



Analytical note

Development of a sensitive analytical method for the determination of cadmium using hydrogen assisted T-shape slotted quartz tube-atom trap-flame atomic absorption spectrophotometry

İpek Şahin, Çağdaş Büyükpınar, Nevim San, Sezgin Bakırdere*

Yıldız Technical University, Department of Chemistry, 34349 İstanbul, Turkey



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ABSTRACT

Cadmium is an element that has several industrial applications and exposure to humans causes serious health problems. Hence, determination of this element in environmental samples surrounding humans is very crucial. In this study, a sensitive, accurate and inexpensive analytical method was developed for the determination of cadmium at trace levels. All the system parameters including acetylene flow rate, T-Shape Slotted Quartz Tube (T-SQT) height, sample flow rate, trapping period and hydrogen flow rate were optimized to obtain lower detection limits. Analytical performance of T-Shape Slotted Quartz Tube-Atom Trap-Flame Atomic Absorption Spectrophotometry (T-SQT-AT-FAAS) was determined under the optimum conditions, and the limit of detection (LOD) was calculated as $0.10 \mu\text{g L}^{-1}$. The percent recovery of tap water samples spiked at 2.0, 3.0, 7.0 and $20 \mu\text{g L}^{-1}$ were found to be between 99.5 and 102.8%. The %RSD values were all below 8.0%, indicating applicability and good accuracy of the method for the water matrix.

1. Introduction

Cadmium is a useful metal for various industrial applications, however, it accumulates in the human body and causes harm to the lungs, liver and kidneys [1,2]. The International Agency for Research on Cancer classified cadmium and its compounds as carcinogenic to the human body [3]. Determination of cadmium at low concentrations needs to be performed in order to better understand its effects on the environment and human health [4]. Due to the relatively low sensitivity of flame atomic absorption spectrophotometry (FAAS), preconcentration prior to analysis [5–7], hydride generation and photochemical vapor generation methods are used to improve analyte absorbance [8–10]. Atom trapping is another popular method used to get lower detection limits for many elements [11].

In this method, analyte atoms adsorbed onto the inner surface of the quartz tube when a lean flame is used. After a certain period of sample introduction, organic solvents like methyl isobutyl ketone are introduced to the system to increase the flame temperature and produce reduced flame medium instantly. The trapped atoms on the inner surface are released to give a transient absorbance signal. Thus, the signal to noise (S/N) ratio is increased significantly to lower the detection limit of the system [12]. Hydrogen can also be used for a more efficient release of the analyte atoms by forming a reducing environment. In

addition, the noise generated by the carbon compounds formed by the combustion of the organic solvents is prevented [13].

This study was aimed at developing a sensitive analytical method using T-Shape Slotted Quartz Tube-Atom Trap-Flame Atomic Absorption Spectrophotometry (T-SQT-AT-FAAS) for the determination of cadmium at trace levels. To the best of our knowledge, this is the first study in literature where T-SQT system is used to get very low detection limit for cadmium by the help of hydrogen in the releasing step. All the system parameters were optimized to obtain lower detection limits, and the developed method was applied to water matrix to check its suitability.

2. Experimental

The operation parameters for the FAAS instrument and the dimensions of the T-tube have been summarized in Table S1 (Appendix A) [13]. FAAS and T-SQT-FAAS studies were carried out with the conventional sample introduction unit, nebulizer. For the T-SQT-AT-FAAS studies, sample solutions were aspirated to the system for a 5.0 min period at a flow rate of 7.0 mL min^{-1} . A lean air-acetylene mixture with a 1:20 acetylene:air ratio was used to generate a proper flame to enable atoms adsorb onto the inner surface of the quartz tube. After the trapping period, hydrogen gas with a 0.85 L min^{-1} flow rate was sent to

* Corresponding author.

E-mail address: bsezgin@yildiz.edu.tr (S. Bakırdere).

system from the arm of T-SQT to instantly produce a reducing medium and to release the trapped atoms at once to obtain a transient signal. Hydrogen flow rate was adjusted using a rotameter positioned prior to the valve. The main pressure regulator of the hydrogen cylinder was set at a constant pressure below 5.0 bar. The hydrogen flow rate was adjusted by the rotameter and a secondary valve positioned close to the T-SQT was used to provide the hydrogen flow into the quartz tube. Absorbance based on peak height values were used throughout the study.

3. Results and discussion

All the system parameters including acetylene flow rate, T-SQT height, sample flow rate, trapping period and hydrogen flow rate were optimized to increase the sensitivity of the system. Each parameter was optimized while the other parameters were kept constant. After the optimization studies, the analytical performance of the system was determined.

3.1. Flame type

Aspirated samples need to be atomized in order for the analyte under study to absorb radiation from the hollow cathode lamp at a peculiar wavelength. In the classical FAAS system, this process is carried out with air-acetylene flame with temperatures between 2300 and 2500 °C. Since the energy required for the atomization of each element varies, the flame temperature is adjusted to a desired temperature by optimizing the fuel flow rate in order to increase the efficiency of the atomization. In atom trapping studies, the flame is kept at a lower temperature compared to the conventional FAAS so that the analyte atoms are adsorbed onto the inner surface of the quartz tube. For this purpose, fuel-lean, stoichiometric and fuel-rich flames were tested with an acetylene:air flow rate ratios of 1:20, 1:10 and 1:5, respectively. Sharp absorption signals with fuel-lean flame were obtained while no signal was obtained for both stoichiometric and fuel-rich flames. In addition, the three flame types without an SQT attachment were tested in FAAS but there was no significant (< 5.0%) difference in the absorbance values recorded. It is clear that temperature in FAAS for Cd determination has no big effect on analytical signal, but fuel-lean flame is very crucial in trapping studies.

