Atomic Absorption Spectrophotometric Determination of Cadmium

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Synopsis. In the determination of cadmium by atomic absorption spectrophotometry(AAS), the interfering effects of different species can be completely eliminated by adding excess cyanide. The mechanism by which the cyanide eliminates interference by influencing the atomization process is discussed. Also the AAS for the analysis of cadmium in complex form is elaborated. The aim of this investigation is to achieve a determinate characterization of compound formation. The way to reach this purpose is the utilization of the continuous titration technique.

The interfering effects on cadmium are rarely mentioned in the literature and what has been published are concerned with its determination.[1-3] In this work the effects of some inorganic and organic compounds have been examined and the feasibility of the compound formation is elaborated.

When solutions of cadmium complexes are examined, the absorption signals are mainly depend on the extent to which the ligands affect the atomization processes of Cd. In this respect, the work of Fujiwara[4] is important. He observed a significant difference in the absorbances in the lower part of the air–acetylene flame for the transition metal complexes. These differences were attributed to the type of complex present in solution.

Cyanide has already been successfully applied in AAS for some metals.[5-7] Since cyanide forms very stable complexes with most of transition metal ions,[8] elimination of the interfering effects by adding cyanide was examined.

Experimental

Atomic absorption spectrophotometer, Unicam SP '90 A series 2 fitted with a new HTA photomultiplier tube No. R 270 from EMI. Air was supplied through PU 9003 air compressor. Acetylene was obtained from cylinders after passing through concentrated sulfuric acid and glass wool for purification. A continuous titration device[9,10] was attached to the instrument and the results were computed using a CASIO FX-502 P type programmable pocket calculator. Absorbance values were recorded with a Philips PM 8251 single-pen recorder.

The instrumental parameters were: Lamp current, 4 mA; wavelength, 228.8 nm; slit width, 0.1 mm; observation height, 0.4 cm; air flow rate, 5 $dm^3 min^{-1}$, fuel flow rate, 1.0 $dm^3 min^{-1}$.

All solutions were prepared from B. D. H. Chemicals, Stock solutions of metals and organic compounds were prepared using twice distilled water; aliquots were suitably diluted to give the desired concentration used for the experiments. Stock solution of cadmium was prepared from $CdCl_2 \cdot H_2O$. The concentration of cadmium in the stock solution was 100 $\mu g\, cm^{-3}$.

The complexes, dibromobis(acetyltrimethylammonium-4-phenylthiosemicarbazide)cadmium(II) chloride [$Cd(H_2atpts)_2Br_2]Cl_2$, bis(1-anthraniloyl-4-phenylsemicarbazide) cadmium(II) [$Cd(Hapsc)_2$], bis(1-benzoyl-4-phenylthiosemicarbazide)cadmium(II) monohydrate [$Cd(Hbpts)_2]\cdot H_2O$, dibromo(acetylpyridinium-4-phenylthiosemicarbazide) cadmium(II) chloride [$Cd(H_2apts)Br_2]Cl$, acetato(1-acetyl-4-phenylthiosemicarbazide)cadmium(II) monohydrate [$Cd(Hapts)(ac)]\cdot H_2O$ and bis(1-anthraniloyl-4-phenylthiosemicarbazide)cadmium(II) [$Cd(Haptsc)_2$] were prepared as mentioned in the literature.[11,12] Other complexes; tris(1,2-propanediamine-*N*,*N*)cadmium(II) dithionate [$Cd(pn)_3]S_2O_6$ and tris(1,2-ethanediamine-*N*,*N*)cadmium (II) hydroxide [$Cd(en)_3](OH)_2$ were also prepared as mentioned earlier.[13] The 4.44×10^{-5} M (1 M=1 mol dm^{-3}) solutions of cadmium complexes were prepared by dissolving the appropriate weight of the solid complex in a few amount of *N*,*N*-dimethylformamide(DMF) and completed to the mark using twice distilled water.

