skills and operations that, although directly related with chemistry fundamentals, constitute an interesting corpus to be implemented in analytical chemistry teaching. A schematic view of the hierarchical relation existing between analytical chemistry, chemical analysis and analytical processes (Pardue & Woo, 1984; Valcárcel & Luque de Castro, 1995) with possibly associated misconceptions are shown in Figure 1.

Classical or "non-instrumental" analytical chemistry is focused on qualitative essays, gravimetry and titrimetry, although introduction of such topics in introductory courses has been subject to discussion (Christian, 1995). The curriculum in instrumental analysis has changed significantly over the past 20 years (Girard & Diamant, 2000). Following Mabrouk (2002), instrumental analysis courses in USA chemistry faculties are focused on ultraviolet-visible (UV-vis) spectroscopy and statistics (94%-98% of faculties), while gas chromatography (GC), atomic absorption spectroscopy, potentiometry, high-performance liquid chromatography (HPLC) and other techniques are treated in a lower percentage of faculties (45%-60%).

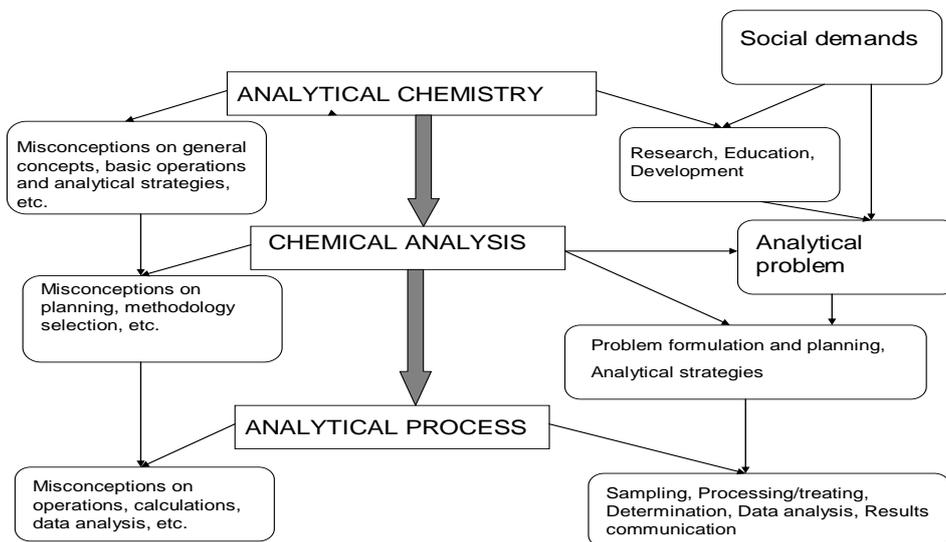


Figure 1 Hierarchical view of analytical chemistry and chemical analysis and directly related misconceptions

In this context, the study of misconceptions dealing with instrumental analysis can involve specific misconceptions associated to each of instrumental techniques and general misconceptions common to all of them. Preliminary data suggested that students' misconceptions on instrumental analysis are directly related with a series of meta-conceptions dealing with the so-called analytical properties (accuracy and precision, reproducibility, etc.), operational concepts (separation and identification) and mathematical tools (linear correlation, integration and derivation), which have to be integrated with social demands for structuring chemical analysis. Many of these issues involve "something more" than strict chemical concepts for which formal definitions hold (Doménech, et al., 2008).

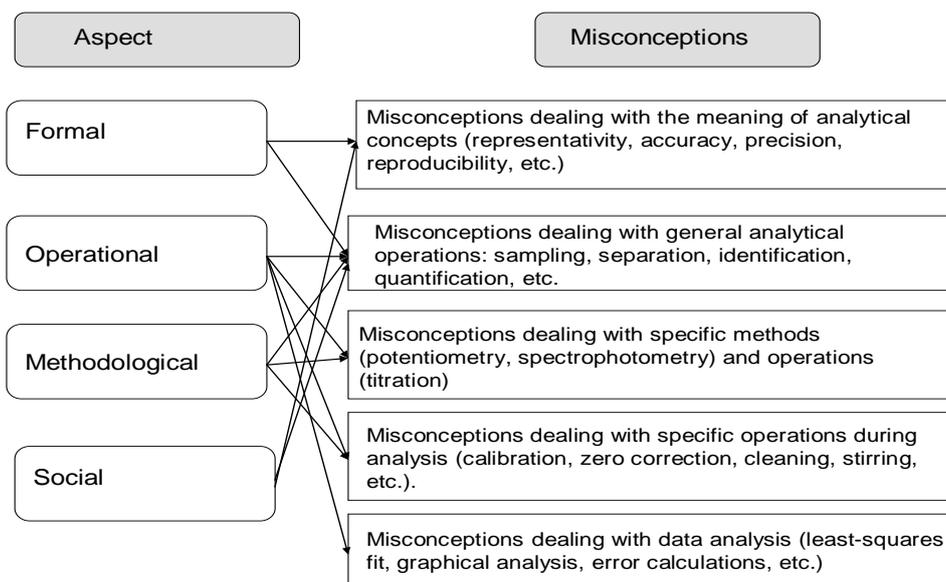


Figure 2 Relationships between formal, operational, methodological and social aspects of misconceptions and possible misconceptions of the students dealing with instrumental analysis

