Spectrophotometric Determination of Nitrous Acid in the Aqueous Streams of Fast Reactor Fuel Reprocessing Using Azo Dye Method

M. Suba, P. Velavendan, N. K. Pandey*, C. Mallika, U. Kamachi Mudali

Reprocessing Research Development Division, Reprocessing Group, Kalpakkam, Kanchipuram, Tamil Nadu, India.

ABSTRACT

A simple spectrophotometric method is optimized for the determination of nitrous acid in nitric acid media. This method is based on the diazotization reaction of nitrous acid with sulfanilamide and N-(1-naphthyl)-ethylene diamine dihydrochloride forming a bright pink colored azo compound. This complex is having an absorbance at 540 nm with molar extinction coefficient of 26,530 L mol^{-1} cm^{-1} and 16,990 L mol^{-1} cm^{-1} for water and nitric acid dilution, respectively; the relative standard deviation was found to be <2% and the detection limit was 1 ppm. The interference studies of nitrous acid determination with uranium and zirconium were carried out, and there is no interference in nitrous acid determination in the range of concentration studied; hence, the optimized method can be employed for the determination of nitrous acid in plant samples.

Key words: Plutonium-uranium recovery by extraction, Nitrous acid, Chromogenic agent, Spectrophotometry.

1. INTRODUCTION

Reprocessing of spent fuel is carried out through plutonium-uranium recovery by extraction (PUREX) process [1-3]. This process consists of fuel receipt, fuel chopping or fuel decladding, dissolution, feed clarification, feed conditioning, solvent extraction, partitioning, scrubbing, stripping, and reconversion steps. In PUREX process, spent fuel assembly is subjected to subassembly handling hardware removal as well as extracting fuel pins from the subassembly before taking for chopping. The fuel pins are chopped by mechanical chopping in a chopper. The fuel element along with fission products is dissolved in nitric acid. Nitric acid concentration employed depends on the nature of fuel element. It is reported that the kinetics of dissolution of uranium oxide (UO_2) is influenced by the concentration of nitrous acid [4]. Plutonium can exist in different oxidation states in dissolver solution due to disproportion reaction, and it is also reported that the distribution ratio for the extraction of Pu^{4+} is higher as compared to Pu^{3+} and $[PuO_2^{2+}]$ [5-8]. Nitrous acid is employed as the redox intermediate for conversion of Pu^{3+} and $[PuO_2]^{2+}$ to Pu^{4+} [3,9]. It is well-established fact that Np also present along with Pu, U in the process solution [3,8]. Np also exists with multiple oxidation states [3,9]. The feed for solvent extraction cycle containing nitrous acid will increase the concentration of $[NpO_2^+]$ [10], which is

not extractable by tributyl phosphate [8]. Therefore, determination of nitrous acid in the reprocessing streams is important.

Determination of HNO_2 in the makeup area samples analyzed by volumetric method [11]. In this method, $KMnO_4$ is used as the titrant and is applicable for the samples having a higher concentration of HNO_2. The samples from the conditioner step have to be analyzed in the hot cell due to higher β, γ activity. In hot cell, the detection of endpoint by color change of $KMnO_4$ is difficult. Hence, a method of HNO_2 determination in the lower dynamic range is essential. Samples obtained from the plant streams can be diluted and can be analyzed by alternate methods such as ion chromatography and spectrophotometric methods. Chromatographic application may be difficult for the radioactive samples this optimized method is suitable for low range nitrous samples which are radioactive. Direct spectrophotometric method for the simultaneous determination nitric acid and nitrite in the presence of uranium has been reported [12]. Characteristic absorption spectrum in the range of 350-380 nm due to nitrous acid is observed. The molar extinction coefficient for nitrous acid is less and not suitable for radioactive samples; therefore, this method not suitable for nitrite determination.

*Corresponding Author:
E-mail: nkpandey@igcar.gov.in

It is well established that a diazonium salt is formed by the reaction of $[NO_2]^-$ with an aryl amine in the HCl medium; subsequently, this diazonium salt reacted with the activated aryl compound to form azo dye [13,14]. The azo dyes are having intense color indicating higher molar extinction coefficient (three to four orders of magnitude as compared direct spectrum). Therefore, detailed studies for application of the spectrophotometric method for determination of HNO_2 in HNO_3 along with interfering elements such as uranium and zirconium were carried out, and the results are discussed in this paper.

