

Fluorometric Investigation of Selected Metals of Environmental Importance

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Summary: A new spectrofluorometric method is investigated for the determination of some selected metals of environmental importance. The method is an indirect one and makes use of the fluorescence enhancement of sodium diethyl dithiocarbamate (NaDEDC), a chelating agent. Effect on the fluorescence behaviour of NaDEDC by different metal cations like Cu(II), Mn(II), Ni(II), Fe(II), Fe(III), Co(II) and Cd(II) was studied and it is observed that almost all of these cations enhance the fluorescence of the ligand to various extents. Optimum wavelength and pH were investigated for maximum complexation of these metals with the ligand and limit of detection for the metal cations.

Introduction

Due to the environmental awareness, the determination of toxic heavy metals in different categories of sample is gaining popularity. Several spectrophotometric methods, for the determination of metal cations like Bi(III), Ni(II), Cu(II), Fe(II) and Co(II) have been reported [2-6]. However, none is satisfactory without prior removal of the interfering substances or making use of the masking agents.

Fluorometric determination of metal cations, although relatively new technique, could be applied for the determination of trace amounts of metal cations by utilizing the enhancement behaviour of certain fluorescent or fluorogenic ligands by the metal cations [7,8]. The more recent trend of the fluorescence phenomenon for the determination of cations and anions is the flow injection technique with fluorimetric detection utilizing the fluorescence enhancement or quenching phenomenon (9%). This work was initiated to investigate such a chelating agent which would cause fluorescence enhancement on chelation and to develop a simple and sensitive procedure for the determination of trace amounts of metal cations having environmental significance. Sodium diethyl dithiocarbamate (NaDEDC) was selected as a chelating agent for this purpose.

Results and Discussion

Preliminary investigation of the fluorescence behaviour of the ligand NaDEDC revealed that the aqueous solution of the ligand is fluorescence active. This may be due to the singlet state excitation of the -C=S bond of the ligand. The effect of concentration on the fluorescence behaviour of the ligand was

investigated in the range of 0.2 to 2%. A regular increase in the fluorescence behaviour with increasing concentration of the ligand was observed upto 1%. Beyond this concentration, no further increase was observed in the fluorescence behaviour of the ligand because of the self quenching phenomenon.

Table 1: Parameters for maximum absorbance and fluorescence intensity

Species/ Cation	Optimum wavelength (nm)		Optimum pH	
	Investig- ated	Repor- ted	Investigated	Reported
Blank (NaDEDC)	340	00	4	
Ni(II)	340	325	3	5-11
Cd(II)	340		D.Water	
Mn(II)	350	355,505	7	6-9
Co(II)	360	367,650	7	5-11
Cu(II)	450	436	7	-11
Fe(II)	350		3	
Fe(III)	350	515	D.Water	

Conditions: Filters: 360, 420 for other case; 400, 420 in case of Cu(II); Buffer: Briton Robinson buffer of pH3-pH7 are used.

The optimum condition of suitable filters, pH for maximum fluorescence phenomenon were investigated and are given in Table-1 along with the literature value of pH for maximum complexation. From the results given in Table-1, it can be seen, that the ligand shows more fluorescence phenomenon in the uv region at 340 nm. The fluorescence intensity of the ligand was found to be dependent on pH. As pH decreases from 7 an increase in the fluorescence intensity is observed. This may be due to the protonation of the ligand, which lead to the utilization of nonbonded electrons. Below pH 4,

decrease in the fluorescence intensity of the ligand was observed which could be due to the decomposition of the ligand.

The effect of chelation of selected metals on the fluorescence behaviour was investigated and an enhancement in the fluorescence behaviour of the ligand was observed. This confirms chelate formation with the metals and as a result of the more rigid nature of the chelates, the fluorescence intensity is enhanced. From the table it is clear that the trace amounts of the metals cations could be detected only in the uv region, while using fluorimetry.

The effect of pH on the maximum complexation leading to maximum fluorescence enhancement was investigated. It was observed that in most cases maximum enhancement was observed in neutral media with the exception of Ni(II) and Fe(II). Therefore the use of buffer was avoided to reduce chemical cost and time. For Ni(II) and Fe(II), pH 3 was found to be the optimum pH, while using Briton-Robinson buffer. The decomposition of the ligand in this media may be reduced due to the presence of mixture of weak acids present in the mixture of borate buffer or the quick formation of the complex at the trace concentration level investigated. The limit of detection, quantification and percentage coefficient of variation was also investigated with and without buffer and the results are given in Table-2. From the detection limit it is clear that the method is for more sensitive than uv visible method.

