

Determination of Selected Cations, Utilizing Fluorescence Enhancement Phenomenon of N-Methyl Anthranilic Acid (NMAA)

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Summary: The effect of cations like Na^+ , K^+ , Cd^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Fe^{3+} , Al^{3+} and Cr^{3+} on the fluorescence intensity of NMAA was studied. All the cations investigated with the exception of Na^+ and K^+ caused an enhancement in the fluorescence intensity of NMAA. Based on the fluorescence enhancement effect, these cations were divided into three groups. The fluorescence enhancement phenomenon was utilized for spectrofluorimetric determination of these cations in aqueous samples. Limit of detection for each cation was also investigated and reported in this paper.

Introduction

The process of luminescence was discovered by Nicholas Monardes [1] a Spanish scientist in sixteenth century. The analytical utility of luminescence was first documented by George Stockes [2] an English physicist in 1864.

Nagashima and Suzuki [3] studied the enhancement of fluorescence in Tb^{3+} and Eu^{3+} ions by the phosphoroly chloride-Tin-Chloride solvent.

Several papers have appeared on the complexation behaviour of Anthranilic acid with transition metals [4-7]. Kallistratos *et al.* [8] synthesized a number of aromatic complexes with rare earths and other elements of group III A of the periodical system. Many of these complexes exhibit a strong monochromatic fluorescence when excited with UV-light. The three mechanisms which could be responsible for the enhancement of the fluorescence were investigated.

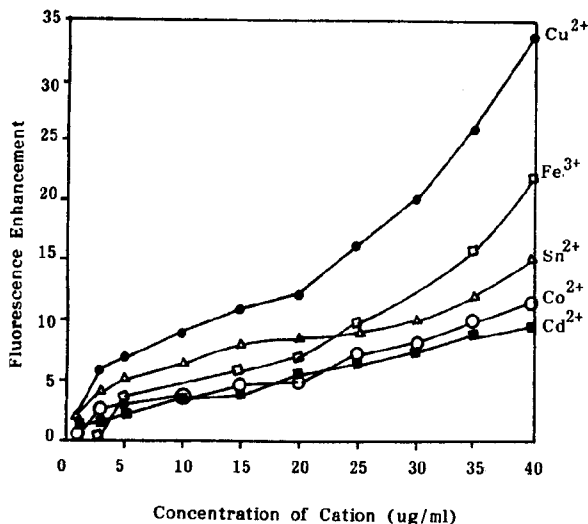
Hiratani [9] reported that Li^+ is the only alkali metal ion which drastically enhances the

fluorescence intensity of 2,2-diethyl-1,3-bis(8-quinolyloxy) propane and 3,3-bis(8-quinolyloxy-methyl) oxetane. In this paper the fluorescence enhancement effect of NMAA after chelation with selected metals have been investigated for its analytical application.

Results and Discussion

The fluorescence enhancement phenomenon of selected cations on NMAA was investigated and the results are shown diagrammatically in Fig. 1-3. As can be seen from figures that the cations studied, could be classified into three categories, based on their effect on the fluorescence behaviour of NMAA. The first category includes Na^+ and K^+ , which have no effect at any concentration on the fluorescence behaviour of NMAA. Fe^{3+} , Zn^{2+} , Cu^{2+} , Cd^{2+} and Ag^+ cause mild enhancement in the fluorescence intensity of NMAA and thus fall in the second category. The third category includes cations like Al^{3+} , Cr^{3+} , Ni^{2+} , Pb^{2+} and Mn^{2+} which cause substantial enhancement in the fluorescence

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Conditions:

Buffer = Phosphate buffer = 0.05N (pH=9)
 Cation solution = 100 µg/ml
 HNAA solution = 10⁻³M
 Emission filter = 420 nm
 Excitation filter = 360 nm.

Fig. 1: Fluorescence enhancement of NMAA by Cu^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} and Fe^{3+} ions. Conditions: Buffer = Phosphate buffer = 0.05 M (pH=9) Cation solution = 100 µg/ml NMAA solution = 10⁻³M Emission filter = 420 nm Excitation filter = 360 nm.

behaviour of NMAA. For spectrofluorimetric behaviour of all of these cations the concentration range of 1-90 µg/ml was investigated.

As can be seen from Figure 1, that a linear enhancement in the fluorescence signal with increasing Cu^{2+} concentration was observed in the concentration range of 1-40 µg/ml. Beyond this concentration (40 µg/ml), there is enhancement, but not linear. For analytical investigation, therefore the range 1-40 µg/ml should be utilized.

