Effects of Solution Physical Properties on Copper and Chromium Signals in Flame Atomic Absorption Spectrometry

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Instrumental techniques are frequently employed in routine analysis. Independently of the technique used, the analyst should know the main instrumental and chemical factors that could affect the analytical results. It is essential to recognize that it is easy to generate data, but the accuracy of these should be demonstrated to obtain acceptable analytical results. In undergraduate courses, it should be emphasized that chemical principles should not be forgotten.

Flame atomic absorption spectrometry (FAAS) was independently proposed by Walsh and by Alkemade in 1955. Nowadays, this technique is extensively employed for metals determination in a broad range of materials. The fundamentals of this technique are clearly explained in classical textbooks (*1–3*). However, there are some aspects that still need to be stressed for students.

Coleman (*4*) proposed an experiment involving the determination of lead in gasoline by FAAS, using a method that avoided the aspiration of organic solvents, but instead involved extracting the metal into an aqueous solvent. This work emphasized the use of wavelengths other than the most sensitive one and the effects of flame stoichiometry and burner height upon the absorbance. Nevertheless, it should be pointed out that the most critical step in FAAS is the introduction of samples, which should be converted to an aerosol in the nebulizer where the process of nebulization occurs. The sample solution is aspirated in the nebulization chamber, where the high flow of gases (ca. 20 L/min) generates drops with different diameters. This chamber is designed to provide a breakage of big drops and to select the suitable drop size (< 5 μm) to reach the flame. The efficiency of this process is typically less than 5% for aqueous solutions; thus when a volume of 5.0 mL of the sample solution is aspirated, only 0.25 mL of this solution reaches the flame. The efficiency of nebulization is affected by viscosity, surface tension, and density (*5–7*). These physical properties strongly affect analytical parameters such as sensitivity and precision, and they should be taken into account to obtain accurate results.

The physical properties of solutions are determined by the solvents used and also by solutes dissolved in this medium. The presence of large amounts of dissolved salts, surfactants, and miscible organic solvents causes changes in viscosity, surface tension, and density. To determine metals in samples with these characteristics, the use of analytical reference solutions prepared in water is not suitable and could lead to erroneous results due to changes in nebulization and atomization processes.

In the work described here we demonstrated the effects of physical properties on chromium and copper signals in FAAS, using solutions prepared in a medium containing surfactant and with mixtures of water and ethanol. Surfactants can be found in a lot of products: for example, motor oils, pharmaceuticals, soaps, detergents, and corrosion inhibitors. Ethanol and other alcohols are employed as fuels. The proposed experiment can be carried out in a 4-h laboratory class, including the preparation of solutions. The main aim is to point out that instrumental analysis, like classical analysis, is dependent on physical and chemical properties and good results cannot be obtained if instruments are considered to be magic black boxes.

Experimental Procedure

Apparatus

All measurements were made using an atomic absorption spectrometer (Intralab/Gemini model AA12/1475) and an air–acetylene flame in a 10-cm one-slot burner. This flame is safe and the occurrence of flashback is highly unlikely. This equipment was supplied with a nebulization chamber with a glass impact bead. To measure the aspiration rate a digital chronometer (Casio) and a graduated cylinder were used. In some experiments a peristaltic pump (Ismatec model IPC-4) was employed for solution propulsion.

Reagents and Analytical Solutions

Five copper solutions containing 5.00 mg/L of Cu^{2+} were prepared in an aqueous ethanol medium with 10, 34, 60, 80, and 96% (v/v) ethanol (Carlo Erba). A pure water solution with the same copper concentration was prepared for reference. An aqueous stock solution containing 1000 mg/L of Cu^{2+} was prepared using $CuSO_4 \cdot 5H_2O$ (Merck).

The effect of surfactant was studied employing solutions containing 5.00 mg/L of chromium and tetrapropylammonium bromide (BTPA, Aldrich) in concentrations of 1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 5.0×10^{-2}, and 1.0×10^{-1} mol/L. A 5.00 mg/L chromium solution was prepared without surfactant for comparison. All solutions were prepared in a 0.012 mol/L hydrochloric acid medium (Merck). The chromium aqueous stock solution (1000 mg/L Cr) was prepared using $K_2Cr_2O_7$ (Merck). Solutions containing dichromate are toxic, and skin contact should be avoided. The BTPA acts as an irritant and its contact with eyes and skin should be avoided.

