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Study of the Effect of Surfactants on the Determination of Gold by Flame Atomic Absorption Spectrometry

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The effect of different surfactants on flame atomic absorption determination of gold is described. Various surfactants such as cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulphate(SDS) and Brij-35 were investigated. All the surfactants enhanced the absorbance and the sensitivity of gold determination by flame atomic absorption. The degree of enhancement was higher for CTAB which has a charge opposite to that of analyte ion, since gold is present as $AuCl_4^-$ or $Au(NO_3)_4^-$ in acidic solutions. The results showed that the reproducibility was increased by a factor of two in the presence of surfactants. The sensitivity (1% absorption) was also improved by a factor of two.

Key Words: Gold, Surfactant, Flame atomic absorption, Cetyltrimethyl ammonium bromide, Sodium dodecyl sulphate (SDS), Brij-35.

INTRODUCTION

The most common method for sample introduction in atomic absorption spectrometry is through the pneumatic nebulization of sample solution. In the nebulization step a primary aerosol is generated, the characteristic of which will have a great influence on the signal intensity and the degree of some interferences. In order to get high transport efficiency and a decrease in the interferences, it is very important that the primary aerosol be as fine as possible for a given set of gas and liquid flow rates[1–3]. Among the physical properties of the solution, surface tension is probably the most influential on the characteristics of primary aerosol. The use of organic solvents can enhance the sensitivity and this has been attributed to the low surface tension of organic solvents[4].

Because of their water solubility and ability to reduce the surface tension of aqueous system it has been suggested that surfactants might improve the sensitivity of FAAS determinations[5–7]. However, there has been a few applications on the use of surfactants in the flame in terms of improved sensitivity and suppression of interferences[8–13]. Kodoma *et al.*[5] reported the use of sodium dodecyl sulfate (SDS) in an improved method for the determination of chromium by AAS using a premixed burner. In a later study Kodoma[7] showed that the increase in sensitivity and reducing interferences in the determination of chromium is related to production of fine aerosol which results from a depression of surface tension of sample containing surfactants.

A model has been proposed for the sensitivity enhancement by surfactants in FAAS using premixed burner by Korahrens *et al.*[10] They suggested that "spectator" ions in FAAS could promote enrichment of the analyte in the double layer at the air-water interface on the surface of large drops. These drops subdivide in the nebulization process to produce smaller drops, which are more efficiently sampled by the premixed burner; therefore an enhancement of analytical signal is observed.

Although flame atomic absorption spectrometry provides a rapid and simple means for the determination of metal ions in various matrices, the sensitivity is not sufficient for some of the elements.

In the present work we wish to report a study of the effect of different surfactants on the determination of gold by flame atomic absorption spectrometry. The aim of this study was to improve the analytical sensitivity of gold determination by AAS.

EXPERIMENTAL

Apparatus

A Varian Techtron atomic absorption spectrometer model AA6 with gold hollow cathode lamp was used. An air-acetylene flame was used for all the determinations. The optimum instrumental parameters for the spectrometer are: lamp current, 5 mA; slit width, 0.2 nm; wavelength 242.8 nm; air flow rate 8 L min^{-1}, and fuel flow rate 2.5 L min^{-1}. A Metrohm pH-meter Model 632 was used for pH measurements with a combine glass electrode combination.

Reagents

All the chemicals used were of analytical grade and distilled de-ionized water was used throughout.

A stock solution of gold (1000 μg mL^{-1}) was prepared by dissolving 0.2002 g of gold (Swiss, 99.99%) in aqua regia and diluting to 200 mL with water in a volumetric flask. This solution was stored in polyethylene bottle. Working standard solutions were prepared by appropriate dilution of this stock solution daily. A solution of cetyltrimethylammonium bromide (CTAB) 0.02 M was prepared by dissolving 3.655 g of CTAB (Aldrich) in water and diluting to 500 mL in a volumetric flask. More dilute solutions were prepared using this stock solution. A solution of sodium dodecyl sulfate (SDS) 13 mM was prepared by dissolving 4.1622 g of SDS (Riedel-Dehaen, 90%) in water and diluting to 1000 mL in a volumetric flask. For preparation of 0.2 M of Brij-35, 23.9681 g of Brij-35 (Merck) was first heated on a hot plate to dissolve, then was transferred to a 100 mL volumetric flask and diluted to the mark with water. Sodium hydroxide (Merck) and hydrochloric acid (Merck) was used for pH adjustments.