Results and Discussion

Effect of potassium cyanide. Figure 1 shows the change in the absorption signal of cadmium as a function of [cyanide]/[Cd] molar ratio. There is a decrease in the signal with distinct break-point corresponding to [CN]/[Cd], 4:1 molar ratio, followed by a sharp enhancement to 130% of the recovery, giving a plateau.

The interpretation of the cyanide behaviour can be discussed on the basis of three main steps which may take place during its continuous increase in the flame, (i) Vaporization of the solid cyano complex particles followed by a decomposition giving Cd atoms which react instantaneously with the oxidizing species in the flame forming cadmium compound(s) essentially CdO, (ii) After the particular stoichiometric ratio is attained at 4:1 for CN:Cd, the excess of CN radical in the flame reacts with the cadmium compound(s) according to the following equation.

$$CdO + CN \longrightarrow Cd + N + CO$$

(iii) The continuous increase of the CN radical scavenging the excess oxidizing species, thus performing a reducing environment for increasing the Cd atom population. There is a balance between the CN

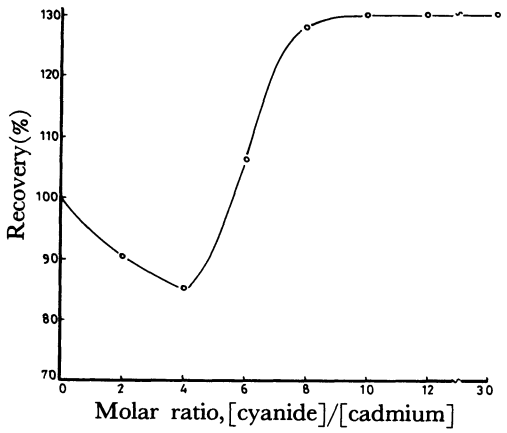

Fig. 1. Titration of 5 ppm Cd (4.44×10^{-5} mol dm^{-3}) with KCN.

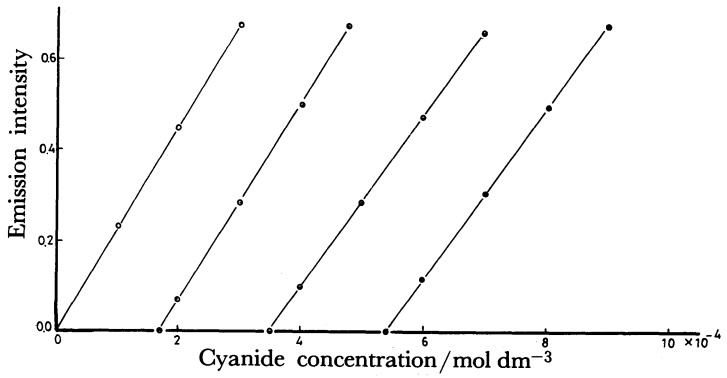

Fig. 2. Changes of cyanide band emission intensity as a function of cyanide concentration, (○) emission signal in absence of Cd, (⊙), (◒), and (●) in presence of 4.44×10^{-5}, 8.89×10^{-5}, and 1.33×10^{-4} mol dm^{-3} of Cd respectively.

radical and the excess oxidizing species in the flame at the plateau.

To assess both the formation of (4:1) molar ratio of CN:Cd and the presence of CN radical in the flame, we measured the emission intensity at 358 nm. Figure 2 curve (o) indicates the initial existence of CN radical in the flame at the starting of the titration process and in absence of the analyte (Cd). On conducting the titration in the presence of 4.44×10^{-5}, 8.89×10^{-5}, and 1.33×10^{-4} M of cadmium, the curves (⊙, ◒, and ●) of Fig. 2 are attained, respectively. These curves show, the emission intensity of CN radical, which disappears at the beginning of the titration and continued till the CN ion concentration reachs the stoichiometric ratio 4:1 for CN:Cd. Thence the emission intensity of CN radical increasing of CN ion.