Procedure

A stoichiometric flame was used for copper and a fuel-rich flame was used for chromium. The observation height and the aspiration rate were adjusted to maximum signal using solutions prepared in aqueous medium. Other conditions were adjusted in accordance with recommendations in the operations manual. All measurements were made in triplicate at wavelengths of 324.7 and 357.9 nm for copper and chromium, respectively. Average values were employed to plot graphics. The aspiration rate for aqueous alcoholic solutions was established by measuring the volume of each solution aspirated during a fixed time of 60 s.
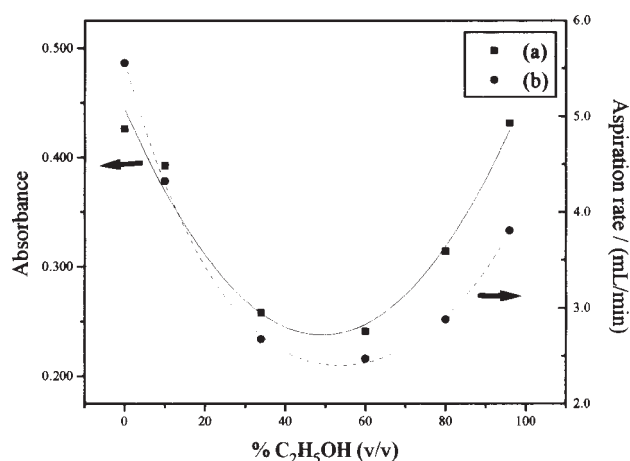
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Figure 1. (a) Absorbance signals for copper (5 mg/L) in different concentrations of ethanol. (b) Aspiration rate for ethanolic solutions.
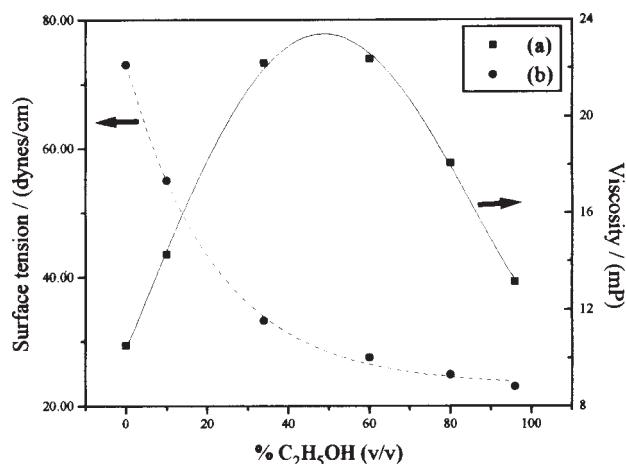

Figure 2. (a) Viscosity of ethanolic solutions at 25 °C. (b) Surface tension of ethanolic solutions at 20 °C (from data obtained in ref *8*).
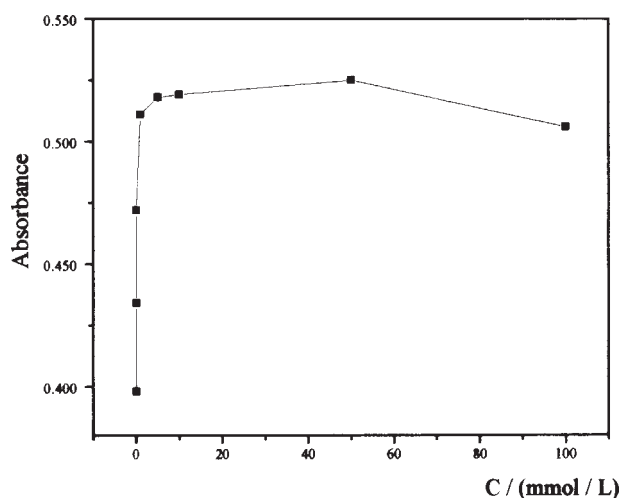

Figure 3. Absorbance signals for chromium (5 mg/L) in different concentrations of tetrapropylammonium bromide.