2. EXPERIMENTAL

2.1. Apparatus
Thermo scientific model double beam spectrophotometer is employed for measuring samples absorbance.

2.2. Reagents
Stock solutions of various concentration nitrous acids were prepared by dissolving A.R grade sodium nitrite substance.

2.3. Sulfanilamide Solution
About 5 g of sulfanilamide was dissolved in a mixer of 50 ml concentrated HCl (1.18 g/cm^3) and 300 ml water and diluted to 500 ml.

2.4. N-(1-naphthyl)-ethylene Diamine Dihydrochloride Solution
Dissolved 0.5 g N-(1-naphthyl)-ethylene diamine dihydrochloride in 500 ml water and stored in a dark bottle.

Nitric acid, sulfanilamide, and N-(1-naphthyl)-ethylene diamine dihydrochloride are of A.R grade. Mille-Q water of conductivity 0.5 µS cm^{-1} used for preparing the solutions.

2.5. Procedure
An aliquot containing different concentrations of nitrous acid is taken in a 10 ml standard flask followed by the addition of 0.1 ml sulfanilamide solution and allowed to react for 8 min, subsequently added 0.1 ml of N-(1-naphtyl)-ethylene diamine dihydrochloride solution and mixed, color is developed, the solution is made up to 10 ml with 1 N HNO_3. Absorbance was measured against reagent blank prepared under identical conditions at 540 nm.

3. RESULTS AND DISCUSSION
Standard nitrous acid solution is reacted with sulfanilamide to form diazonium salt, and this reaction is diazotization and is well-known reaction in organic synthesis. Diazonium salt is reacted with N-(1-naphthyl)-ethylene diamine dihydrochloride to form corresponding azo dye. The absorption spectrum of the azo dye as a function of nitrous acid with and without uranium and zirconium are given in Figures 1-3. The data given in these Figures 1-3 indicate that the complex is having a broad absorption band with maximum absorbance at 540 nm wavelength, and this is taken for measuring the absorbance of the samples. The formation of intense deep colored complex in visible region as compared to its precursors is explained below. The azo dyes absorb in the longer wavelengths of light. Specifically, they absorb in the visible region than the
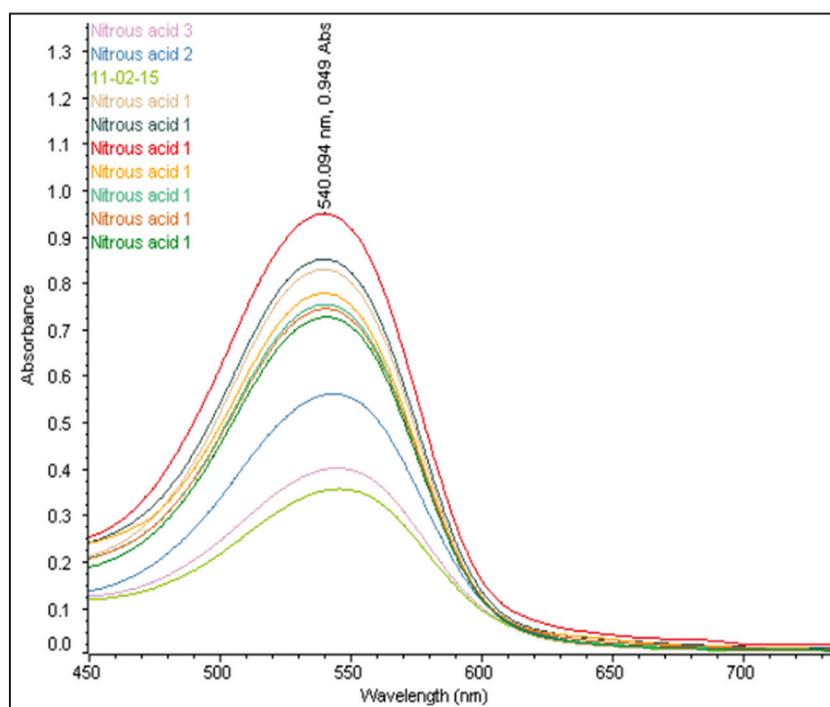

