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# Colorimetric Method for Beryllium Surface Contamination Detection

**by**
**Scott McWhorter and Amy Ekechukwu**

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**Westinghouse Savannah River Company**
**Savannah River Site**
**Aiken, SC 29808**

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## ABSTRACT

To address the need for real-time accurate total beryllium analyses, Savannah River Technology Center (SRTC) Analytical Development Section (ADS) personnel evaluated and modified a colorimetric screening method developed at Los Alamos National Lab (LANL) to measure beryllium on surfaces. This method was based on a color complex formed by beryllium and chromium azurol s (CAS). SRTC converted this visual method to a quantitative analysis method using spectrophotometric detection. The addition of a cationic surfactant (hexadecyltrimethylammonium bromide, CTAB) to the Be-CAS system shifted the complex absorbance away from the CAS absorbance and allowed for the detection of 1.80 μg/L (1.80 ppb) $Be^{+2}$. Assuming complete dissolution and a 10 mL rinse solution volume to remove the beryllium from the wipe, the detection limit was calculated to be 0.018 μg/wipe, which is comfortably below the free release limit of 0.200 μg/wipe. The spectrophotometric method was rugged and simple enough that it could be used as a field method.

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## 1.0 SUMMARY

To address the need for real-time accurate total beryllium analyses, SRTC ADS personnel evaluated and modified a colorimetric screening method developed at Los Alamos National Lab (LANL) to measure beryllium on surfaces. This method was based on a color complex formed by beryllium and chromium azurol s (CAS). SRTC converted this visual method to a quantitative analysis method using spectrophotometric detection. The addition of a cationic surfactant (hexadecyltrimethylammonium bromide, CTAB) to the Be-CAS system shifts the complex absorbance away from the CAS absorbance and allowed for the detection of 1.80 μg/L (1.80 ppb) $Be^{+2}$. Assuming complete dissolution and a 10 mL rinse solution volume to remove the beryllium from the wipe, the detection limit was calculated to be 0.018 μg/wipe, which is comfortably below the free release limit of 0.200 μg/wipe. The spectrophotometric method was rugged and simple enough that it could be used as a field method.

## 2.0 INTRODUCTION

The Department of Energy (DOE) Beryllium (Be) Rule (10 CFR Part 850) is applicable to both soluble and insoluble forms of beryllium metal, compounds and alloys containing a minimum of 0.1% beryllium that may be released as an airborne particulate. The Savannah River Site (SRS) Industrial Hygiene (IH) organization is tasked with assuring that materials and/or components released for general use outside of declared Be work areas meet the criteria established in the Code of Federal Regulations (CFR). As part of this program, SRS industrial hygienists collect wipe samples of materials contained within a Be work area prior to free release. Additionally, IH field personnel wipe areas suspected of having Be contamination. These wipe samples are transported to an American Industrial Hygiene Association (AIHA)-accredited lab and are analyzed according to the National Institute for Occupational Safety and Health (NIOSH) standard protocol. The SRS Environmental Monitoring – Industrial Hygiene lab is accredited, and so many of the samples are submitted to the on-site facility. Others are transported to AIHA-accredited contract labs. In either instance, the sample turnaround time can be upwards of several weeks. Ultimately, a reliable near real-time, field-portable method for determining Be at the DOE free release limit would reduce this analysis time from days or weeks to less than two hours.

Approximately one year ago, an apparent discrepancy in Be wipe results was found between the Westinghouse Savannah River Company (WSRC) IH lab and a commercial IH Lab using the NIOSH standard protocol to analyze the samples. Owing to this discrepancy, SRS IH began an extensive evaluation of the data from previous analyses, the standard analytical procedure used, and the instrumentation employed by each

laboratory to perform Be analysis. In cooperation with several entities both on and off-site, IH identified several areas of potential deficiencies in the standard Be analysis protocol including sample digestion, analytical method employed, and lack of compensation for concomitant interferences present in the wipe samples. Owing to the findings of this evaluation coupled with information gleaned from the experiences of other DOE complex and commercial entities, the DOE Be Advanced Technical Action Team (ATAT), and the DOE Be Working Group, SRTC scientists began the development of improved techniques for analyzing total Be in wipe samples. The ADS was tasked with developing a colorimetric monitoring method which would meet the DOE Be Rule detection criteria. This report documents all colorimetric method development activities pursued by the ADS along with a detailed discussion of the results obtained.

## 3.0 EXPERIMENTAL

### 3.1 Conduct of Testing

This work was in support of Defense Programs Operations. The work was scoping in nature and involved exploratory research of new technologies. The work followed the SRTC research guidelines for exploratory activities and used a technical notebook (WSRC-NB-2001-00131) as the primary means of documentation.