The meaning of misconceptions can involve, following prior treatments for analyzing students' definition of fundamental science concepts (Doménech, et al., 1993), formal, operational/topical, operational, methodological

and social aspects. The formal aspect of misconceptions is related with the use of specific concepts and formulations used in instrumental analysis. Apart from generic concepts (spectrophotometry and potentiometry), fundamentals on specific concepts and formulations (intensity, Lambert-Beer law, etc.), “analytical” concepts such as accuracy or reproducibility are involved. Misconceptions can also involve an operational aspect concerning the specific capabilities, problems and operations in instrumental analysis, for instance with operations, calculations or error counting. The methodological aspect of misconceptions can be ascribed to peculiar methods of analytical chemistry and data treatment, and, finally, the social aspect of misconceptions involve the social implementation of analytical chemistry and chemical analysis. Figure 2 presents a schematic view of possible formal, operational, methodological and social misconceptions.

### 3. Analysis of students' misconceptions

#### 3.1 Background

The investigation was performed after the students followed a course (in the preceding 2006-2007 academic year) on classical analytical chemistry where gravimetry and volumetry methods (classical or non-instrumental) were extensively treated. This course also covered fundamental concepts in analytical chemistry and error calculations. The questionnaires were passed along the 2007-2008 academic period after the students covered a significant portion of theoretical lessons on instrumental analytical chemistry. Lessons covered general topics on instrumental data analysis (calibration curves, standard additions method and internal standards) and spectrophotometry (visible/ultraviolet spectrophotometry and Lambert-Beer law). As far as the students studied extensively acid-base titrations during the preceding course, all questions were focused on the problem of determining the concentration of a sample solution of an acid from titration with an aqueous NaOH standard solution.

#### 3.2 Sample and procedure

A mixed written response/interview protocol was used for detecting misconceptions of university students on instrumental analysis. The structured interviews comprised four questionnaires (Q1-Q4, see Tables 1-4) to be completed in the analytical chemistry laboratory during regular classes. Possible misconceptions related with each one of the proposed items are summarized in Figure 2. Each item of the questionnaires was first accomplished by the students and immediately, their responses were commented and discussed in group. Individual responses were recorded conjointly with observations and comments along the session. The structure of the research protocol is described in Tables 1-4 for Q1-Q4, respectively. The Q1 and Q2 presented in two separate laboratory sessions were a problem-based approach (Fitch, et al., 1996; Clark & Rest, 1996), which was used for studying instrumental monitoring of acid-based titrations. In the first session (Q1), an orthodox instrumentation (Crison pH 2000 pH-meter) was used, thus obtaining a typical s-shaped titration curve as illustrated in Figure 3. In the second session, the students were challenged to develop a single instrumentation with minimal laboratory equipment. Conductimetry was selected for this purpose. Here, an a.c. generator (Enosa generators with 1.5V issue were used) coupled with two graphite electrodes (two bars of pyrolitic graphite, of 0.5cm diameter were used) and an amperemeter (Enosa polymeters) were used using the scheme depicted in Figure 4. Variations of the measured current during the titration were mainly due to the large variations in the concentration of  $H^+(aq)$  and  $OH^-(aq)$  ions, so that two typical straight lines plots of current vs. added volume of NaOH were obtained (Skoog & West, 2006) as shown in Figure 5.

**Table 1 Structured Q1**

Question	Student's action	Interviewer participation
1.1 We dispose of a pH-meter for determining the acidity of an aqueous solution. Describe (briefly) the sequence of all operations to be performed	Written response	Remembering the need for calibration, temperature control, electrode cleaning and continuous stirring during measurement
1.2 Indicate the results after measurements	pH measurements on a problem solution followed by written response	Asking about the validity (accuracy and precision) of the results, comment on the need for repeating measurements Calculations (mean value, standard deviation)
1.3 Describe the operations for monitoring an acid-base titration	Written response/group interview	Discussing with the students the need for concentration determination, difference between primary and secondary standards; Limitations in the use of chemical indicators; Fundamentals of the potentiometric titration method
1.4 Determine the concentration of acid from data in Figure 3	Calculations/group interview	Repeating calculations, error estimation and comment on responses of the students

**Table 2 Structured Q2**

Question	Student's action	Interviewer participation
2.1 Open problem: How to determine the concentration of a solution of a "strong" acid with minimal instrumentation (a 0.10 M HCl aqueous solution is taken as a problem)	Open responses in group interview	Comments on possible techniques after discarding classical titration with chemical indication
2.2 Describe possible instrumental methods	Group interview	Potentiometric and conductimetric monitoring of titration with a NaOH solution of known concentration Presentation of a home-made conductimeter (see Figure 3); Brief discussion of fundamentals and operation mode
	Group interview	Performing titration experiment and discussing with the students the need for decarbonatation of NaOH solution and repeating measurements
2.3 Data handling and determination of the concentration of the problem solution	Written response/group interview	Discussing responses and commenting the "two straight lines" method for determining the end point of the titration
2.4 Are the accuracy and precision of this method larger, identical, or lower than that based on the use of a commercial pH-meter?	Written response	