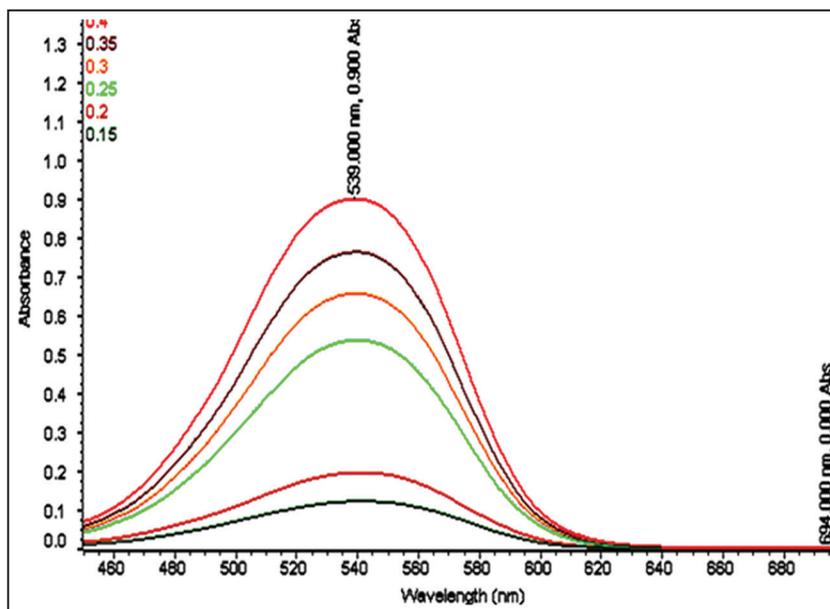**Figure 1:** Typical absorbance spectrum of nitrous acid at 540 nm.

Figure 2: Absorption spectra of azo dye formed in the presence of uranium.
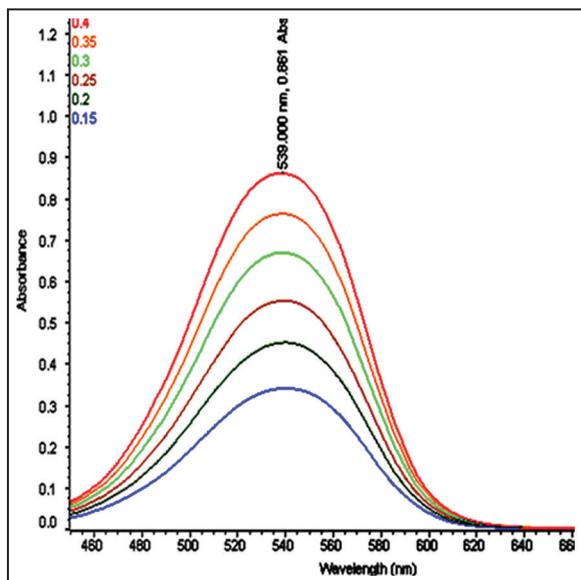

Figure 3: Absorption spectrum of azo dye formed in the presence of zirconium.

reactants due to increased conjugation also with high absorption probabilities.

Data in Figure 1 also indicate that absorbance at absorption maximum increases with increase in the nitrous acid concentration. This increase is attributed to increased absorbing species in the medium increased the probability of absorption so that increased absorbance is obtained. The variation of absorbance trend as function of nitrous acid in the presence of uranium (0.03 mg mL^{-1}) and zirconium (0.01 mg mL^{-1}) in a fixed concentration can also be explained in a similar way. In these studies, different concentrations of nitrous acid starting from 0.15 to

0.4 mm in 10 ml standard flask were taken, and the experiment was carried out in a similar way. The absorbance spectrums for interference studies at 540 nm were given in the Figures 2 and 3.

3.1. Calibration of HNO$_2$ in Water Medium
The absorbance data as a function of nitrous acid are used for obtaining the calibration plot.

The absorbance values at absorption maximum as a function of nitrous acid diluting with water and results are given in Figure 4.