3.2. T-SQT height

The T-SQT is fixed horizontally on the flame burner head but its height on the burner can be varied to maximize trapping efficiency. A closer position between the quartz tube and the burner causes the atoms to leave the quartz tube in a short period, while an increase of this distance causes a loss in the amount of analyte entering the narrow slit of the tube. The optimization studies of the T-SQT height was conducted between 0.0 and 3.0 mm, at 1.0 mm intervals. Similar absorbance values were obtained at 1.0 and 2.0 mm heights, whereas at 0.0 and 3.0 mm heights, a decrease in absorbance values was observed. For this reason, 1.0 mm was selected as the optimum tube height.

3.3. Sample flow rate

In the FAAS system, the sample solution is introduced to the flame as an aerosol by a nebulizer. The flow rate of the sample drawn from the nebulizer changes the nebulizer efficiency. An increase in the sample flow rate increases the amount of sample reaching the flame unit at a given time. In trapping studies where fixed volumes of sample solutions are used, the homogeneity of liquid droplets in the aerosol greatly affects the activity of atoms in the flame and hence the amount of atoms collected on the surface of the quartz tube. The sample flow rate optimization was carried out at flow rates of 3.6–7.0 mL min⁻¹ using a sample volume of 15.0 mL. The absorbance values increased significantly after 5.0 mL min⁻¹, reaching a peak at 7.0 mL min⁻¹ as

shown in Fig. S1 (Appendix A). For the lower sample flow rates, the prolonged period needed to aspirate entire sample could have led to releasing of trapped atoms from the inner surface of quartz tube, resulting in lower absorbance. The high sample flow rate ensured rapid transfer of entire sample with high nebulization efficiency, and an immediate hydrogen gas transfer after trapping of analyte atoms caused immediate releasing of trapped atoms.

3.4. Trapping period

The basic principle of atom trapping studies is the introduction of sample solution for a certain period and the releasing of adsorbed atoms at once to obtain a sharp signal. The amount of atoms trapped is proportional to the sampling period to a certain extent. The inner surface of the quartz tube is covered with adsorbed atoms over time and this reaches a maximum adsorption capacity after a period of time. Therefore, no significant change is observed in the absorbance values for excess amounts of sample introduced. In this optimization step, trapping periods between 15 and 360 s were tested and absorbance signals increased from 15 to 300 s after which a plateau was reached due to the limited surface area to trap further analyte atoms. Increasing the trapping period to 360 s did not result in a significant increase in absorbance signal; thus, 300 s was selected as optimum trapping period to avoid using excessive amounts of sample solution and prevent time consumption. The correlation between trapping period and absorbance can be seen in Fig. S2 (Appendix A).

3.5. Hydrogen flow rate

It is essential to produce reducing flame medium within a short period of time to instantaneously release trapped atoms from the inner surface of the quartz tube. For this purpose, organic solvents such as methyl ethyl ketone, methyl isobutyl ketone, isopropyl alcohol are generally used via the sample introduction system [14]. Other analytical methods have been reported using externally heated quartz tube atomizer where volatilization and atomization of trapped analyte atoms were achieved by turning off oxygen flow to allow only hydrogen into the system [15]. Hydrogen gas was used in this study to release the trapped atoms from the inner surface of the quartz. The addition of hydrogen likely causes the production of hydrogen radicals that attack the trapped Cd atoms and remove them from the inner surface of the SQT [15,16]. In case of the usage of different organic solvents, the instruments quartz windows can be easily effected and covered with burning products of the solvents. In addition, fluctuation in the deuterium signal as background correction tool could be lowered by using hydrogen gas in the releasing step. This improves the signal/noise ratio to get lower detection limits. The hydrogen gas flow rate optimization was carried out between 0.85 and 2.1 L min⁻¹. Although a lower standard deviation was obtained with 2.1 L min⁻¹ flow rate, 0.85 L min⁻¹ was determined as optimum one as presented in Fig. S3 (Appendix A) to protect the device from horn shaped flames formed through the exit slots of the quartz tube. During the study, the main hydrogen gas valve was maintained below 5.0 bar and the secondary valve connected to the quartz tube was opened instantaneously for a rapid hydrogen combustion. The secondary valve with a pressure regulator also served as a precautionary measure to control hydrogen explosion. After the analytical signal was obtained, the secondary valve was opened and closed several times to ensure atoms were not left on the surface of the tube walls. This was used as a cleaning process for the quartz tube before performing ensuing trapping. The absence of a signal was indicative of complete removal of atoms from quartz's surface.

3.6. Analytical figures of merit

Analytical performance of the system including limit of detection (LOD), limit of quantitation (LOQ), relative standard deviation and

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