RESULTS AND DISCUSSION

Preliminary investigations showed that presence of surfactants affect the atomic absorption signal of gold in flame. Therefore the effect of different surfactants such as sodium dodecylsulfate (SDS) as anionic, cetyltrimethylammonium bromide (CTAB) as cationic and Brij-35 as nonionic surfactants on the determination of gold by flame atomic absorption was studied.

The optimum concentration of each surfactant was established by measuring the absorbance of a solution containing 10 [10 μg mL^{-1} of gold and different concentration of each surfactant. The results are shown in Fig. 1 for SDS and Brij-35 and Fig. 2a for CTAB. As it can be seen all three surfactants tested increased the absorbance of gold. SDS and Brij-35 caused an increase of only 30% while CTAB showed an increase of 50% in the absorbance of gold. This indicates that the charge of the surfactant is important in the observed enhancement of the signal. Since gold is present as $AuCl_4^-$or $Au(NO_3)_4^-$ in acidic solutions, therefore the cationic surfactant CTAB shows the maximum degree of enhancement for the absorbance of gold. It has been suggested that surfactant molecules accumulate around the analyte ions to form reverse micelles during the aspiration process[14]. In addition reverse micelle formation could also protect the analyte from chemical interferences from foreign ions. In solutions containing surfactants, micelle formation occurs above a certain concentration called critical micelle concentration (CMC). Fig. 2a shows the dependence of the absorbance of a 10 μg mL^{-1} gold solution on the concentration of CTAB. The break in the curve

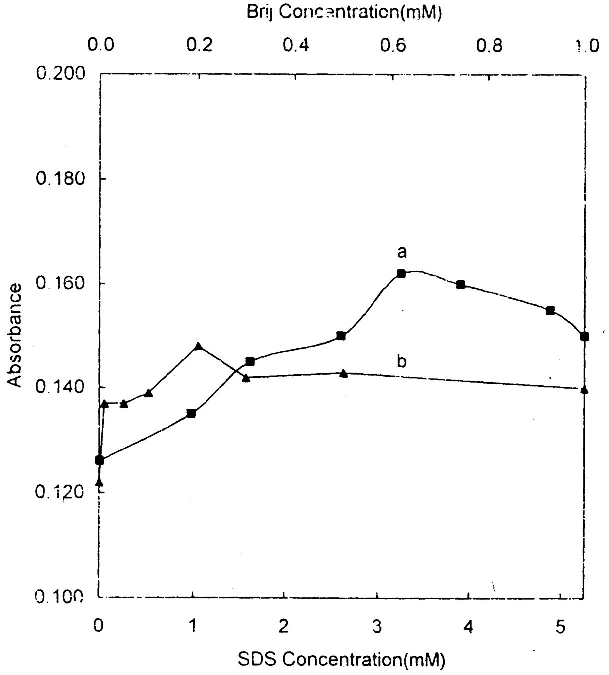

Fig. 1. Effect of surfactant concentration on the absorbance of 10 μg mL^{-1} of gold: (a) SDS (b) Brij-35.

is an indication of onset of micellization. At CTAB concentrations below the CMC, the absorbance is enhanced by increasing the concentration of CTAB. In order to make sure that the surfactant concentration used was above the CMC point, the CMC of the surfactant was also determined by conductometric method. The results presented in Fig. 2b indicate that the break in the curve (CMC point) is exactly at the same concentration as CMC point in Fig. 2a.