The data given in this Figure 4 indicate that the absorbance varies linearly with nitrous acid concentration. The R^2 was found to be 0.998. This indicating the applicability of linear relation for measuring the concentration of nitrous acid in the unknown samples and is given by the following equation.

$[HNO_2]$ = ([Absorbance − 0.016]/[26.53])*Dilution factor

3.2. Calibration of HNO$_2$ in Nitric Acid Medium
It is known that the concentration of nitrous acid present in the nitric acid generates nitrogen peroxide whose solubility in aqueous is limited [15]; hence, the effect of nitric acid concentration on determination of the nitrous acid medium is studied, the results of this indicated that beyond 1.4 M nitric acid concentration the nitrous acid present in nitric acid decreases drastically. Hence, acidity range of 0.8-1.4 M nitric acid has to be maintained. Therefore, the solution is made up with 1 M nitric acid to maintain acidity in this range.

The absorbance variation as a function of nitrous acid by diluting with 1 M nitric acid is studied, and the results are given in Figure 5. The data obtained are subjected to linear regression analyses. The R^2 value is found to be 0.963 and concentration of nitrous acid in the unknown sample can be determined by the following equation.
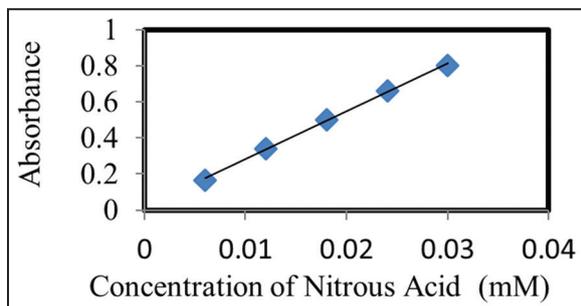

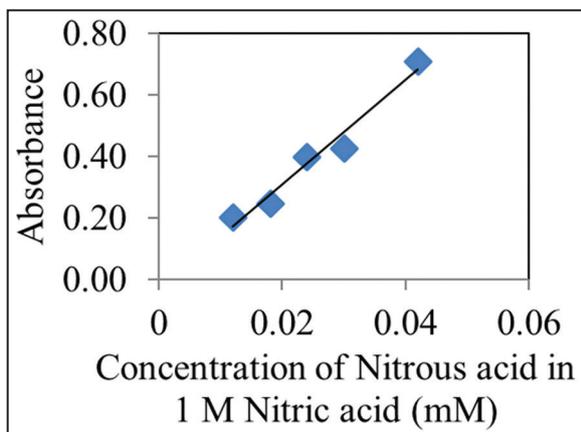**Figure 4:** Calibration graph for nitrous acid in water at 540 nm.

Figure 5: Calibration graph for nitrous acid in nitric acid at 540 nm.

$$[HNO_2] = ([Absorbance - 0.031]/[16.99])*Dilution\ factor$$

3.3. Effect of Uranium and Zirconium Concentration in the Nitrous Acid Determination

The samples from the reprocessing plant consist of uranium and plutonium as well as zirconium apart from other fission products. A preliminary study of the effect of uranium and zirconium on the determination of nitrous acid in nitric acid is studied.

3.4. Effect of Uranium Concentration in the Nitrous Acid Determination

The presence of uranium interference during the determination of nitrous acid in HNO_3 was studied. Different concentrations of nitrous acids were taken to this solution, fixed amount of (0.031 mg mL^{-1}) uranium was added, and the nitrous acid estimation procedure was followed, the absorbance values were taken at 540 nm wavelength, and calibration graph was drawn; the R^2 value was found to be 0.999 and shown in Figure 6.

3.5. Effect of Zirconium Concentration in the Determination of Nitrous Acid

The determination of nitrous acid in HNO_3 medium at fixed (0.010 mg mL^{-1}) concentration of zirconium ion is carried out; the absorbance of different concentrations of nitrous acid containing zirconium in HNO_3 is obtained at 540 nm and plotted the calibration graph and shown in Figure 7; the linear regression coefficient R^2 value was found to be 1.0 showed that there was a linearity between the different nitrous acid concentrations.