**Table 3 Structured Q3**

Question	Student's action	Interviewer participation
3.1 Provide a description of phenomena involved in spectrophotometric measurements	Written response	Remembering and detailing concepts of spectrometry, colorimetry, spectrophotometry, absorption, reflection, diffusion, absorbance, etc.
3.2 Describe all operations involved in the record of the absorption spectrum in the visible region of a colorant X in solution	Written response/group interview	Discussing involved concepts (spectra, spectrophotometry/colorimetry, absorbance, Lambert-Beer law, etc.)
	Record of the spectrum of a solution of a colorant	Discussing with the students the need for zero adjust, possibility of wavelength error (need of instrument calibration) and repeating measurements (precision).
3.3 Describe the characteristics of the spectra in Figure 6	Written response/group interview	Comment on responses; Determination of characteristic parameters, wavelength at the maximum of absorbance ( $\lambda_{\max}$ ) and the coefficient of molar absorptivity ( $\epsilon$ ); Discussion of possibilities

Table 4 Structured Q4

Question	Student's action	Interviewer participation
4.1 The figure shows the absorption spectrum obtained in aqueous solutions of two colorants X and Y (Figure 6a) and the spectrum of a sample solution. Indicate if the spectrum in Figure 6b can correspond to a mixture of solutions of the colorants X and Y	Group interview	Discussing responses and claiming for a "mathematical" method for ensuring the response
Propose a quantitative method for properly asserting or reject this possibility	Group interview	Developing an analytical method from measurements at two selected wavelengths
4.2 Describe the spectra represented in Figure 8	Group interview	Description in terms of the combination of two different one-peak spectra exhibiting an isosbestic point
Describe a possible experiment whose results agree with spectra in Figure 8	Group interview	Discussion on the possible meaning of the isosbestic point and comparison of spectra in Figures 7 and 8 Description in terms of the spectral response of a chemical indicator during an acid-base titration

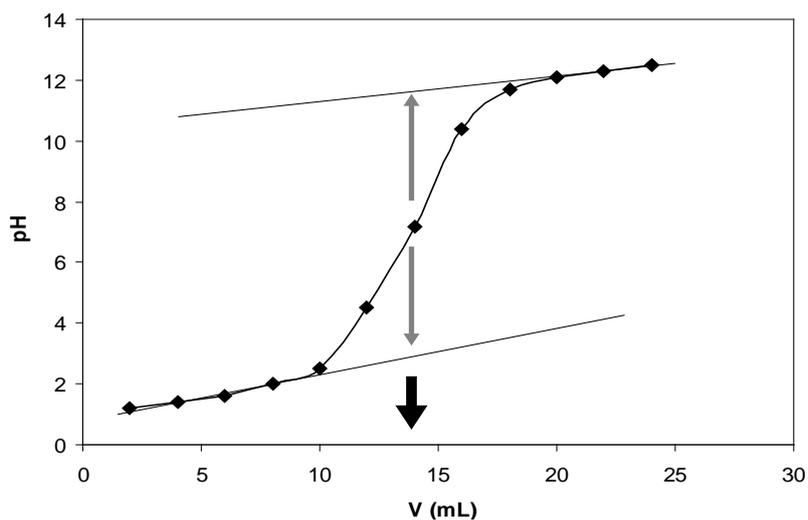


Figure 3 pH vs. volume titration curve for query 1.4 in Q1 (Arrows indicate the auxiliary elements for graphically determining the endpoint of the titration)

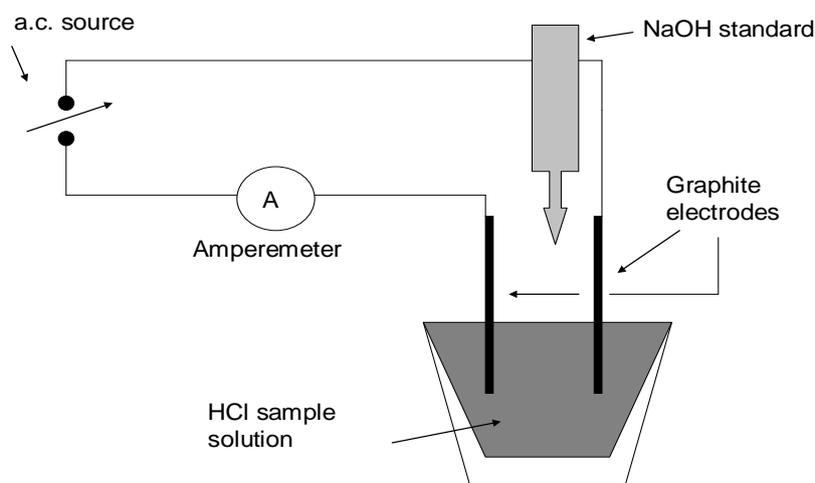
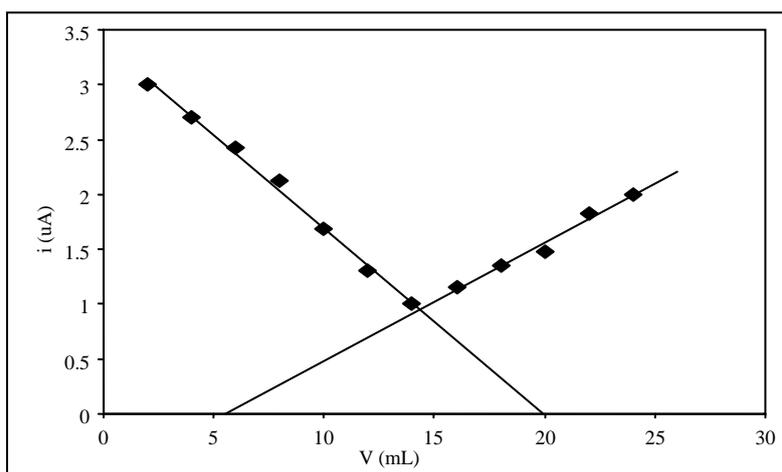