### 3.2 Reagents

Distilled deionized (DI) water was used for making all solutions. The $Be^{+2}$ used in the study was a 10 ppm atomic absorbance (AA) standard in 2% $HNO_3$ obtained from High Purity Standards and diluted to 1 ppm in DI water for the stock solution. The chromeazurol, 2",6"-dichloro-3,3"-dimethal-4'-hydroxy-3"-sulfofuchson-5,5'-dicarboxylic acid (CAS) was purchased from Aldrich Chemicals (dye content approx. 65%) and used by diluting to a concentration of 0.1 wt% in DI water without further purification. The absorbance of the CAS stock solution was tracked before each use to ensure reagent stability over time. Fifty milli-molar borate (pH = 9.2) (Agilent Technologies) was used as the buffer system in this study. Myristyltrimethylammonium bromide (CTAB) was purchased from Acros Organics and diluted to 50 mM in DI water.

### 3.3 Reagent Mixing

Because of the sensitivity of the color development of this colorimetric system on kinetic effects [1], all solutions were prepared for spectrophotometric analysis by pipetting the appropriate volume of stock solution into a 30-mL plastic container in the following order: $Be^{+2}$, borate, CAS, CTAB and $H_2O$. The solutions were allowed to equilibrate for 30 minutes prior to analysis.

### 3.4 Apparatus

A TIDAS II UV/VIS spectrophotometer shown in Figure 1 was used for all absorbance measurements. The spectrophotometer was allowed to equilibrate for at least 30 minutes before making measurements. One-centimeter matched quartz cuvettes were used. The blank in all cases was DI water (neither the surfactant nor the buffer exhibited any absorbance in the 400-700nm region).

## 4.0 RESULTS AND DISCUSSION

### 4.1 Color Development Equilibration

In order to ensure that all measurements occurred at equilibrium conditions, time studies of the color development for the Be:CAS:CTAB system were performed. Figure 1 shows the absorbance of the Be:CAS:CTAB complexes at 598 nm ($\lambda_{max}$) over time. Be:CAS ratios were tested (1:2 and 1:20) in order determine if there was any influence from concentration on the reaction kinetics. In both cases, the reagents were mixed and the complex formation was monitored over a 40 minute period by measuring the absorbance every 2 minutes. As observed in Figure 2, after 12 minutes the absorbance of the complexes reached a steady state so a time of 30 minutes was chosen as an adequate equilibration period for further analysis. In each case the formation of a distinct blue hue was indicative of Be:CAS:CTAB ternary complex formation.

### 4.2 Optimization of CTAB Concentration

The addition of CTAB to enhance UV/VIS spectroscopy of the Be:CAS complex system has been studied while the mechanism of the surfactant-induced changes is not well understood [1-3]. In this study, CTAB was added to the Be:CAS system in order to enhance sensitization and resolution as compared to uncomplexed CAS. Figure 3 shows the optimization of the CTAB concentration at both low and high Be concentrations. For both cases (low and high $Be^{+2}$ concentrations), the absorbance of the complex becomes uncertain immediately after the critical micelle concentration (CMC) (CMC of $4.0 \times 10^{-4}$ M in aqueous solutions from literature [2, 4, 5]) of CTAB is reached. Cook et al reported a similar occurrence noting that the uncertainty corresponded with precipitate formation in solution [2]. In our case, no visible precipitates were noted although the concentrations were very dilute. Also, further addition of CTAB resulted in a stabilization of the absorbance (dissolution of the precipitate) In any case, maximum absorbance was observed at a CTAB concentration of $3.0 \times 10^{-4}$ M, while further additions caused a decrease in the absorbance which indicates that surfactant monomer interactions serve to sensitize the Be:CAS system through formation of ternary complexes up to the CMC.

### 4.3 Optimization of Be:CAS Molar Ratio

To determine the optimum Be:CAS molar ratio, the absorbance of several complexes were monitored while varying the CAS concentration. Absorbance spectra were

collected at both the upper and lower $Be^{+2}$ levels (i.e. 10 ppb and 100 ppb). The results are shown in Figure 4(a-b). For the 10 ppb case, the maximum absorbance was observed at a CAS concentration of $3.3 \times 10^{-5}$ M which correlates to a 1:30 Be:CAS molar ratio, while further additions of CAS in excess of the 1:30 ratio resulted in a decrease in absorbance. Previous reports of the Be:CAS system have suggested that a 1:2 metal:dye ratio was optimum [1-3]. In this case, the metal:dye ratio could not be reduced to 1:2 due to the detection limit constraints of the spectrometer. This could be due to several factors including CAS purity, pH, and salt effects. In this case, the purity of the CAS reagent was reported to be 65% which lowers the effective CAS concentration to $2.1 \times 10^{-5}$ M (i.e. Be:CAS molar ratio of 1:19) in solution. Also, the Be:CAS binding would have been greatly influenced by the unknown dye content (35% impurities) which would serve as an interferences with the Be:CAS binding efficiency.