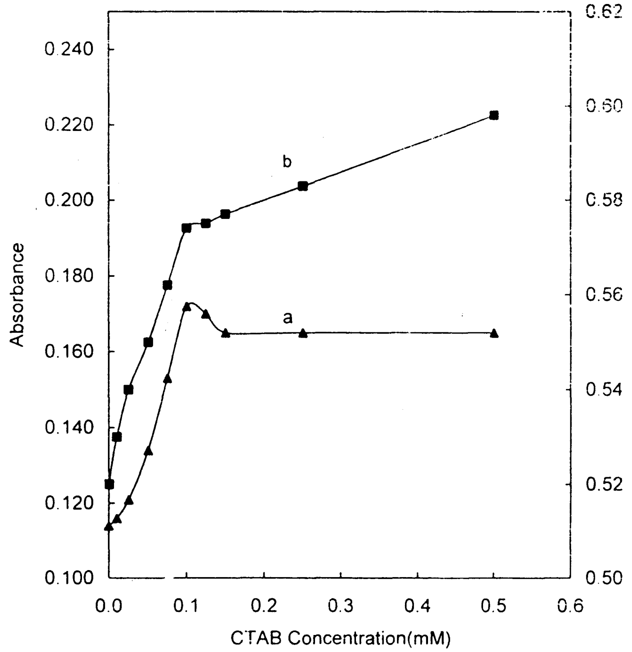

Fig. 2. CMC point for CTAB: (a) absorbance measurement (b) conductivity measurement.

The effect of pH on the absorbance of gold in the presence and absence of surfactants was also studied. In Fig. 3 the absorbance of gold is plotted as function of pH over the pH range of 1.2–11. As it can be seen, increasing the pH decreases the absorbance of gold solution. This could probably be due to the formation of aurate(III) salts such as $NaAuO_2 \cdot H_2O$ or $KAuO_2 \cdot 3H_2O$ in alkaline solutions which are less volatile than compounds such as $H[AuCl_4] \cdot 3H_2O$ or $H[Au(NO_3)_4]$ formed in acidic solutions[15]. However, the absorbance of gold in the presence of surfactants is constant at all pH values, which could probably be due to prevention of formation of stable compounds in the presence of micelles.

The effect of burner height on the absorbance of 5 μg mL^{-1} of gold in the presence and absence of surfactants was investigated. Fig. 4 shows the dependence of absorbance on the burner height. As it is observed the flame profiles differ in both systems with and without surfactant. The results ruled out the possibility that the presence of certain surfactant could alter the flame composition and therefore the distribution of gold atoms in the flame.

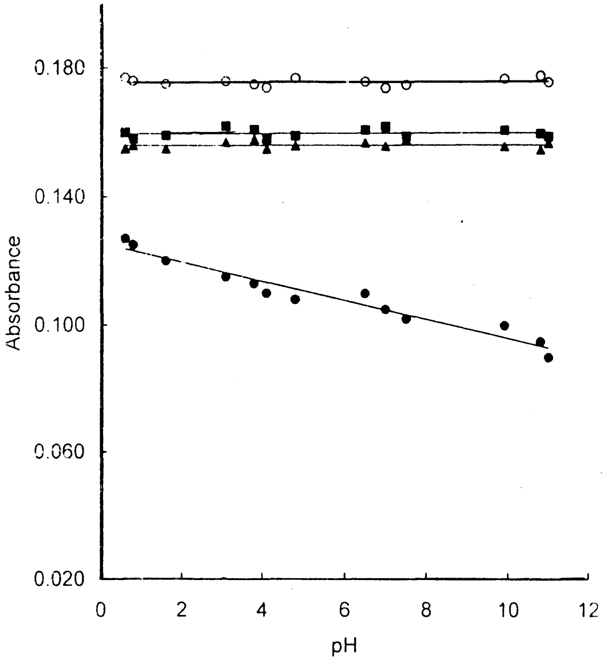

Fig. 3. Effect of pH on the absorbance of 10 μg mL^{-1} of gold in the presence of different surfactants: (•) gold, (▲) gold + SDS, (■) gold + Brij-35, (○) gold + CTAB

