Use of Reaction between Melamine and Bioxalate Ions for Monitoring Melamine Content of Petrochemical Wastewater

M. A. Farajzadeh* and N. Abdi Rahmani
Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran

This study describes a turbidimetric technique for determination of melamine in wastewater of petrochemical companies. A single reagent (bioxalate ions) is used and an insoluble ion-pair (melamine:bioxalate 1:3) produced. The reproducibility of the method is excellent and relative standard deviation for six repeated experiments is 1.5%. An interferences study was carried out, and it was found that the common species occurring in wastewater has no interference effect on the determination of melamine. The interference effect of Al^{3+} was eliminated by its precipitation as $Al(OH)_3$ at pH 7. Finally this method was successfully used in the determination of melamine content of Urmia Petrochemical Company, a local melamine producer.

Keywords: Melamine; Turbidimetry; Wastewater; Bioxalate.

INTRODUCTION

The outstanding characteristic of melamine, usally a white crystalline material, is its insolubility in most organic solvents. This property is also evident in melamine resins after they are used. On the other hand, melamine is appreciably soluble in water and its solubility increases with temperature. Extensive investigations have been performed with melamine in experimental animals. These suggest that the compound may have a low order of biological activity. The acute oral LD for mice was found to be 4/55 g/kg, approximately the same for rats.[1] Although melamine was prepared for the first time in 1834 by Liebig, almost a century passed before its properties and reactivity were thoroughly investigated. In the late 1930 s a commercial process was developed. Since then, uses for melamine have been developed rapidly in a variety of fields, including plastics, surface coating, bonding agents, paper and textile finishes, tanning agents, pharmaceuticals, petroleum, and rubber chemicals.[2,3]

Only a few analytical techniques have been proposed in the determination of melamine and its degradation products. High performance cation-exchange chromatography using phosphate buffer as the eluent was proposed for determination of melamine and its degradation products, melame, meleme, ammeline, and ammelide.[4-6] In another HPLC method isocyanuric acid, ammelide, ammeline, and melamine in crude isocyanuric acid were determined using potassium chloride – hydrochloric acid – acetonitril solution as mobile phase and a UV detector at 215 nm.[7] Raman spectroscopy has also been used in determination of free melamine content in melamine-formaldehyde (MF) resins. In contrast to the conventional liquid chromatography method, the Raman spectroscopic method can be directly applied to cured resins without sample preparation. In addition, Raman imaging was used to determine the homogeneity of the free melamine content in cured MF resins.[8]

In previous work,[9] we proposed a new turbidimetric method based on the reaction of Hg^{2+} with melamine to evaluate melamine content of petrochemical wastewater. Here, another turbidimetric technique is presented in which three moles of bioxalate ions react with one mole of melamine to produce an insoluble ion-pair. This reaction is performed at pH 3-4. This method is less sensitive than the previous method, but uses bioxalate ions instead of mercuric ions, a highly polluting cation.

$$C_3N_6H_6 + 3HC_2O_4^- + 3H^+ \rightarrow (C_3N_6H_9)^{3+}, 3HC_2O_4^-\downarrow$$

In comparison of the present method with other methods such as chromatographic and spectroscopic methods, it is fast and simple. A gas chromatography method[10] requires a preliminary derivatization procedure, which is considered a disadvantage because of the longer time required for sample preparation and the concomitant source of analytical errors. Two HPLC methods were also found to be unsuitable for this particular application. The first one[11] (using a Lichrosorb RP-18 column, potassium phosphate buffer-methanol gradient, and a temperature of 2 °C) produced broad, tailing peaks

* Corresponding author. E-mail: farajzade@yahoo.com

that were not completely separated. Although the second one[12] (using a Zorbax NH_2 column and acetonitrile-phosphate buffer solution) resulted in improved separations, the chromatograms were difficult to produce. Maybe this was due to batch differences in Zorbax NH_2. Similar problems were also experienced with a method developed on a Diol column, which failed after replacing the column with one from a different batch. This implies that the above methods are very sensitive to small changes in stationary phase and are therefore unsuitable for routine use. Other methods such as Raman spectrometry need a specific and expensive instrument, which makes its application in routine analysis not commercially feasible.

EXPERIMENTAL

Apparatus

An LKB spectrophotometer model 4045 equipped with an automated cell driver was used in turbidance measurements. Determinations were performed using 1-cm plastic cells.

Chemicals

$C_2H_2O_4$, NaOH, NaCl, Na_2SO_4, $NaHCO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, K_2HPO_4, NH_3, urea, ethanol and other chemicals were supplied from E. Merck (Darmstadt, Germany) and used as received. All chemicals were analytical grade. Melamine was supplied from a local melamine producer (Urmia Petrochemical Company) with a purity > 99%.