For the 100 ppb case, the maximum absorbance was observed at a CAS concentration of $16.5 \times 10^{-5}$ M (1:16.5 molar ratio). After accounting for the CAS purity, the CAS concentration is reduced to $10.7 \times 10^{-5}$ M (1:10.7 molar ratio). The increased Be:CAS molar ratio sensitization can be attributed to micellular effects since the surfactant concentration used at $3.0 \times 10^{-4}$ M CTAB is reasonably close to the CMC of CTAB in buffer (~ $4.0 \times 10^{-4}$ M). Additionally, unique binding chemistry was observed beyond the 1:10.7 molar ratio (see Figure 5). Examination of the absorption spectra reveals that at lower molar ratios, reduced free dye absorbance occurred at ~486 nm, while at larger molar ratios (> 1:10.7) increased free dye absorbance at 486 nm and also a disappearance of the shoulder at ~ 640 nm occurred. The change in free dye absorbance is expected as the CAS concentration is increased while the disappearance of the shoulder at 640 nm is indicative of a solvatochromic effect which could be caused by changes in the surfactant concentration or variations in the electrolyte concentration due to the higher impurities contributed from the CAS solution. These hypotheses cannot be confirmed at this time due to the limited nature of the data collected but can be inferred from previous studies [2].

### 4.4 Effect of Be:CAS Molar Ratio on Detection Limits

Working curves for the Be:CAS:CTAB systems were prepared for pre- and optimized conditions over a $Be^{+2}$ concentration range of $5.5 \times 10^{-7}$ M to $1.1 \times 10^{-5}$ M. The results of these determinations are plotted in Figures 6 and 7. At pre-optimized conditions, one can observe that the slope of the curve is non-linear. These conditions were selected solely on literature reported data for similar systems. For this curve, the CAS and CTAB concentrations were held constant at $1.4 \times 10^{-5}$ M and $3.0 \times 10^{-4}$ M, respectively, creating Be:CAS:CTAB molar ratios ranging from 1:25.5:545 to 1:1.27:27.3. The two distinct slopes that are observed can be attributed to excess CAS being available at the lower $Be^{+2}$ concentration levels for binding while at the higher concentration level (100 ppb), the nearly equilmolar ratio of Be:CAS was not sufficient to complex all of the available $Be^{+2}$.

At optimized conditions, a relatively linear curve is observed with a correlation coefficient ($R^2$) of 0.99937. The CAS and CTAB concentrations determined from the

above experiments were $1.4 \times 10^{-4}$ M and $3.0 \times 10^{-4}$ M, respectively. From these results, an estimate of the detection limit can be obtained. The detection limit in this case is defined as the Be concentration at which the absorbance exceeds the base line by 3 standard deviations ($\sigma$'s) of the noise. The $\sigma$ of the noise for these optimized conditions was found to be $1.92 \times 10^{-4}$ absorbance units, and the background was $7.41 \times 10^{-3}$ absorbance units (absorbance of free dye at 598 nm). Thus, the detection limit was reached at $7.99 \times 10^{-3}$ absorbance units which corresponds to a concentration of $1.8 \times 10^{-7}$ M (1.80 ppb) $Be^{+2}$ after graphical extrapolation of the plot. This value compares well with detection limits reported in the literature [1-3].

## 5.0 CONCLUSIONS AND FUTURE WORK

The results of this study demonstrate that enhancements in the metal-dye complex spectroscopy can be achieved through the formation of ternary complexes with CTAB surfactant monomers. The degree of sensitization varies appreciably with CAS and surfactant concentration, while further sensitization has been reported to occur by addition of electrolytes [Cook 1982 and 1984]. In these studies, a detection limit of 1.80 ppb $Be^{+2}$ was achieved along with a relatively linear calibration plot over a range from 5.0 to 100 ppb $Be^{+2}$ ($R^2 = 0.99937$). This detection limit clearly meets the DOE Be Rule detection criteria. Also, it is likely that this system will be employed in the presence of high ionic strength samples in order for complete dissolution of all oxides. In order to use this system as a predictive analytical tool, further studies will be necessary to determine the effects of metal interferents (i.e. Cu, Fe, etc.) and ionic strength, as well as, precisely defining the parameters of the dissolution matrix.

