Short Communication

# Occurrence of cadmium in water: Its determination by flameless atomic absorption spectrophotometry

M.Z. Hasan, Animesh Kumar and S.P. Pande
National Environmental Engineering Research Institute, Nagpur 440 020.

**Abstract**

A simple and sensitive method has been described for the determination of cadmium in potable water by flameless atomic absorption spectrophotometry. Major elements like sodium, potassium, calcium and magnesium were observed to interfere severely in the atomization of cadmium. Interference by these elements was, however, successfully overcome by matrix modification. The matrix modification reagent consists of 1 per cent ammonium nitrate plus 1 per cent diammonium hydrogen phosphate. The detection limit of the method is 0.15 $\mu g/l$. Cumulative frequency distribution of cadmium in waters showed that the $Cd^{2+}$ was chiefly contributed by anthrapogenic sources rather than industrial or sewage discharges.

**Key words:** Cadmium, flameless atomic absorption spectrophotometry, matrix modification, pollution, water.

## 1. Introduction

Flame atomic absorption spectrophotometric method cannot be used directly for cadmium as its detection limit is higher than 10 $\mu g/l$, the criteria guidelines for potable water[1]. Concentration of cadmium by complexation coupled with extraction in organic solvent is not suitable due to non-stability of cadmium complexes for longer duration[2]. Flameless atomic absorption spectrophotometry provides sensitive methods for cadmium determination. However, this method suffers from the drawback of matrix interference[3,4]. The vaporization characteristics of cadmium and major metals—sodium, potassium, calcium and magnesium—are too close for their complete separation. It makes difficult to effectively eliminate the matrix in the charring stage of heating cycle of a graphite furnace without partial or complete loss of relatively volatile cadmium. In order to remove the matrix which causes background absorption, a selective volatilization and atomization technique has been used[5-7]. The matrix has also been separated from the analyte by chemically modifying the matrix so that it is removed during charring stage. This technique is termed as matrix modification[8]. Matrix modifying reagent consisting of ammonium nitrate and orthophos-

phoric acid has been observed to provide interference-free atomization of cadmium in the presense of calcium and magnesium[9]. The present communication describes a sensitive flameless atomic absorption spectrophotometric method for cadmium.

## 2.  Materials and methods

*2.1 Samples:*  River water samples from Kanhan river and ground water samples from wells of different wards of Nagpur Minicipal Corporation were collected.

*2.2 Sampling procedure:* Samples were collected by using a clean stainless steel water sampler which was introduced to water system with the help of rope and water taken out. The water was filtered immediately through 0.45 micron filter paper acidified with 6 N nitric acid (8 ml/l) and transferred to sampling bottles.

*2.3 Equipment:* A Perkin-Elmer atomic absorption spectrophotometer Model-372 equipped with HGA-2200 graphite furnace, a deuterium background corrector and a cadmium hollow cathode lamp was used. The instrument was operated in peak height mode and signals were recorded on a 10 mV span recorder (Perkin-Elmer Model 56). The cadmium hollow cathode lamp was operated at 6 mA lamp current with a wave length settling of 228.8 nm, spectral slit width of 0.7 nm and nitrogen as purge gas at a flow rate of 45 ml/min.

*2.4 Standard cadmium solution (5 $\mu$g/1):* The solution was prepared by two step dilution of stock cadmium solution containing 1000 mg/1 cadmium with 1 per cent nitric acid.

*2.5 Matrix modifying reagents:* Ammonium nitrate ($NH_3NO_3$), 1 g and diammonium hydrogen phosphate ($NH_4$)$_2$ $HPO_4$ 1 g was dissolved in 100 ml of deionized distilled water.

## 2.6  Experimental

A 20 $\mu$l of the water sample was transferred into graphite tube and then 20 $\mu$l of matrix modifying reagent was also added to it. The graphite furnace was programmed for optimum drying (100°C for 30 seconds), charring (650°C for 50 seconds without ramping) and atomization (2300°C for 5 seconds). Background corrector was used throughout the analysis. Results were computed from duplicate readings. Standards and blanks were run identically and reagent blanks were compensated for.