Solutions

A melamine solution 0.04 M (5000 mg/L) and oxalic acid 0.1 M adjusted to pH 3-4 with NaOH 5 M in distilled water was prepared.

Procedure

In each series of 25-mL volumetric flasks, an appropriate volume of melamine solution was placed. Then 3 mL oxalic acid (pH = 3-4) was added into the flasks. After dilution by distilled water, it was agitated manually, turbidance recorded at 400 nm against the blank solution using 1-cm plastic cells and was used in the calibration curve plotting and other calculations.

Procedure for real sample

pH of real sample (Urmia Petrochemical Company wastewater) was adjusted at 7 by adding 1 M HNO_3 and the produced precipitate (see the section of determination of the melamine content of the real samples, in this study) filtered. The filtered solution was used after appropriate dilution in the determination of melamine.

RESULTS AND DISCUSSION

Selection of the optimum pH

For this purpose, pH of 0.1 M oxalic acid solution was adjusted between 2-12 by adding 1 M HNO_3 or NaOH solutions and tested as a turbidimetric reagent. From the obtained results in Fig. 1, the optimum pH range can be selected at 2-4. In pH < 2 and pH > 4 the formed precipitate was dissolved and hence the turbidance decreased. It is mentioned that at pHs 2-4 the preferable species of turbidimetric reagent is bioxalate ($HC_2O_4^-$) ($H_2C_2O_4$, pK_{a1} = 1.25 and pK_{a2} = 4.27). This shows that in the reaction performed in this study $HC_2O_4^-$ ions react with melamine to produce precipitate. In Fig. 1 the variations of turbidance and mole fraction of bioxalate as a function of pH have the same pattern, in which participation of bioxalate ions in producing solid materials in melamine solution is verified.

Influence of bioxalate concentration

For this purpose, bioxalate solutions with different concentrations were added to the solutions having a constant concentration of melamine (0.004 M). The turbidance was plotted vs. bioxalate concentration at 400 nm. As shown in Fig. 2 the turbidance increases with concentration of bi-

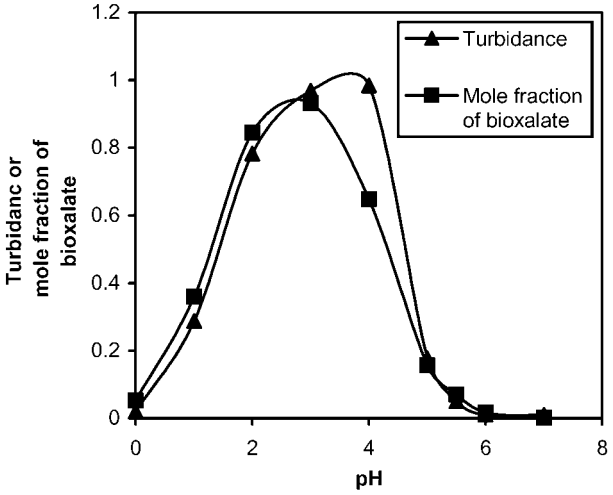

Fig. 1. Influence of pH on the mole fraction of bioxalate and turbidance produced after reaction between bioxalate ions and melamine.

oxalate ions and reaches the constant value at 0.012 M. It is mentioned that the reaction between bioxalate ions and melamine is a well known reaction, which was used in the gravimetric determination of melamine. The product of reaction is a less soluble ion-pair in water. From the results obtained in Fig. 2 we conclude that three bioxalate ions react with one molecule of melamine (0.012:0.004 or 3:1). This is expected because melamine has three amino groups of which each of them interacts with one bioxalate ion.

Influence of solution volume

For this study, different volumes of melamine solution (2.5, 5 and 10 mL) and appropriate volumes of bioxalate solution (3, 6 and 12 mL) were added into different volumetric flasks (25, 50 and 100 mL) and diluted with distilled water. In these conditions the concentration of melamine and bioxalate in all flasks were equal. As shown in Fig. 3 the solution volume has no considerable effect on the turbidance.

Study of stirring speed

In this study, effect of stirring speed was considered at minimum, medium and maximum speeds of the magnetic stirrer. As shown in Fig. 4 increasing stirring speed has no major effect on the turbidance amounts and almost the same results were obtained with and without stirring, with a little preference at 500 rpm stirring speed.

Study of stirring time

For optimizing the stirring time, the turbidance was recorded at 0.5 min intervals over the range 0-10 min. The results show that after 2 min turbidance decreased (Fig. 5). This decrease in turbidance can be explained by producing aggregates from smaller particles size of precipitate, which scatter the light to a less extent, compared to smaller ones.

Turbidance reading in different wavelengths

In the present study, the turbidance of melamine after adding reagent was recorded at different wavelengths at the intervals of 50 nm over the range of 400-700 nm and is shown in Fig. 6. A slight decrease in turbidance is observed by increasing wavelength. This is expected from the literature, which states turbidance must be decreased at longer wavelengths. However 400 nm was selected as an optimum wavelength in this study, in order to achieve a relatively higher sensitivity and to eliminate absorption of radiation in the ultra violet region by other compounds, which probably are present in the real samples.