## 6.0 ACKNOWLEDGEMENTS

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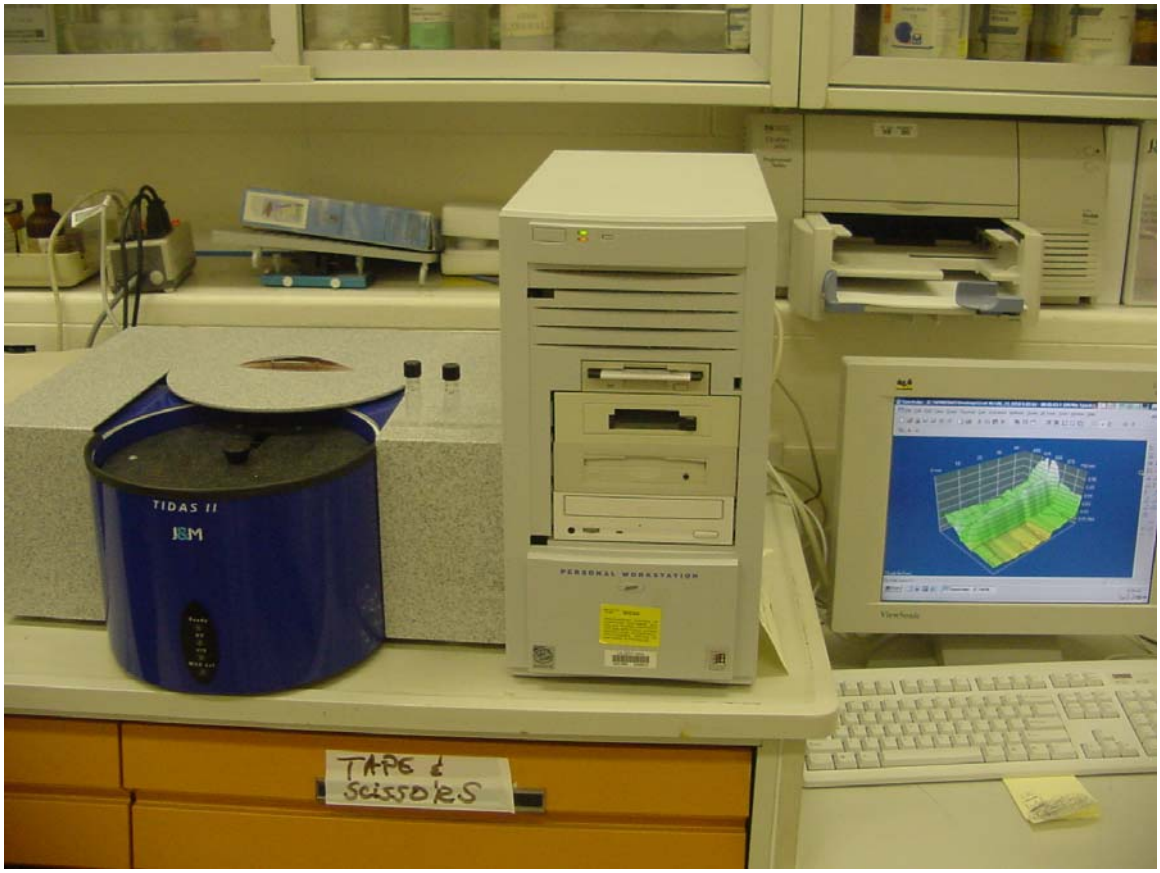