## 3.  Results and discussion

*3.1. Atomization:* Experimental curves were plotted from the atomic absorption signals obtained using a synthetic water sample containing 5$\mu$g/1 of cadmium. It was observed that loss of cadmium occurred after charring temperature exceeded 300°C. Atomization signals were recorded even at 700°C indicating that some atoms of cadmium were produced even at this temperature (fig. 1). When cadmium was atomized in the presence of matrix modifying reagent, insignificant loss of cadmium was observed up to 650°C (fig. 2). This is perhaps achieved due to the formation of cadmium pyrophosphate, which is stable up to quite high temperature and yields gaseous cadmium atoms consistently on decomposition.
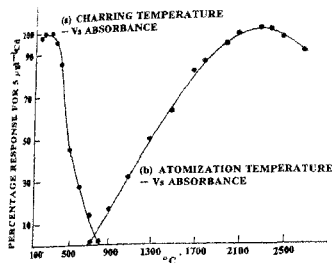
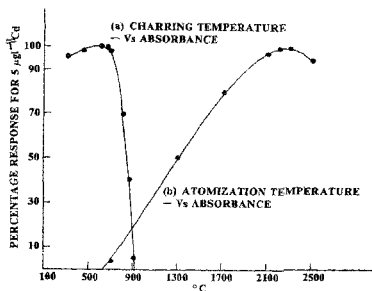FIG. 1. Char and atomization curve for cadmium without matrix modifying reagent.

FIG. 2. Char and atomization curve for cadmium with matrix modifying reagent.

**3.2 Background absorption:** Experiments were carried out to find the effectiveness of deuterium background corrector in case of cadmium determination in water. Absorbance for $1 \mu g \, Cd/ l$ was measured with and without using deuterium background corrector under various conditions. The measured absorbance of $1 \mu g \, Cd / l$ in the absence of interference (a) with $D_2$ correction and (b) without $D_2$ correction were 0.07 and 0.071 respectively. In the presence of alkalinity of 285 mg/l the corresponding values were 0.069 and 0.098 respectively. Moreover the background absorption was much lower in matrix modifying reagent added samples than in plain samples. As long as atomizing time was less than 5 seconds, background absorption was not high and it was possible to remove background absorption by deuterium background corrector.

**3.3 Interference effects of diverse ions:** In order to assess the effects of cations and anions, a solution containing 5 $\mu g/l$ cadmium was spiked with varying amounts of diverse ions. Metals were added as their chloride and anions as their respective acids. Significant interference effects were observed to be produced even at low levels of spiking. These interferences were, however, removed by the addition of matrix modifying reagent. The tolerance of these ions in the presence and absence of matrix modifying reagent is given in Table I. It was evident from these results that cadmium could be successfully estimated in water samples of normal composition.

**3.4 Accuracy, precision and minimum limit of detection:** The accuracy of the method was evaluated by determination of percentage recovery of spiked samples of ground water (intrinsic content 3.0 $\mu g/ l$) and river water (intrinsic content 0.5 $\mu g/ l$). The recovery was found to vary between 93 and 105 per cent for various spiking concentrations of cadmium (Table II). Precision was determined as percentage scatter of replicate analysis in terms of relative standard deviation (RSD). The highest relative standard deviation was 7.9 per cent for ground water and 5.3 per cent for river water. Minimum detection limit is defined as $\bar{X}_{Bl} + 3 \sigma_{Bl}$ where $\bar{X}_{Bl}$ is the mean of blank replicates and $\sigma_{Bl}$ is the standard deviation of blank replicates. Computation of these values gave a minimum detection limit of 0.15 $\mu g/l$ of cadmium.