Among the cations placed in second category, Cu^{2+} is the most sensitive cation and causes greatest enhancement in the fluorescence behaviour of NMAA. There is a linear enhancement in the fluorescence behaviour with increasing Zn^{2+} concentration upto the range of 40µg/ml as observed for Cu^{2+} . Beyond this concentration there is enhancement, but not proportional to the concentration. For analytical investigation, therefore the range 1-40 µg/ml like for Cu^{2+} should be utilized.

The fluorescence enhancement behaviour of the cations of the second category is given Fig. 1. As is clear from Figure 1, that there is a continuous enhancement in the fluorescence signal of NMAA, with increasing concentration of Cd^{2+} . The concentration range of 1-90 µg/ml may be used for analytical investigation.

Cd^{2+} caused less enhancement than that caused by the rest of the cations except Ag^+ of the second category.

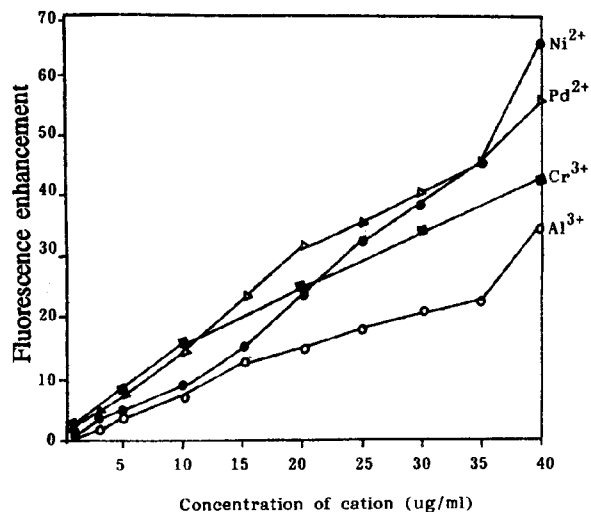
Figure 1 also shows that in the concentration range of 1-25 µg/ml of Fe^{3+} , the enhancement in fluorescence intensity of NMAA may be considered linear and should be utilized for analytical investigation.

Fe^{3+} causes more enhancement than that caused by Ag^+ , Cd^{2+} and Co^{2+} but less enhancement than that caused by Cu^{2+} in the same category. As can be seen from Fig. 1 that there is a regular enhancement in the fluorescence behaviour of NMAA with increasing concentration of Co^{2+} and therefore the concentration range of 1-90 µg/ml like for Cd^{2+} may be used for analytical investigation of Co^{2+} . In the second category Ag^+ is the least sensitive of the cations and therefore causes lowest enhancement in the fluorescence intensity of NMAA with increase in the concentration. The concentration range of 1-90 µg/ml like Co^{2+} and Cd^{2+} may be used for analytical investigation.

The fluorescence enhancement behaviour of the third category cations is shown in Fig. 2. As is clear from this figure that the fluorescence intensity of NMAA increases proportionally with the increase in concentration of Ni^{2+} . The concentration range of 1-90 µg/ml may therefore be utilized for analytical investigation.

It can also be seen from Fig. 2, that the fluorescence enhancement of NMAA caused by Pb^{2+} is quite linear in the concentration range of 1-90 µg/ml. This concentration range could be utilized for the analytical investigation. Pb^{2+} causes more enhancement than that of Mn^{2+} and Al^{3+} of the third category in the overall concentration range investigated.

As is clear from Figure 2 that the fluorescence behaviour of NMAA increases



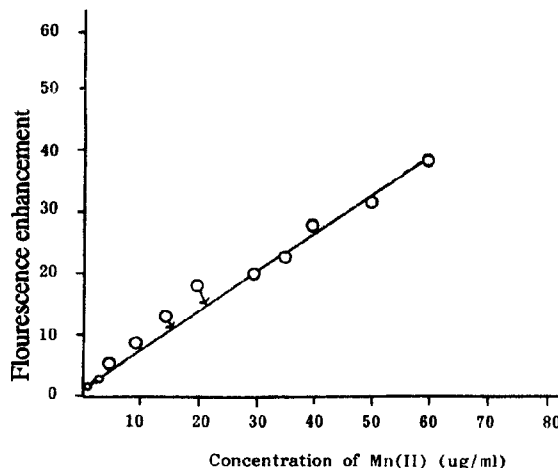
Conditions:

Buffer = Phosphate buffer = 0.05M (pH=9)
 Cation solution = 100 ug/ml
 NMAA solution = 10^{-3} M
 Excitation filter = 360 nm
 Emission filter = 420 nm

Fig. 2: Fluorescence enhancement of NMAA by Al^{3+} , Cr^{3+} and Ni^{2+} and Pb^{2+} ions. Conditions: Buffer = Phosphate buffer = 0.05M (pH=9); Cation solution = 100 $\mu\text{g/ml}$; NMAA solution = 10^{-3} M; Excitation filter = 360 nm; Emission filter = 420 nm.