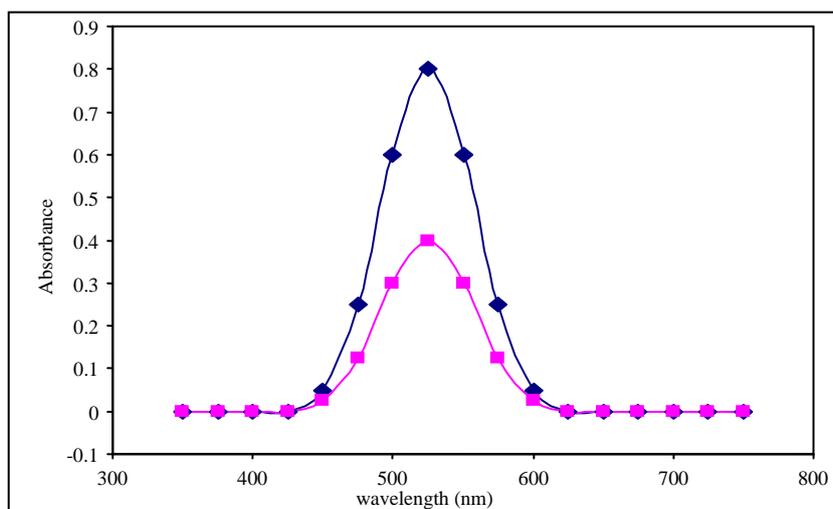
Figure 4 Scheme for a single conductimeter device to be used for monitoring acid-base titrations



**Figure 5** Typical current vs. added volume of standard NaOH solution recorded for acid-base titrations monitored by means of the experimental arrangement depicted in Figure 4

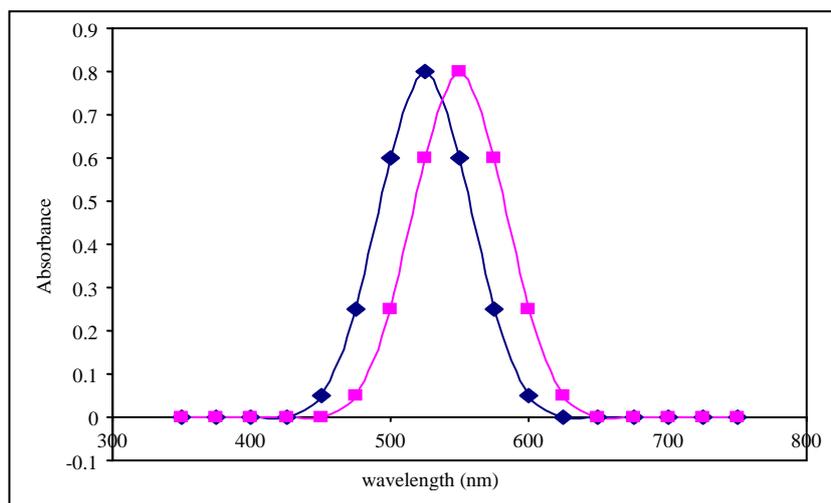
The Q3 and Q4 were introduced during two separate laboratory sessions devoted to visible spectrophotometry. Again experiments were introduced in the context of solving analytical problems about solutions of colorants. A Perkin Elmer Lambda 35 spectrophotometer was used in these laboratory sessions. The visible spectra was obtained using a point-to-point method at 25nm spaced wavelengths. In structured interviews, the spectra for two colorants (Figure 6), a possible mixture of them (Figure 7) and a possible spectrophotometric acid-base titration (Figure 8) were presented to the students.

The sample consisted of 45 chemistry students (3rd year) and 32 chemical engineering students (3rd year) from the University of Valencia. The interview protocol was applied to the students during laboratory sessions (instrumental analysis lessons) along the ordinary 2007-2008 period. The chemistry students were divided into three groups of 12 (C1), 15 (C2) and 18 (C3) students respectively, while the chemical engineering students were divided into two groups (CE1 and CE2), each comprising 16 students. The students were told that this study was part of educational research that was intended to help improve their instruction and its outcome would have no effect on their grades. Ordinary pH-meters and single-beam educational spectrophotometers were used by the students during the sessions.

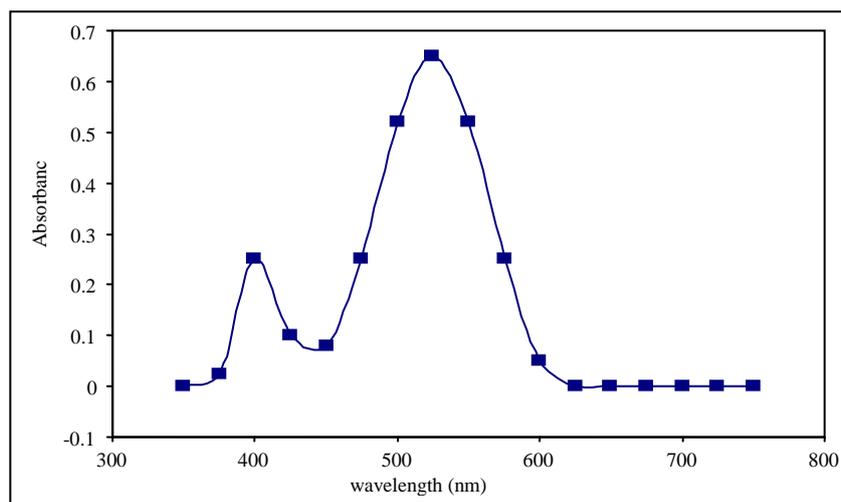


(a)