## Table I

**Effect of various ions on the analysis of cadmium solution (5 $\mu$g/l)**

| Ions | Tolerance limit * of interfering ions | |
|------|------------------------------------|---|
| | Without matrix modifying reagent | With matrix modifying reagent |
| $Cl^-$ | $20 \times 10^3$ | $100 \times 10^3$ |
| $SO_4^{-2}$ | $8 \times 10^3$ | $40 \times 10^3$ |
| $PO_4^{-3}$ | $100 \times 10^3$ | $100 \times 10^3$ |
| $Na^+$ | $2 \times 10^3$ | $40 \times 10^3$ |
| $K^+$ | $0.1 \times 10^3$ | $10 \times 10^3$ |
| $Ca^{2+}$ | $1 \times 10^3$ | $100 \times 10^3$ |
| $Mg^{2+}$ | $1 \times 10^3$ | $20 \times 10^3$ |
| $Mn^{2+}$ | $5 \times 10^3$ | $10 \times 10^3$ |
| $Fe^{3+}$ | $2.8 \times 10^3$ | $10 \times 10^3$ |

* The tolerance limit represents the ratio of the concentrations of the interfering ions to that of the analyte for less than 5 per cent deviation of absorbance from expected value.

## Table II

**Accuracy and precision results for cadmium determination**

| Cadmium added ($\mu$g/l) | Ground water (intrinsic content 3.0 $\mu$g/l) | | River water (intrinsic content 0.5 $\mu$g/l) | |
|---|---|---|---|---|
| | Percentage recovery | RSD % | Percentage recovery | RSD % |
| 1 | 93 | 7.6 | 96 | 4.3 |
| 2 | 95 | 6.4 | 94 | 5.1 |
| 5 | 94 | 4.9 | 99 | 5.3 |
| 10 | 98 | 7.9 | 98 | 4.9 |
| 20 | 105 | 5.7 | 103 | 4.3 |
| 25 | 103 | 6.3 | 101 | 4.9 |

***3.5 Cumulative frequency distribution:*** Cumulative frequency distributions are shown in figs. 3 & 4. In these curves, the smaller the angle with the $X$-axis the greater is the range of variation of cadmium concentration[10]. The ratio (Q) between $C_{99}$ (not exceeded 99 per cent of all the results) and $C_1$ (not exceeded 1 per cent of the samples) indicates the extent of variation, *i.e.*
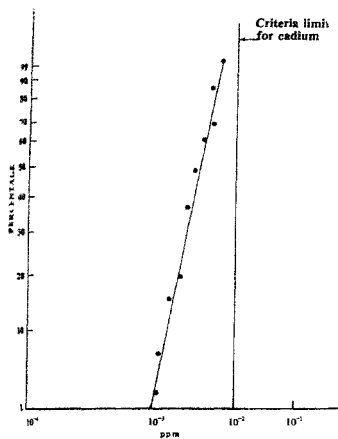
$$Q = \frac{C\ 99\%}{C_1\%}$$

Fig. 3. Cumulative frequency distribution of cad-mium in ground water.
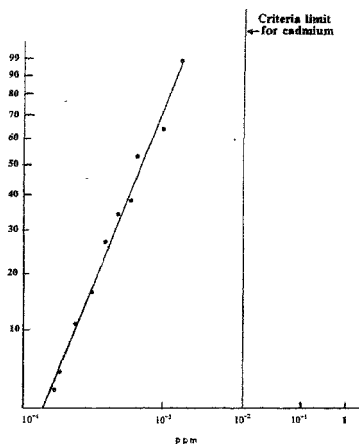


Fig. 4.   Cumulative frequency distribution of cad-mium in river water.

High value of Q shows that the metal is predominantly discharged from industrial sources and low value shows that this is mainly of anthrapogenic nature. In the present study, the values of Q for ground water and river water were 7.3 and 9.3 respectively. This indicated that cadmium levels of waters were chiefly from anthrapogenic sources.

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