**Figure 1 TIDAS II Spectrometer system used for absorbance measurements.**

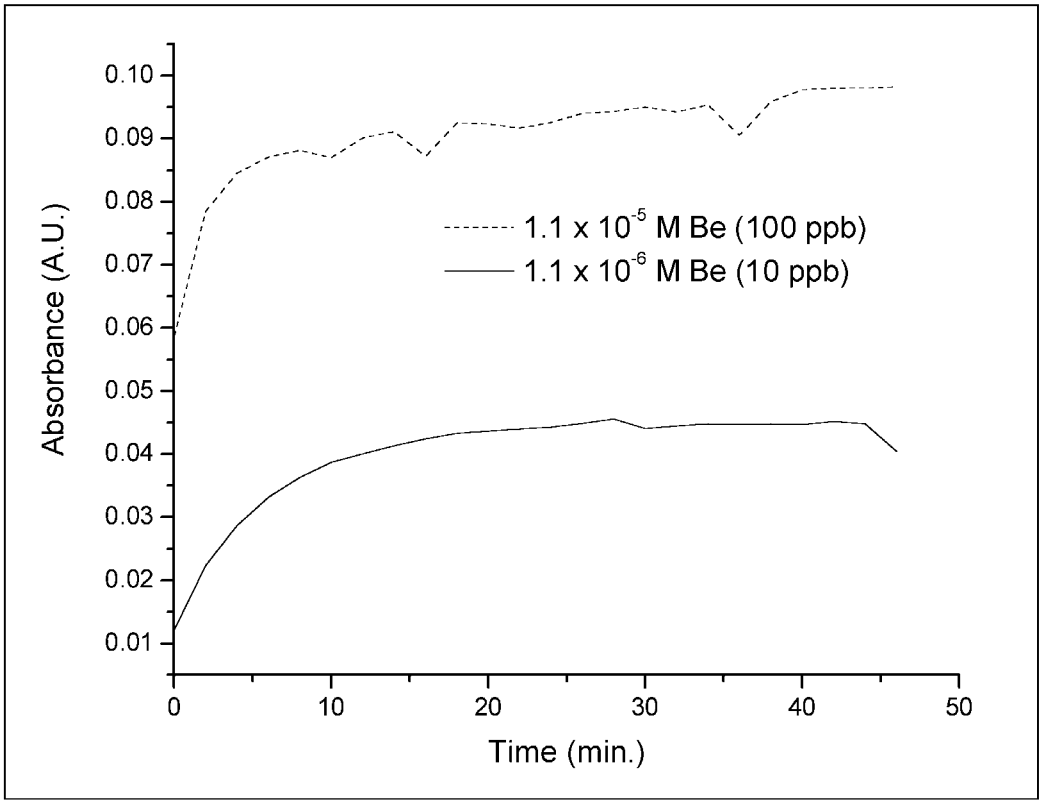


**Figure 2 Be:CAS:CTAB color development studies.**

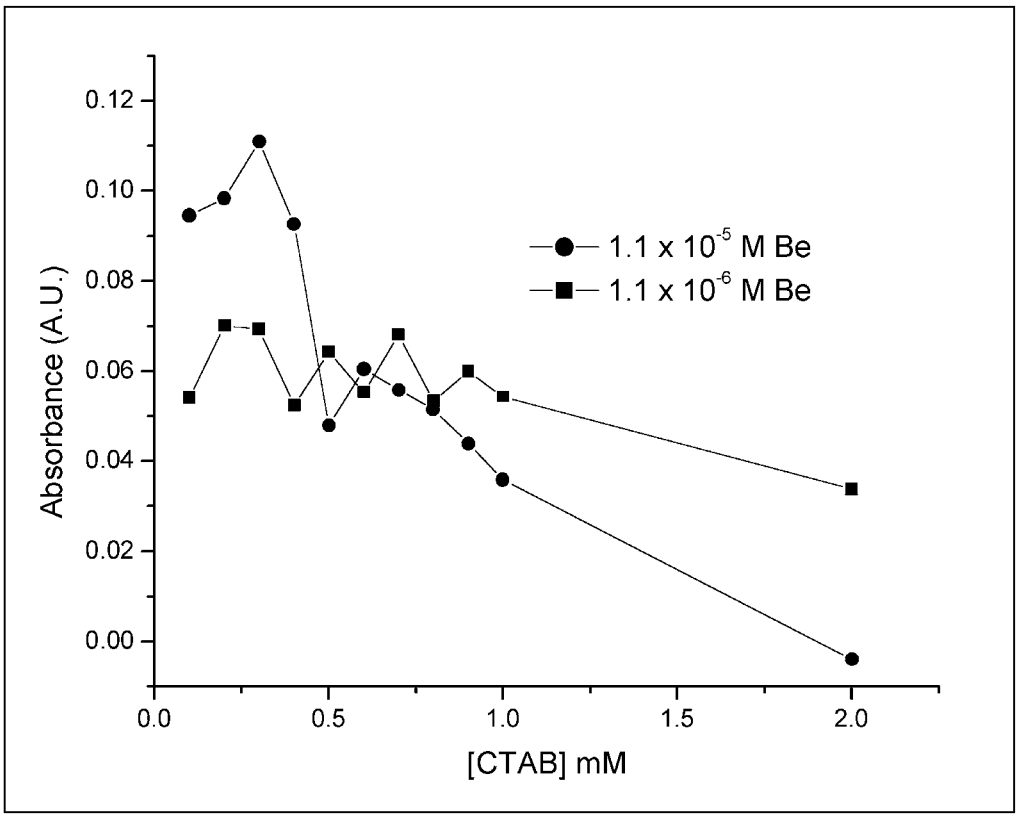


**Figure 3 Absorbance dependence of Be:CAS:CTAB complexes on CTAB concentration: (squares) [$Be^{+2}$] = 10 ppb; (circles) [$Be^{+2}$] = 100 ppb; [CAS] = 2.2 x $10^{-5}$ M; [Borate buffer] (pH = 9.3) = 1.0 x $10^{-2}$ M.**