(to be continued)

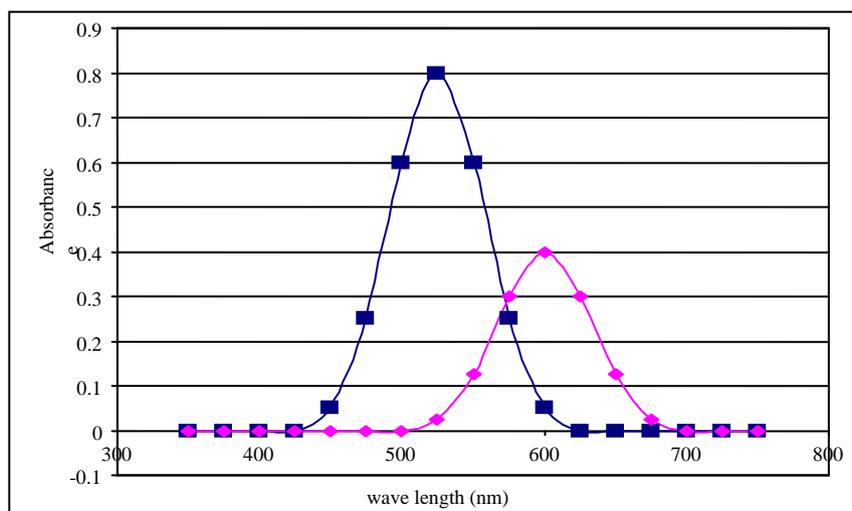


(b)



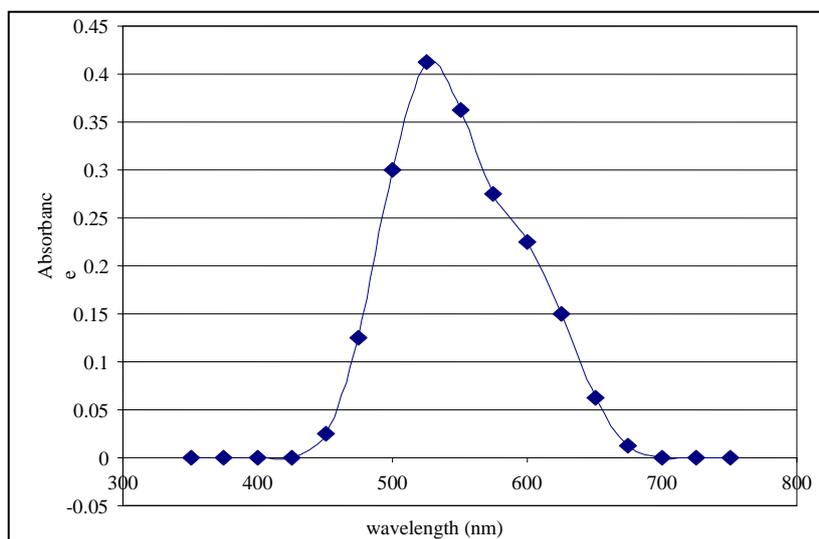
(c)

Figure 6 Visible spectra for two solutions (a, b) and one solution of unknown coloured (c) components



(a)

(to be continued)



(b)

Figure 7 Visible spectra for: (a) two colorants X (squares) and Y (rhombs) in aqueous solutions of concentration  $2.0 \times 10^{-4}$  and  $4.0 \times 10^{-4}$  M respectively, and (b) for an unknown solution presumably consisting of a mixture of colorants X and Y

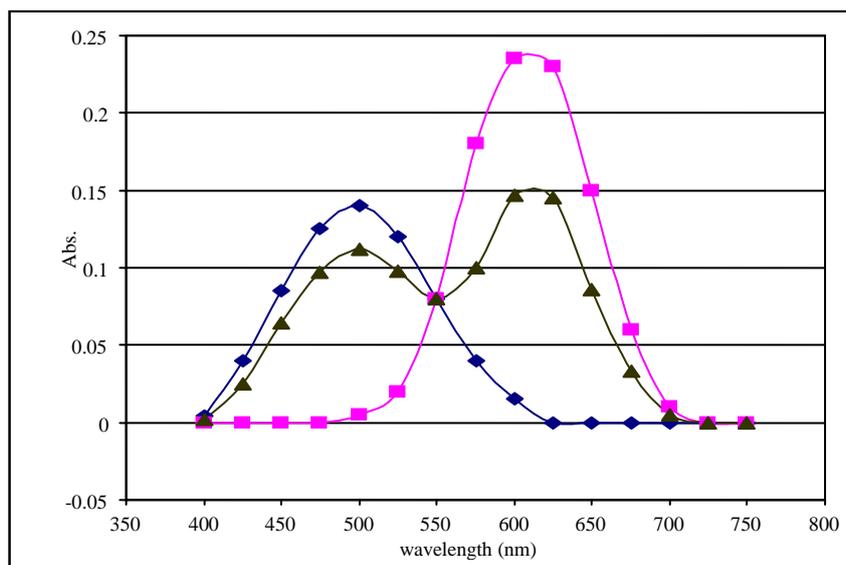


Figure 8 Visible spectra for a solution of a colorant Z in concentration  $2 \times 10^{-4}$  M at pH values of 3.0 (rhombs), 7.0 (triangles) and 10.0 (squares)

#### 4. Results and discussion

The obtained results for Q1 and Q2 are summarized in Tables 5 and 6, results for Q3 and Q4 are summarized in Table 7. No significant differences were observed between the results obtained for the five tested groups of students. The responses to the 1.1 item revealed that only a small proportion of students were aware of the need for calibration, cleaning, repeating measurements and stirring during measurements in pH measurements. In response to the 1.2 item, the mean value is generally used as a representative pH value, attachment of the corresponding standard deviation when express the result of the pH measurement was not unanimously made.