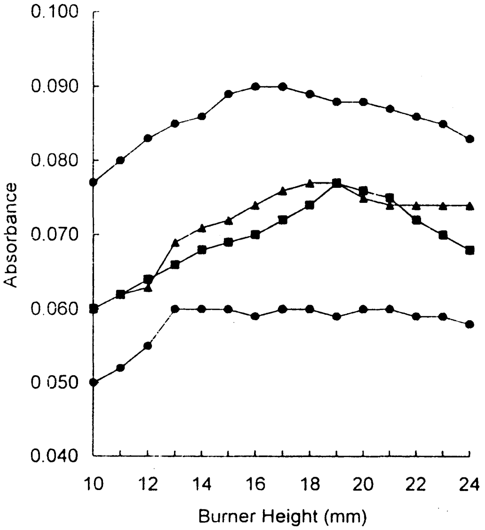

Fig. 4. Effect of burner height on the absorbance of 5 μg mL^{-1} of gold in the presence of different surfactants: (•) gold, (▲) gold + SDS, (■) gold + Brij-35, (○) gold + CTAB

Analytical Characteristics

The calibration curves were found to be linear with and without surfactants (Fig. 5). The surfactants increased the sensitivity and improved the reproducibility. The comparison of the analytical figures in the presence of different surfactants is shown in Table-1.

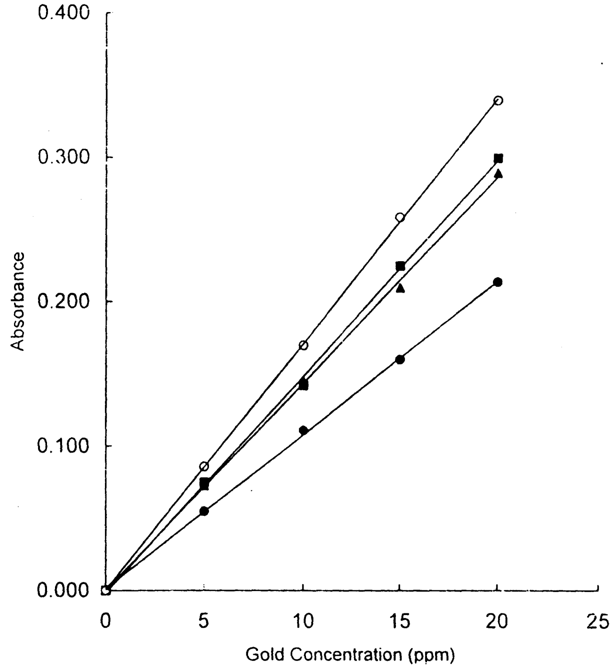

Fig. 5. Calibration curves for gold in the presence of different surfactants: (•) gold, (▲) gold + SDS, (■) gold + Brij-35, (○) gold + CTAB.

TABLE-1
COMPARISON OF DETECTION LIMIT, SENSITIVITY AND % RSD IN THE PRESENCE OF DIFFERENT SURFACTANTS

	Gold	Brij 35	SDS	STAB
Detection limit (μg mL^{-1})	0.49	0.46	0.40	0.31
% RSD	4.10	2.30	2.70	1.90
Sensitivity (μg mL^{-1}) 1% Absorption	0.41	0.31	0.29	0.21

Conclusions

The use of surfactants resulted in an increased signal for the determination of gold. The results revealed that the micellar system could modify both the nebulization aerosols and the analyte atomization processes. The flame profiles indicate that some of the enhancement is due to the combustion of organic matter when surfactant is present which can effect the atomization process. The results also showed that the surfactant charge was important since CTAB with a charge opposite to the analyte [$AuCl_4^-$ or $Au(NO_3)_4^-$] gave the highest enhancement.

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