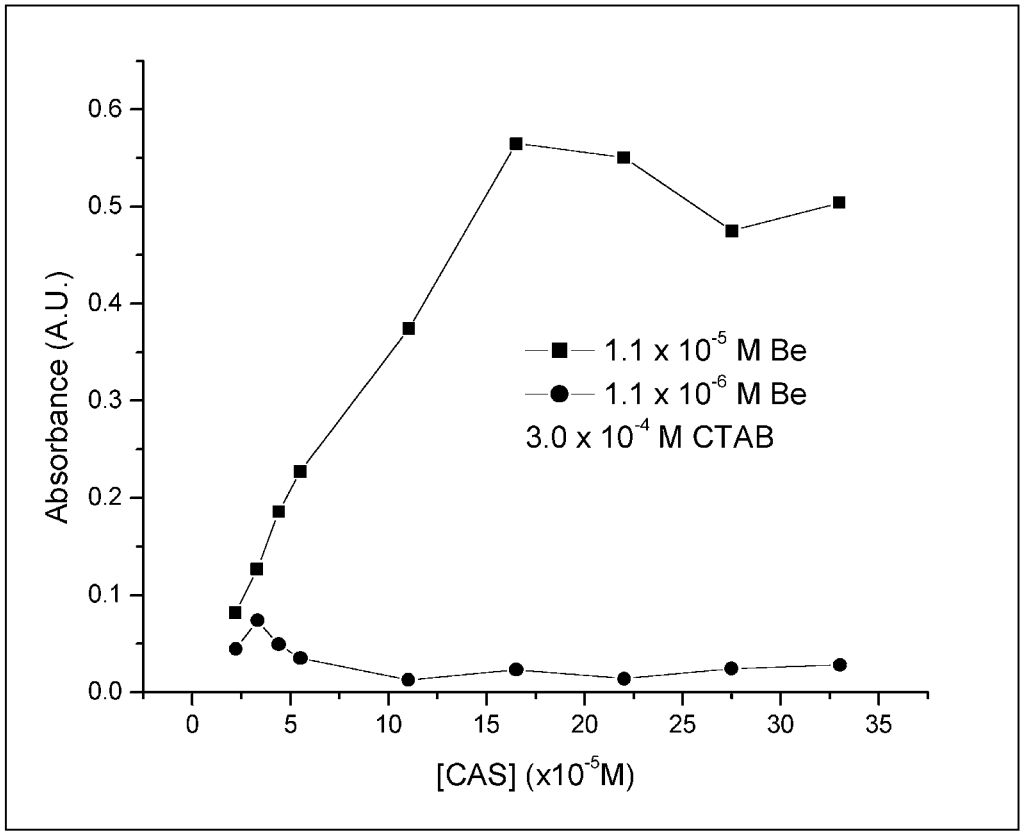


**Figure 4 Absorbance dependence of Be:CAS:CTAB complexes on CAS concentration: (circles) [$Be^{+2}$] = 10 ppb; (squares) [$Be^{+2}$] = 100 ppb; [CTAB] = 3.0 x $10^{-4}$ M; [Borate buffer] (pH = 9.3) = 1.0 x $10^{-2}$ M.**