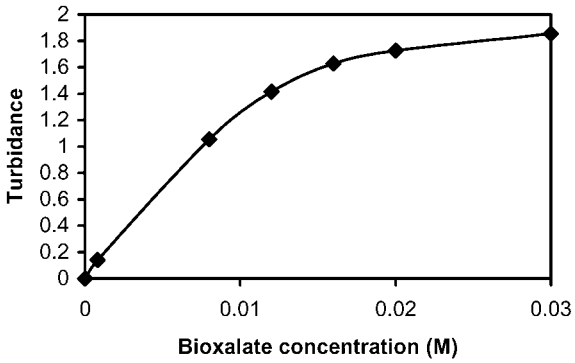

Fig. 2. Studying stochiometry of reaction between bioxalate ions and melamine. Concentration of melamine is 0.004 M in all solutions.

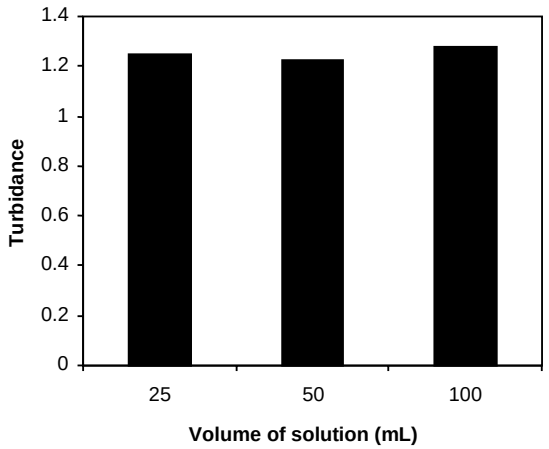

Fig. 3. Effect of solution volume on the turbidance produced by adding bioxalate ions into melamine solution.

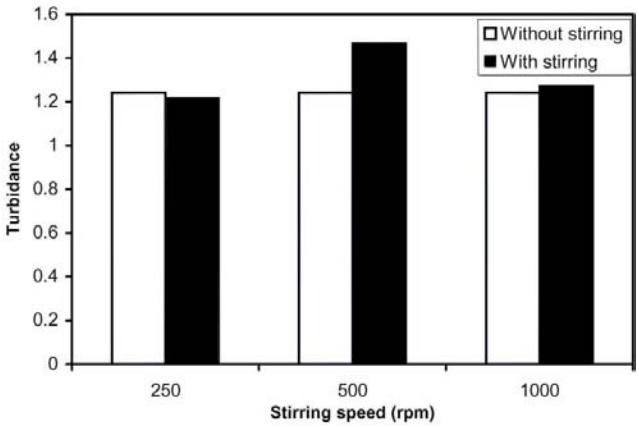

Fig. 4. Effect of stirring speed on the turbidance resulted by adding bioxalate ions to the melamine solution.

Interferences study

Here, we studied different compounds, which previously in determination of melamine by Hg^{2+} were mentioned as probable interferences.[9] The following results were obtained:

We did not observe any considerable effect for species such as Cl^-, HCO_3^-, Mg^{2+}, PO_4^{3-}, urea and ammonia up to concentrations 1000, 600, 16000, 400, 30000 and 170 mg/L, respectively. On the other hand, the effect of ionic strength on the turbidance was evaluated in the presence of NaCl at different concentrations and it was ineffective on the measurements.

The presence of SO_4^{2-} ions in the concentrations higher than 400 mg/L decreased turbidance amounts. Therefore, we determined SO_4^{2-} concentration in wastewater by the standard method (turbidimetric method by Ba^{2+}) and obtained 150 mg/L. Therefore the SO_4^{2-} level of the studied sample was not critical in our work. Also melamine content of petrochemical wastewater was very high and the further dilution was performed for its fitting in the linear region of calibration graph; therefore, the effect of sulfate ions become negligible.

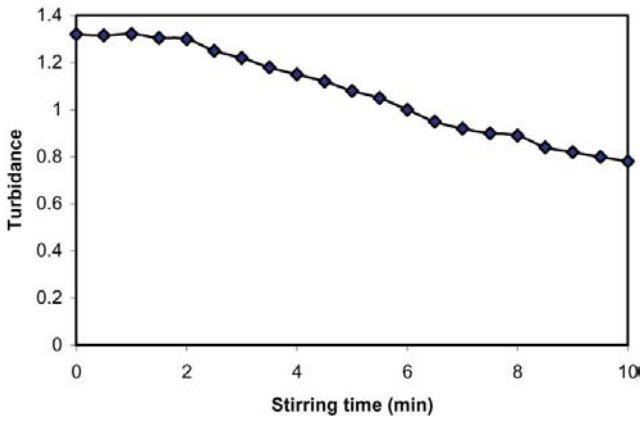

Fig. 5. Effect of stirring time on the turbidance of melamine solution after adding bioxalate ions.