Table 5 Results on Q1

Item	Response	C1 N=12	C2 N=15	C3 N=18	CE1 N=16	CE2 N=16
1.1	Need for calibration	3 (25.0)	4 (26.7)	4 (22.2)	4 (25.0)	3 (18.8)
	Need for cleaning	3 (25.0)	5 (33.3)	6 (33.3)	4 (25.0)	5 (31.2)
	Need for repeating measurements	3 (25.0)	2 (13.3)	3 (16.7)	3 (18.8)	3 (18.8)
	Need for stirring	1 (8.3)	1 (6.7)	2 (11.1)	2 (12.5)	1 (6.2)
1.2	Mean value of 3-5 measurements	10 (83.3)	10 (66.7)	12 (66.7)	10 (62.5)	12 (75.0)
	Standard deviation	4 (33.3)	4 (26.7)	6 (33.3)	4 (25.0)	5 (31.2)
	Distinction between accuracy and precision	3 (25.0)	4 (26.7)	5 (27.8)	3 (18.8)	3 (18.8)
1.3	Measuring with precision	10 (83.3)	9 (60.0)	14 (77.8)	12 (75.0)	11 (68.8)
	Need for standardization of NaOH	2 (16.7)	2 (13.3)	4 (22.2)	2 (12.5)	2 (12.5)
	Need for decarbonation of NaOH solution	1 (8.3)	2 (13.3)	5 (27.8)	1 (6.2)	2 (12.5)
	Need for indicator selection	2 (16.7)	3 (20.0)	4 (22.2)	2 (12.5)	2 (12.5)
	Possibility of potentiometric (conductimetric, spectrophotometric) titrations	2 (16.7)	2 (13.3)	2 (11.1)	1 (6.2)	2 (12.5)
1.4	Graphical extrapolation of quasi-linear regions	1 (8.3)	0 (0.0)	1 (5.6)	1 (6.2)	1 (6.2)
	Estimated midpoint	8 (66.7)	12 (80.0)	14 (77.8)	2 (12.5)	3 (18.8)
	Maximum/minimum apparent points	3 (25.0)	3 (20.0)	3 (16.7)	3 (18.8)	3 (18.8)

Table 6 Results on Q2

Item	Response	C1 N=12	C2 N=15	C3 N=18	CE1 N=16	CE2 N=16
2.3	Correct calculation of concentration					
	Yes	10 (83.3)	14 (93.3)	14 (77.8)	14 (87.5)	14 (87.5)
	No	2 (16.7)	1 (6.7)	4 (22.2)	(12.5)	(12.5)
2.4	Commercial instrumentation					
	more	12 (100)	15 (100)	18 (100)	16 (100)	16 (100)
	equal	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)
	less	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)
	to be decided by data precise and accurate than home-made	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)

Table 7 Results on Q3 and Q4

Item	Response	C1 N=12	C2 N=15	C3 N=18	CE1 N=16	CE2 N=16
3.1	Intensity, absorbance, transmittance, etc.	6 (50.0)	9 (60.0)	7 (38.9)	9 (56.2)	6 (37.5)
	Dispersion/absorption, reflection, etc.	6 (50.0)	5 (33.3)	9 (50.0)	7 (43.8)	8 (50.0)
3.2	Need for zero correction	1 (8.3)	2 (13.3)	2 (11.1)	1 (6.2)	2 (12.5)
	Need for cleaning	2 (16.7)	5 (33.3)	5 (27.8)	3 (18.8)	4 (25.0)
	Need for repeating measurements	0 (0.0)	1 (6.7)	0 (0.0)	0 (0.0)	2 (12.5)
	Need for calibrating wavelength	0 (0.0)	1 (6.7)	1 (5.6)	0 (0.0)	0 (0.0)
3.3	Single peak aspect of spectra in Figure 6a	5 (41.7)	5 (33.3)	6 (33.3)	5 (31.2)	6 (38.5)
	Determination of $\lambda_{\max}$	3 (25.0)	5 (33.3)	5 (27.8)	5 (31.2)	5 (31.2)
	Determination of $\epsilon$ at $\lambda_{\max}$	2 (16.7)	3 (20.0)	3 (16.7)	3 (18.8)	2 (12.5)
	Different colorants in Figure 6a	3 (25.0)	5 (33.3)	6 (33.3)	6 (37.5)	6 (38.5)
	Similar colorants in Figure 6b	8 (66.7)	9 (60.0)	14 (77.8)	12 (75.0)	12 (75.0)
	Possibility of wavelength error in Figure 6b	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)
Mixture of compounds in Figure 6c	5 (41.7)	8 (53.3)	9 (50.0)	6 (37.5)	8 (50.0)	
4.1	Correct qualitative interpretation of the spectrum	8 (66.7)	9 (60.0)	14 (77.8)	8 (50.0)	12 (75.0)
	Estimating of the concentrations of the colorants X and Y	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)
4.2	Combination of two different one-peak spectra	10(83.3)	9 (60.0)	14 (77.8)	12 (75.0)	12 (75.0)
	Isosbestic point as denoting species in equilibrium	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)
	Spectral response identical to that expected for a chemical indicator during an acid-base titration	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)	0 (0.0)