4. CONCLUSION

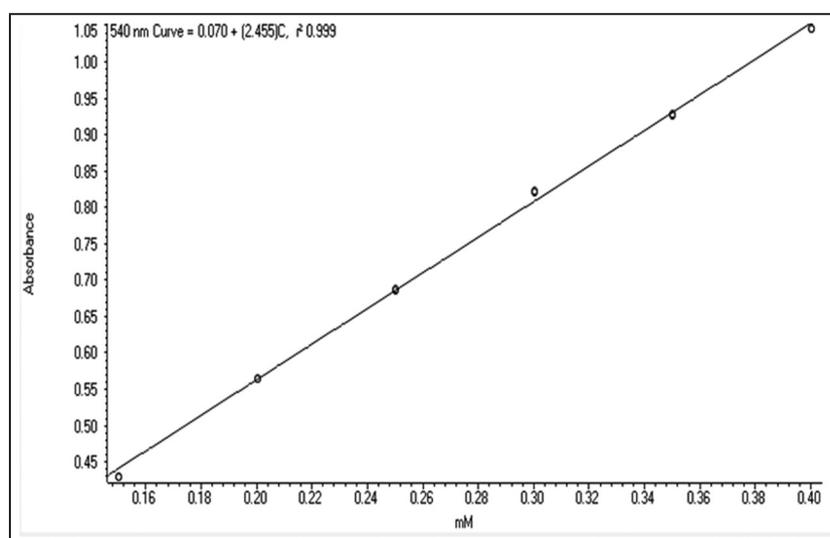The optimized method for the determination of nitrous acid in the nitric acid medium is simple,

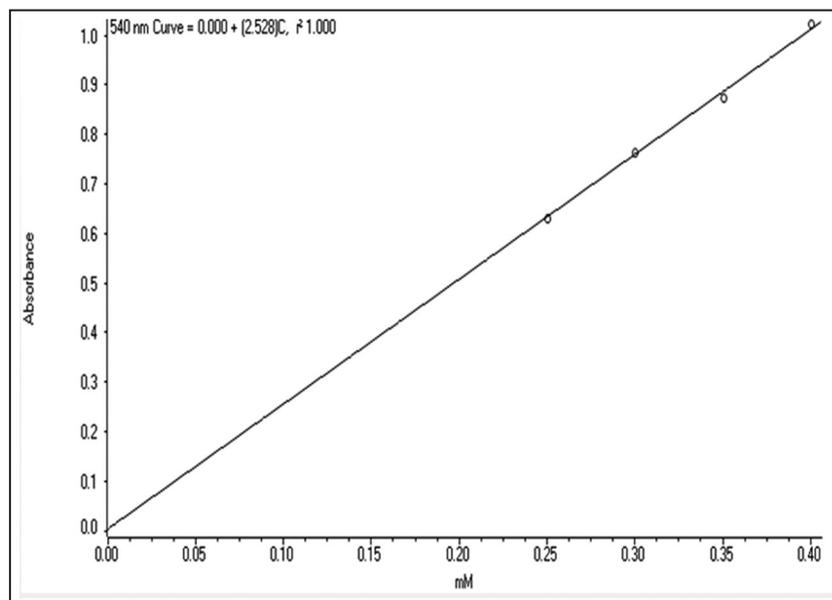**Figure 6:** Calibration of nitrous acid in the presence of uranium.

Figure 7: Calibration of nitrous acid in the presence of zirconium.

accurate, and highly precise, sensitive method for the nitrous acid samples from spent fuel reprocessing plant. In this method, the interference from uranium and zirconium was studied and found that there is no interference of these ions during the determination of nitrous acid in nitric acid, and suitable for the samples with low concentrations of nitrous acid in HNO_3.

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*Bibliographical Sketch

N.K. Pandey (BS, Chemical Engineering, BIT Sindri, Dhanbad, India, 1984) is a senior research engineer with the Department of Atomic Energy at Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, India. He is currently Head of Process Engineering & Modeling Section of Reprocessing Group. He has research interest is in the area of modeling & simulation of solvent extraction process especially related to fast reactor fuel reprocessing. He has developed for the spent solvent purification process based on vacuum distillation process. He is an expert in mass transfer, reaction engineering, and thermodynamics. He has about 60 publications in various national and international journals, seminars, and symposia.