Results and Discussion

To demonstrate the effects of physical properties on analytical signals in FAAS, we used solutions containing copper prepared in an ethanolic medium and solutions containing chromium plus tetrapropylammonium bromide.

Copper solutions containing 0–96% (v/v) ethanol were aspirated in the nebulizer. The results are shown in Figure 1a. All solutions contained the same concentration of copper, but the absorbance signals varied by about a factor of two, reaching a minimum at about 50% ethanol. In Figure 1b is shown the measured variation of aspiration rate for ethanolic solutions. It can be observed that a lower aspiration rate results in a lower absorbance signal, since the analyte mass that reaches the flame is decreased when the aspiration rate diminishes. A mathematical manipulation of the experimental data showed a reasonable linear correlation between absorbance and the log of the aspiration rate ($r = 0.9116$):

$$A = 0.5635 \text{ (log aspiration rate)} + 0.04692$$

As expected, this equation confirms the close correlation between aspiration rate and absorbance signal, and it can be concluded that analytical results obtained by FAAS will only be accurate when the aspiration rate remains constant for analytical reference solutions and samples.

The effect of the medium on absorbance signals can be explained by considering the physical properties of ethanolic solutions, such as surface tension and viscosity, and how these properties might affect aspiration rate and nebulization.

The effect of ethanol on viscosity is showed in Figure 2a, from which it can be observed that viscosity attains a maximum at about 50% (v/v) ethanol. From Figures 1b and 2a it can be concluded that viscosity strongly affects the aspiration rate: higher viscosity causes lower aspiration rate. To understand this effect it is necessary to recall how solutions are aspirated in pneumatic nebulizers, which are the most frequently used systems for introducing samples into spectrometers. In these systems, the solutions are aspirated by the Venturi effect, which is caused by the high flow rate of gases in the tip of a needle positioned in the entrance of the nebulization chamber. This high flow of gases generates a low-pressure zone in the needle tip, thus promoting the aspiration of solutions. Analytical errors generated by viscosity effects can be corrected by coupling a peristaltic pump to the pneumatic nebulizer (*9*).

Another physical property that could be considered to explain the variation of absorbance signals with ethanol concentration is surface tension. It is well known that solutions with lower surface tension are more easily nebulized and the formation of a larger population of small drops is facilitated (*5*). Surface tension decreases with increasing ethanol concentrations (Fig. 2b). Thus one would expect higher absorbance signals with solutions containing higher ethanol concentrations. However, this effect cannot be used to explain the results obtained, since the changes in aspiration rate with viscosity were the most pronounced effect.

The influence of physical properties on absorbance signals was also demonstrated using solutions containing chromium and a cationic surfactant (Fig. 3). In this case, the variation in absorbance signals was not due to changes in viscosity because similar results were obtained when a peristaltic pump was coupled to the nebulizer for introduction of solutions. However, the presence of sur-

factant causes a decrease in the surface tension of the solution. It can be observed in Figure 3 that up to a concentration of 5.5×10^{-3} mol/L of tetrapropylammonium bromide, a continuous increase in absorbance signals occurred due to diminution in surface tension. After that the variation in signals was less pronounced because physical properties remained practically constant [since, according to literature data (*10*), the critical micelle concentration was attained].

Conclusions

These experiments with a flame atomic absorption spectrometer are useful to demonstrate that all analytical work, even when based on a well established instrumental technique, requires careful examination of physical and chemical properties of solutions containing analytes.

It is important to emphasize that, as experimentally demonstrated, even solutions containing the same concentration of the analyte can yield different results due to physical characteristics of the solutions. Determination of metals by FAAS in samples containing surfactants or organic solvents, such as alcoholic beverages, fuels, and motor oils, could only be done accurately if physical effects were taken into account. These effects could be corrected by using the standard additions method, so that all solutions are prepared in the same media and conse-quently present the same physical properties. The analyst needs to consider the sample characteristics and the fundamentals of the instrumental technique adopted, and only on the basis of this information is it possible to choose a suitable analytical procedure that will generate accurate results.

Acknowledgments

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