In response to query 1.3, the need for de-carbonation of the solution of NaOH and the need for its standardization (using a primary standard, typically potassium hydrogen phthalate) are omitted by the majority of

students. All these factors were theoretically studied in “ordinary” classroom sessions as well as indicators performance. Remarkably, however, few students indicate that it is needed an adequate choosing of indicator for a correct titration and a lower proportion of students recognize the possibility of using a non-chemical end-point determination procedure, namely via potentiometric, conductimetric and spectrophotometric monitoring, etc.

Analysis of graphical data demanded by the item 1.4 was in general performed correctly from the midpoint in the central portion of the pH vs. NaOH solution volume titration curve. This midpoint was obtained, however, with no definite criteria and only a few students use the extrapolation of pre- and post-end-point almost linear regions. In all five groups, several students take incorrect points (at the beginning or at the end of the central regions of the titration curve) for determining the end-point for the titration experiment.

Open interviews for the proposal of instrumental methods for monitoring acid-base titrations indicated that the students refer to instrumental techniques in a generic way (potentiometry and spectrophotometry), but they find gross difficulties for providing an operational view of the instrumentation. The single conductimetric device described in Figure 4 was accepted by the students with reluctance as a possible method for monitoring the titration. Again, relevant aspects in the analytical process (need for standardization of the NaOH solution, need for decarbonation of such solution and need for testing the repeatability of the electrical measurements) were generally omitted.

Interestingly, the two straight lines graph in Figure 5 obtained for conductimetric monitoring of the titration were qualified by several students as erroneous because they expected an s-type graph such as in potentiometric monitoring (Figure 3). The calculation of the concentration of acid from the conductimetric titration was generally corrected, using the intersection point between the two straight lines fitted from experimental data, but several students used an incorrect end-point for the titration by using the experimental point of minimal conductivity.

The most remarkable feature corresponded to the item 2.4, where the students were asked about the relative accuracy and precision of the conductimetric titration relative to the potentiometric one. Unanimously, the students considered more precise and accurate the potentiometric titration, performed with a commercial equipment than the conductimetric one performed with a home-made device.

With regard to concepts involved in spectrophotometry (item 3.1), there was a set of vague responses regarding the general involved phenomena (distinction between light absorption, reflection and dispersion), its description in terms of modern physics (photon absorption, quantum transitions, etc.) and magnitudes and laws to be used (absorbance, Lambert-beer law, etc.). Responses to the 3.2 item were qualitatively similar to those for item 1.1; however, the percentage of responses claiming for the need for repetitive measurements in order to minimize non-systematic errors in 3.2 are approximately half than those obtained in the case of pH measurements (item 1.2). Apparently, the more sophisticated instrument, the spectrophotometer, produces a level of confidence larger than that attributed to a less expensive instrument, the pH-meter. Remarkably, few students indicate the need for previous zero adjust in spectrophotometric measurements and none consider the possibility of any instrument derive causing wavelength error.

Qualitative description of spectra in query 3.3 was in most cases naive, so that the one-peak character of the represented spectra for both X and Y species in Figures 6a and 6b is frequently omitted and only in relatively few cases and it determines the wavelength at the maximum absorbance as a part of the written description. Remarkably, students in a relatively high percentage (25%-40%) do not recognize that the spectra in Figure 6a can correspond, simply, to two solutions of the same colorant with different concentrations. The spectra in Figure 6b can be attributed to two similar colorants and to two spectra of the same solution when a systematic error is

produced in the wavelengths. This second possibility is entirely absent in the students' responses. Remarkably, the spectrum in Figure 6c is attributed by most students (35%-50%) to the existence of a mixture of compounds in the solution, i.e., the possibility of a two- or multiple-peak spectrum is neglected.

Qualitative description of the possible combined spectrum of X and Y in item 4.1 was to any extent, erratic. Most students stated that the represented spectrum (Figure 7b) corresponds to a combination of the spectra for X and Y in Figure 7a, but the students were generally unable to detail a method for properly verifying this possibility from absorbance measurements at (at least) two different wavelengths.

Similarly, the students were unable to provide a satisfactory description of spectra in Figure 8, corresponding to query 4.2. Here, the students attempted to describe spectral curves in terms of mixtures of colorants, partly as a result of a "contamination" from item 4.1. Even after insisting in the different experimental situation summarized in Figure 8 (spectra for a same solution at different pH values), the students were unable to correlate this situation with the colour changes experienced by a chemical indicator upon varying the pH. This is of particular interest because the association of different spectral responses to different species in solution is a crucial aspect for studying chemical equilibria, which generally and probably underlines a more profound misconception: the confusion between chemical substance and chemical species.