proportionally with the increase in concentration of Cr^{3+} within the range of 1-90 $\mu\text{g/ml}$. This concentration range like that of Pb^{2+} may therefore be utilized for analytical investigation. The fluorescence enhancement caused by Cr^{3+} is greater than that by Mn^{2+} and Al^{3+} in the third category. The curve obtained for Al^{3+} in the concentration range of 1-40 $\mu\text{g/ml}$ is linear. Beyond this concentration upto 70 $\mu\text{g/ml}$, the increase in enhancement is comparatively less. The third linear portion of the curve shows that in the concentration range of 70-90 $\mu\text{g/ml}$, there is a great increase in the fluorescence enhancement.

The effect of Mn^{2+} on the fluorescence behaviour of NMAA is shown in Figure 3. As can be seen from this figure that a linear enhancement is observed upto 60 $\mu\text{g/ml}$ of the added metal. Beyond this concentration the enhancement is not proportional to the concentration. The concentration range of 1-60 $\mu\text{g/ml}$ may be used for



Conditions:

Buffer = Phosphate buffer 0.05N (pH=9)
 NMAA solution = 10^{-3} M
 Mn(II) Solution = 100 ug/ml
 Excitation Filter = 365 nm
 Emission filter = 425 nm

Fig. 3: Fluorescence enhancement of NMAA by Mn^{2+} . Conditions: Buffer = Phosphate buffer 0.05M (pH=9); NMAA solution = 10^{-3} M; Mn^{2+} solution = 100 $\mu\text{g/ml}$; Excitation Filter = 360 nm; Emission filter = 420 nm.

analytical investigation. Mn^{2+} causes less enhancement than Ni^{2+} , Pb^{2+} and Cr^{3+} in the overall concentration range investigated. Thus Mn^{2+} is the least sensitive cation (except Al^{3+} in the concentration range of 1-25 $\mu\text{g/ml}$) of all the cations in the third category.

Experimental

Apparatus and instruments

Spectrofluorimeter, Model 930 (Made in China) was used for fluorescence measurement, while digital pH meter (Model CD 660, WPA) with combined glass electrode was used for pH measurement and for preparation of buffers.

Materials

The nitrate salts of the cations were chosen for this investigation. The cations studied are Na^+ , K^+ , Al^{3+} , Pb^{2+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , and Cd^{2+} .

The salts of above mentioned cations were purchased commercially and were used without further purification.

Preparation of solutions

i) Preparation of buffer

0.05M phosphate buffer solution was prepared by dissolving 7.1g of disodium-hydrogen phosphate (Na_2HPO_4) in distilled water and diluted to one litre.

ii) Preparation of NMAA solutions

10^{-2}M solution of NMAA was prepared by dissolving 0.0755g of NMAA in methanol and diluted to 50ml with methanol. One ml of 10^{-2}M NMAA solution was then diluted to 10ml with phosphate buffer (0.05M, pH-9) to obtain 10^{-3}M solution of NMAA.

iii) Preparation of cation solutions

1000 $\mu\text{g/ml}$ stock solution of each cation was prepared by dissolving an appropriate amount of the nitrate salt of each cation in distilled water and diluted to 100 ml with distilled water.

100 $\mu\text{g/ml}$ solution of each cation was then prepared by dilution.

Procedure

A number of clean dried, 10 ml volumetric flasks were taken. For samples preparation, added to each flask, 1 ml of NMAA solution (10^{-3}M) varied amounts (0.1-9.0 ml) of metal ion solution of 100 $\mu\text{g/ml}$. Dilution was made upto 10 ml with phosphate buffer (pH-9). All the resulting solutions were 10^{-4}M in NMAA and had metal ion concentration in the range of 1-90 $\mu\text{g/ml}$.

Similarly a separate blank was prepared for each sample of metal ion using the same procedure as for sample preparation, except, the metal ion solution in each case was replaced by distilled water.

For the measurement of fluorescence phenomenon of each solution, zero of the instruments was adjusted with the blank and the fluorescence readings of the solution were noted at excitation filter of 360 nm and emission filter of 420 nm. Excitation filter of 360 nm is used because of the maximum absorptivity of the NMAA at 360 nm. Since emission radiations are of larger wavelength therefore, emission filter of 420 nm was used.

Conclusion

Fluorescence enhancement phenomenon of N-methyl anthranilic acid by selected cations could be applied for analysis of some of these metals, especially if they are present individually. These metals could be determined down to concentration of 1 ppm using this technique.

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