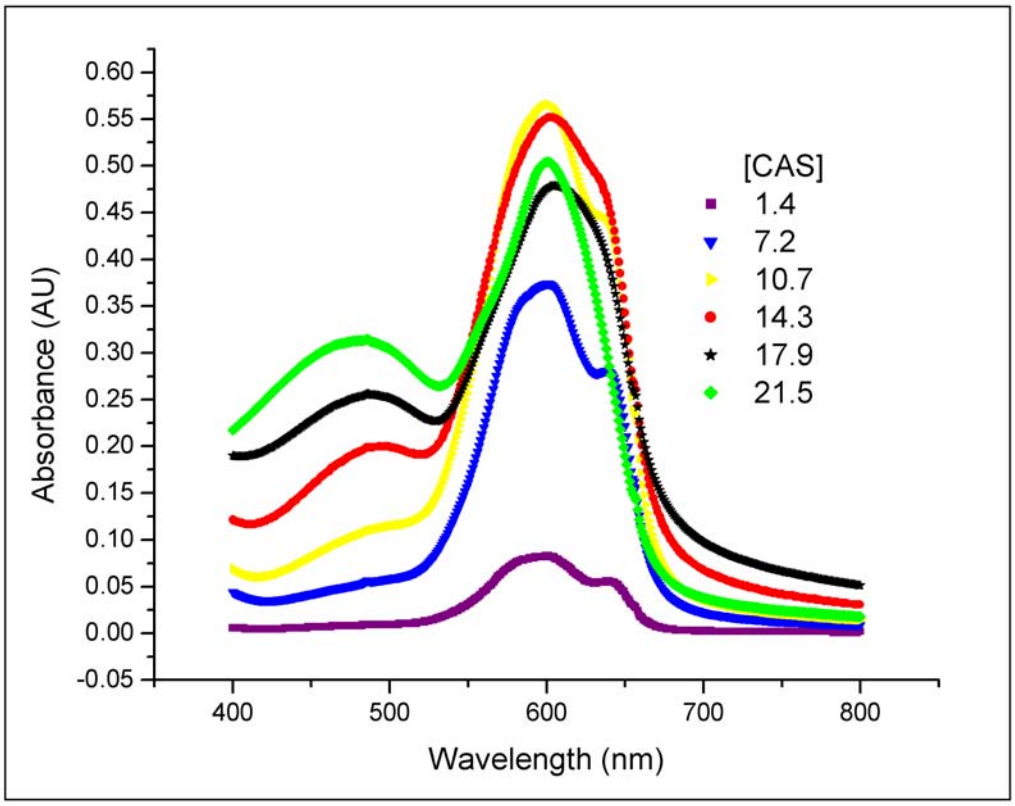


**Figure 5 Change in the vis-Absorbance spectra of the Be:CAS:CTAB complexes with CAS concentration. All conditions were same as in Figure 4.**