Table-2: Limit of detection and quantification of selected metals at optimum conditions.

Metal Cations	With Buffer			Without Buffer		
	LOD (ppb)	LOQ (ppb)	C.V. %	LOD (ppb)	LOQ (ppb)	C.V. %
Cu(II)	131.6	177.0	4.3	74.0	110.0	5.5
Fe(II)	6.3	7.2	2.0	8.2	9.3	1.5
Fe(III)	34.0	44.4	2.9	34.0	44.4	2.9
Cd(II)	26.5	31.2	1.1	26.5	31.2	1.1
Ni(II)	9.0	11.6	3.7	24.5	34.5	3.5
Mn(II)	5.6	5.9	0.6	5.6	5.9	0.6
Co(II)	3.7	5.0	4.7	3.7	5.0	4.7

Conditions: Final concentration of NaDEDC in all cases = 0.04%
Filters: Excitation 360, Emission 420. For Cu(II) excitation filter 400 is used.
Buffer: Briton Robinson buffer was used. Eqab. Time = 20 minutes.

The interferences effect of selected cations and anions on the determination of Cu(II), Fe(II), Ni(II), Fe(III), Mn(II), Co(II) and Cd(II) were investigated. Among the anions investigated, none was observed to interfere with the fluorimetric determination of all the metals investigated. Due to the non specific nature of the ligand, most of the metal compete for the ligand, leading to additive interferences. Among

the metals investigated only Zn(II) and Cu(II) were found to be tolerated upto 50 and 25 ppb respectively.

Conclusion

Aqueous solution of NaDEDC is fluorescence active and the metal cations investigated enhances the fluorescence of the ligand to various extent. Due to the fluorescence enhancement, the techniques could be used for trace determination of these metals when present individually. When present in mixture prior separation before by solvent extraction method using specific chelating agent, masking or ion-exchange separation is recommended before spectrofluorimetric determination.

Experimental

i. Apparatus and instruments

Spectrofluorometer, Model 930 (Made in China) was used for fluorescence measurements, while digital pH meter (Model CD 860, WPA) with combined glass electrode was used for pH measurement and for the preparation of buffers, wavelength optimization for maximum absorbance was done by spectronic 20 D.

ii. Reagents

All reagents used were of Analytical Grade and were mostly of BDH chemicals and E. Merck. Distilled water was used throughout for the preparation of solutions.

iii. Solutions

- 0.2 % stock solution of NaDEDC was prepared in distilled water in a 100 ml volumetric flask.
- 100 ppm stock solutions of the various metal cations were prepared by dissolving the appropriate amounts of their chloride salts in distilled water.
- Working standard solutions were prepared fresh each day from the stock solutions.

iv. Procedure

In order to have an idea about the fluorescence behaviour of the ligand (NaDEDC), a dilute (0.02%) aqueous solution was subjected to the spectrofluorometer adjusting zero of the instrument with distilled water. As the aqueous solution was colorless, therefore excitation filter 360 and emission

filter 420 were used in the spectrofluorometer. As the scale reading was more than that of distilled water, so wavelength optimization for maximum absorbance of the ligand solution was carried out using spectronic 20D. Effect of concentration on the fluorescence behaviour was then investigated. After these preliminary investigations, the effect of various metal cations on the fluorescence behaviour of the ligand was carried out by subjecting different solutions having 0.01% ligand and 2 ppm of respective metal cation using excitation filter 360 and emission filter 420 nm. As enhancement in the fluorescence was observed, so optimization of wavelength for maximum absorbance and optimization of pH for maximum fluorescence enhancement was conducted. For wavelength optimization of solution containing 0.001% NaDEDC and 2 ppm metal cation in the respective cases were subjected to varied wavelength study. For pH optimization Britton Robinson buffers were prepared and the enhancement in fluorescence at different pH for each metal were noted using solutions having a constant amount of the ligand, that of the respective metal cation and 10 ml of the buffer in 25 ml volume. Separate solutions having the same composition but with no buffer were used in each case for comparison of fluorescence enhancement. Effect of the metal ion concentration was then studied for each metal ion at the optimum wavelength, both in distilled water and at optimum pH, each time adjusting zero of the instrument with

distilled water. Standard deviations for the lowest limit of detection for each metal cation were then obtained using six samples of the same composition in each of the respective metal cations. The interference effect of various metal cations and anions on the fluorescence behaviour of the respective complex was investigated.

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