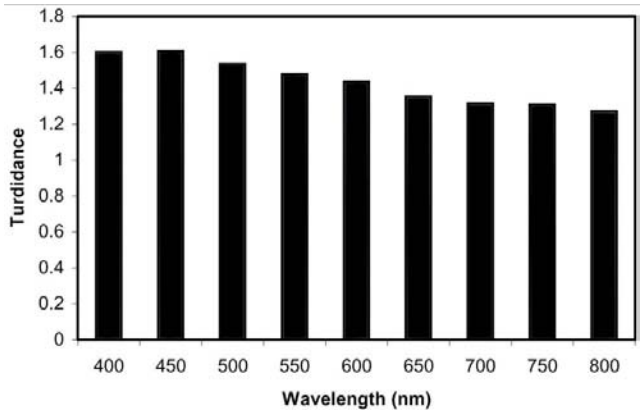

Fig. 6. Turbidance vs wavelength.

Ca^{2+} increased turbidance amounts in the concentrations higher than 40 mg/L. To evaluate the effect of Ca^{2+} and other species occurring in the natural waters on the efficiency of the presented method, two series of solutions were prepared. In the first series the constant volumes of bioxalate solution (3 mL) were added to melamine solutions with different concentrations (250, 500 and 750 mg/L) and diluted with distilled water. In the second series similar solutions were prepared except that tap water was used instead of distilled water. Turbidances of the two sets of solutions were read at 400 nm and are shown in Table 1. As seen from the obtained results matrix effect is negligible in tap water.

Quantitative characteristics of the method

Under the described experimental conditions, linear correlation is obtained in the range 100-1200 mg/L, with a calibration curve equation $T = 0.0021C + 0.0651$ ($r^2 = 0.9946$). T and C are turbidance and concentration of melamine (mg/L), respectively. The limit of detection (LOD) is 30 mg/L. Six repeated determinations were performed on the solution having 500 mg/L melamine in order to evaluate the repeatability of the method. The relative standard deviation (RSD%) was obtained at 1.5%, indicating that the proposed method is reproducible.

Determination of the melamine content in real sample

When the diluted or undiluted wastewater of a petrochemical company was used by this method no precipitate was produced. When we tested the pH of the sample, it was 8.5. Nitric acid solution (1 M) was used for pH adjusting at 4. But at pH 7 a bulk precipitate was formed which redissolved at lower pH by adding further HNO_3 solution. This shows that the previous precipitate is an amphoteric compound that is produced in neutral pHs. We guessed that this precipitate is $Al(OH)_3$. This assumption was confirmed when bioxalate ions were added to the sample and precipitate was not formed

Table 1. Matrix effect (tap water) study

Melamine Concentration (mg/L)	Turbidance of standard solutions prepared in	
	Distilled water	Tap water
250	0.594	0.750
500	1.320	1.351
750	1.539	1.654

Table 2. Added-found method to evaluate matrix effect in wastewater

Melamine concentration (g/L)		Recovery (%)
Added	Found	
0.00	2.15	-
1.00	3.18	103
2.00	4.04	94.5
3.00	5.16	100
4.00	6.08	98.3

at optimum experimental conditions. Bioxalate ions were consumed in complexation reaction with Al^{3+} and thereby the formation of ion-pair between bioxalate ions and melamine was disturbed. However, in order to eliminate Al^{3+} interference, the pH of the real sample was adjusted at 7 by adding 1 M HNO_3 and the obtained precipitate was removed by filtration. The filtered solution was used in the determination of melamine. The obtained result was 2.09 g/L, which is in agreement with the result (2.20 g/L) obtained by the previously presented method.[9]

In order to evaluate the matrix effect in analysis of melamine in real samples, the added-found method was used. To wastewater of a petrochemical company, melamine was added in three levels, and the obtained concentrations were compared with the added concentrations (Table 2). The obtained recoveries were in the range of 94-103%, revealing that the matrix effect in wastewater is negligible.

CONCLUSION

In this study the well-known reaction between bioxalate ions and melamine used in the gravimetric analysis of melamine was experienced in the determination of melamine in petrochemical wastewater by turbidimetric method. The proposed method is more sensitive than the gravimetric method and less sensitive than previously presented method by authors.[9] The reproducibly of the method is good and RSD% was obtained at 1.5% (n = 6). Simplicity, cheapness of reagent, and short time analysis are the major advantages of the proposed turbidimetric method compared with other instrumental methods such as HPLC, GC, and Raman spectroscopy. It covers well the range of melamine in the wastewater of a melamine production unit.

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