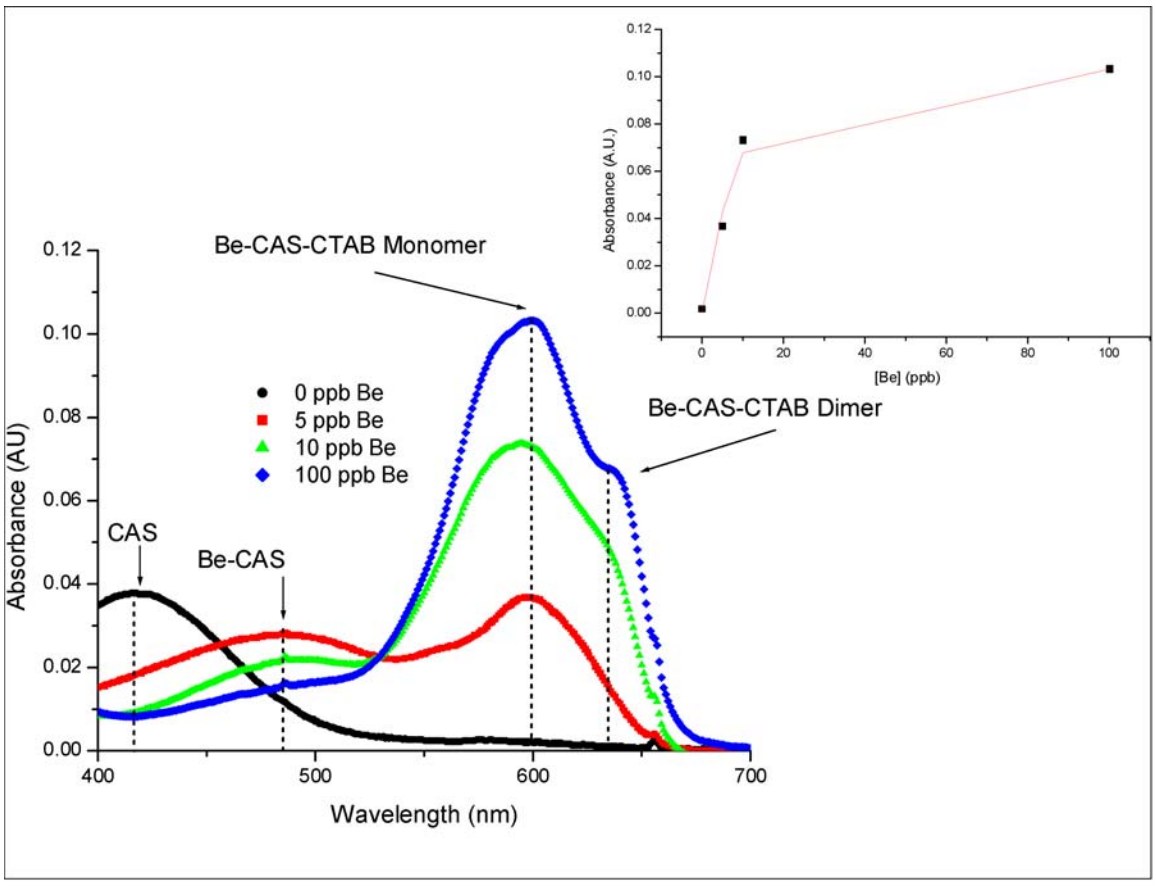


**Figure 6 Pre-optimized calibration plot of the Be:CAS:CTAB system: [CAS} = 1.4 x $10^{-5}$ M; [CTAB] = 3.0 x $10^{-4}$ M; [Borate buffer] (pH = 9.3) = 1.0 x $10^{-2}$ M.**

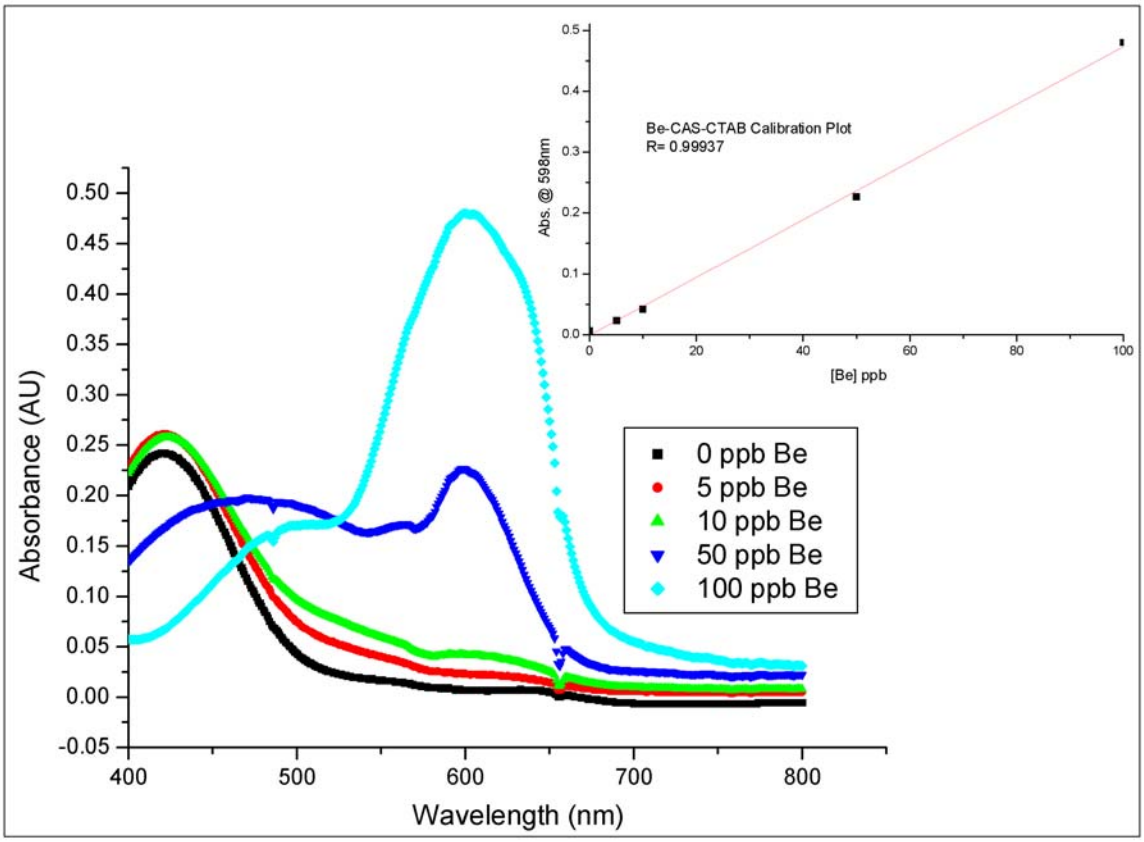


**Figure 7 Optimized calibration plot of the Be:CAS:CTAB system: [CAS} = 1.4 x $10^{-4}$ M; [CTAB] = 3.0 x $10^{-4}$ M; [Borate buffer] (pH = 9.3) = 1.0 x $10^{-2}$ M.**