Elimination of interferences. Different and diverse Cd(II) complexes are investigated. The relationship between the free Cd atom population and the height of measurement above the burner top is measured. The distribution curves in Fig. 3 clearly indicate the differences in the thermal stabilities of the tested complexes. Different times in the flame are required to achieve the same ratio of free atoms from various compounds. The general applicability of the cyanide addition to Cd(II) complexes is indicated by the data in Table 1.

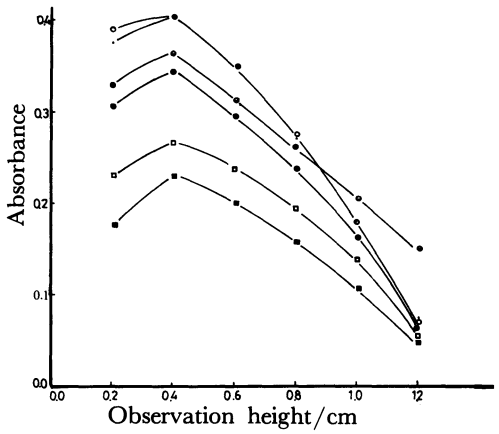

Fig. 3. Distribution of cadmium atoms as a function of observation height for different cadmium(II) complexes (5 ppm of Cd), (○)[$Cd(H_2atpts)_2Br_2]Cl_2$, (·) $CdCl_2$, (◒)[$Cd(Hapsc)_2$], (●)[$Cd(Hbpts)_2]\cdot H_2O$, (□)[$Cd(pn)_3]S_2O_6$, and (■)[$Cd(en)_3](OH)_2$.

Table 1. Determination of Cd(II) complexes without and with masking by 0.05 M KCN (in all cases, the amount of complex taken corresponds to 5 μg cm^{-3} of Cd)

Cd(II) Complex	Cd Recovery/%	
	without masking	with masking
$[Cd(H_2atpts)_2Br_2]Cl_2$	100	100
$[Cd(Hapsc)_2]$	90	100
$[Cd(Hbpts)_2]\cdot H_2O$	86	98
$[Cd(H_2apts)Br_2]Cl$	100	100
$[Cd(Hapts)(ac)]\cdot H_2O$	108	98
$[Cd(Hptsc)_2]$	110	102
$[Cd(pn)_3]S_2O_6$	66	98
$[Cd(en)_3](OH)_2$	58	100

References

1) R. T. T. Rantala and D. H. Loring, *At. Spectrosc.*, **6**, 163 (1980).
2) W. M. Blakemova and S. M. Billedeau, *J. Assoc. Anal. Chem.*, **64**, 1284 (1981).
3) B. Magnusson and S. Westerlund, *Anal. Chim. Acta*, **131**, 63 (1981).
4) K. Fujiwara, H. Haraguchi, S. Toda, and K. Fuwa, *Bunseki Kagaku*, **25**, 255 (1976).
5) M. M. M. El-Defrawy, J. Posta, and M. T. Beck, *Anal. Chim. Acta*, **115**, 155 (1980).
6) M. M. M. El-Defrawy, J. Posta, and M. T. Beck, *Anal. Chim. Acta*, **102**, 185 (1978).
7) M. M. M. El-Defrawy, M. A. Mostafa, and A. M. Abdallah, Egyptian Chemical Society, XII Egyptian Chemical Conference, Cairo, 7—10 April, 1984.
8) A. G. Sharpe, "The Chemistry of Cyano Complexes of Transition Metals," Academic Press, London (1976).
9) R. W. Looyenga and C. O. Huber, *Anal. Chim. Acta*, **55**, 179 (1971).
10) J. Posta and J. Lakatos, *Magy. Kem. Folyoirat*, **86**, 284 (1980).
11) A. A. El-Asmy and M. M. Mostafa, *Polyhedron*, **2**, 591 (1983).
12) A.M. Shallaby, M. M. Mostafa, and A. A. El-Asmy, *Acta Chim. Hung.*, **114**, 9 (1983).
13) G. Marcu, M. Somay, and C. Varhelyi, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **23**, 3 (1978).