The above results, although corresponding to a limited sample of university students, suggest that there is a set of misconceptions on instrumental analysis. With regard to formal and operational aspects of misconceptions, one can mention that:

(1) Concepts, terms and symbols involved in instrumental analysis are frequently used in imprecise and interchangeable meaning (e.g., absorption by absorbance);

(2) Connection between laws and associated experimental measures is often viewed as a monolithic relation, which necessarily has to be accomplished regardless experimental conditions;

(3) The foundations of the instrumental method and the operation of the equipment are generally viewed as secondary or trivial insights during analysis;

(4) There is a generalized weak view of errors and a vague notion of analytical properties. The students, although orthodox instruction in theory of errors, tend to use a vague concept of error without discerning, for instance, between accuracy and precision or between systematic and random errors. Students are aware of the importance of error consideration, but tend to identify manual errors in handling instrumentation as the main or even unique source of experimental error. In particular, the students know "theoretically" the importance of error consideration and expression, but tend to neglect such aspects when performing instrumental analysis, in agreement with results from Tomlinson, et al. (2001);

(5) Students tend to consider only one or, eventually, two coupled variables when performing instrumental analysis, and, in this case, only linear relationships between variables are expected. Possibility of multiparametric methods and non-linear functional dependences are frequently omitted.

With regard to methodological and social aspects of misconceptions, reported data suggest that:

(1) Instrumental analysis is frequently considered from a pseudo-empiricist view, so that measurements could be theory-insensitive and/or can be performed without link with theoretical foundations;

(2) The foundations of the instrument performance are frequently taken as irrelevant for measurement purposes. Thus, the instrument appears as a black box mysteriously displaying the demanded results. Equipment is frequently regarded as an exact, self-sufficient and semi-automatic device. Component degradation, biased measurements, etc., are generally not considered. Concomitantly, there is no need for cleaning, calibration, etc.

Apparently, when more sophisticated the instrumentation is, more accurate and precise it is considered by the students;

(3) Instrumental analysis appears frequently as an autonomous step which becomes non-integrated within a more complex analytical process. Explicit integration of the instrumental analysis step with sampling, sample pretreatment, etc., is generally omitted. Apparently, analytical procedures are taken as independent of social demands resulting from variable situations in the real world. Considerations on inter-laboratory trials, need for quality assessment and quality control, etc., are entirely absent in students' considerations;

(4) Additionally, the students tend to display a linear view of analytical strategies, so that analysis proceeds through a succession of operations (sampling, preliminary operations and signal measurement) with no need of revisions;

(5) Remarkably, the students tend to perform an "automatic" analysis of data where alternatives or complications are ignored. This is clearly perceived in their interpretation of spectral curves where the majority of students apparently apply a "one compound, one peak" rule, or ignore correlation between spectral changes with pH variations.

Much of these misconceptions can be ascribed to a pseudo-empiricist view of science that impregnates a significant part of science teaching (Duschl, 1985; Hodson, 1985) and partly focuses the dichotomy between science and technology education (Gilbert, 1992). As recently reported by Davidowitz, et al (2001) on the reasons given by second year chemical engineering and science students for making repeat measurements, the majority of students perceive the purpose to be either to identify a recurring (correct) value or to perfect measuring skills.

Students misconceptions on instrumental analysis can be viewed, at least partly, within the frame provided by Taber (2002) on chemistry misconceptions and Cousin (2006) and Meyer and Land (2003; 2006) on treating threshold concepts. Then, students appear to adhere, to a large extent, to ritual (they are able to perform superficial tasks and techniques to get a result, but fail to understand the complexity that lies behind it) and inert (concepts are understood but not actively used or connected to the "real world", a failure to see the "big picture") knowledge. Such factors define, apparently, a learning style dominated by a trivial view of the role of instrumentation in chemical analysis where the apparatus seems like an autonomous "black box" and the student acts merely as a "button-pusher", as commented by Mabrouk (2002).

Threshold concepts appear as difficult but key ideas characterized by being core to understanding the subject, seismic (getting that it brings about a significant shift in perception of the subject), irreversible (the change in perspective that comes with understanding), integrative (understanding threshold ideas exposes previously ignored interrelatedness) and bounded with other concept areas. Translation of such ideas to the studied misconceptions in instrumental analysis suggests that several "threshold abilities" have to be acquired by the students in order to obtain an educationally satisfactory view of that sub-discipline. Tentatively, these "threshold abilities" refer to:

(1) integrated view of instrumental analysis within the general frame (concerning aims, methods, steps and social links) of analytical processes;

(2) non-empiricist view of science and reasonable understanding of the complexity between measurement and theoretical approaches;

(3) critical view of instrumentation, in particular with regard to theory, measurement and errors;

(4) critical view of data collection and data analysis, in particular with regard to deviations from ideal behaviour, factors of uncertainty, etc., and consideration of possibilities.

Apparently, such abilities act as preconditions for properly acquiring adequate skills for handling

instrumentation and interpret experimental data.

## 5. Conclusions

Analysis of university students' misconceptions on instrumental analysis using a "mixed" set of written questionnaires and structured interviews during laboratory sessions suggests that there are definite misconceptions for which formal, operational, methodological and social aspects can be remarked. There is a generalized view of analytical procedures like "automatic" operations performed by error-free instruments with no need of control, maintenance and verification, and instruments being as "black boxes" operating autonomously-like.

Misconceptions on instrumental analysis reveal the appearance of a pseudo-empiricist view of science which impregnates students' learning styles where instrumentation is viewed as an automatic and autonomous element to be used in chemical analysis.

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