
Continuous Spectrographic Analysis of Vanadous and Vanadic Ions

Prepared by
J. V. Bishop, R. A. Dutcher, M. S. Fisher, S. Kottle, R. A. Stowe

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ABSTRACT

Spectroscopic methods were investigated for the determination of vanadium ions in aqueous solutions arising in the production of vanadium (II) formate and its use in the LOMI (Low Oxidation-state Metal Ion) process for the chemical decontamination of systems in nuclear power plants.

In the LOMI process, a dilute solution of vanadous formate and picolinic acid is used. The vanadous formate reduces metal oxides in the scale on the equipment, causing the scale to break up and become suspended. The picolinic acid chelates these materials and makes them soluble. During the decontamination the progress is followed by analyses of the metal ions and of the radioactivity. When the values stop increasing, the decontamination is terminated. At present, it cannot be determined if the values are no longer changing due to all the scale being removed or due to the vanadous ion being spent.

Infrared and ultraviolet-visible analysis were investigated as the means of analyzing for vanadium species. It was found that the complex formed by V(II) with picolinic acid could be used for colorimetric analysis for V(II) in the range of 0 - 0.011 moles/liter, which encompasses the concentration range used in the LOMI process. The findings will be used to develop an on-line instrument for continuously monitoring V(II) during decontamination.

TABLE OF CONTENTS

	Page
Abstract	iii
List of Figures	vi
Introduction	1
Apparatus and Materials	2
Discussion of Results	
I. Reflectance Spectroscopy	
A. Infrared Region	3
B. Visible Region	3
II. Transmission Spectroscopy	
A. Monitoring Production of V(II) from V(IV)	5
B. Monitoring V(II) at LOMI Concentration	5
Conclusions and Recommendations	12
References	18

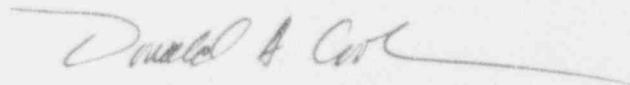
LIST OF FIGURES

Figure No.		
1	Reflectance Infrared Spectra	4
2	Absorbance of 0.2 M Vanadium Formate Solutions	6
3	Vanadous Formate/Picolinic Acid (1:3 Ratio)	7
4	Vanadous Formate/Picolinic Acid, Absorbance as a Function of Concentration (1:3 Ratio, 675 nm)	9
5	Vanadous Formate/Picolinic Acid (1:9 Ratio)	10
6	Effect of Picolinic Acid Concentration	11
7	pH of Vanadous/Picolinic Solutions	15
8	Wavelength Shifts	16
9	Spectra of Interfering Ions	17

FOREWORD

The NRC supports high-quality research proposals from small business firms on important scientific or engineering problems and opportunities that could lead to significant advancement in the safety of nuclear operations. One of the topic areas where proposals are solicited is the area of radiation protection and health effects, including improved decontamination technologies that will reduce personnel dose or decontamination cost or improve decontamination effectiveness. The Continuous Spectroscopic Analysis of Vanadous and Vanadic Ions project was selected because it met these criteria. Under this project two spectroscopic methods were tested for determining the time when the decontamination process is complete or the process solution has been expended. The approach used was to analyze the test solution for the presence of vanadium ions in concentrations that would be normally found in the LOMI decontamination solution to determine when the process was complete.

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INTRODUCTION

Vanadium in the +2 oxidation state is a powerful reducing agent which is used with a chelating agent in the Low Oxidation-state Metal Ion (LOMI) method (Ref. 1, 2) for removing refractory metal oxide deposits from the interior surfaces of stainless-steel equipment in nuclear power plants. This process is one of several methods which are employed for decontamination in boiling water and pressurized water plants. If those deposits are not removed, the radiation field in the vicinity of the piping and associated pumps rises, primarily because of the presence of Co-60. That adversely affects permissible safe working times available to plant operating personnel.

In a LOMI cleanup, a dilute mixture of vanadous formate and formic and picolinic acids is circulated in deionized water through the system which is to be cleaned. The reducing agent and chelant, acting in concert, solubilize deposited iron, nickel, cobalt, chromium, etc. At the completion of the cleaning process the dissolved metals are removed and concentrated for disposal by means of an ion exchange bed. During the course of a decontamination it is necessary to monitor radioisotope concentrations and the concentration of metal which is solubilized. When these values no longer increase, the decontamination is terminated. At present it cannot be determined whether these values are no longer changing because scale removal is complete or because of vanadous ion depletion. If the vanadous ion is being spent before the scale is completely removed, perhaps the process could be modified to make it more effective. It was the objective of the research described herein to assess the feasibility of performing a spectrometric analysis for V(II) which could be made on-line, continuous, and automatic.

Clark (Ref. 3) reviewed the older gravimetric, volumetric and colorimetric methods for the determination of vanadium. In the titrametric method which was used in the present work V(II) was titrated with aqueous potassium permanganate solution (Ref. 4). Total vanadium was determined by reduction of all vanadium present to V(II) by means of a Jones reductor, followed by permanganate titration (Ref. 5). The analysis is somewhat time-consuming for concentrations in the range of 0 - 1 M, which is the range of interest in the manufacture of vanadous formate. At concentrations in the vicinity of 0.005 M, as used in the LOMI process, it is inadequate.

The spectra of vanadous and vanadic ions have been investigated. (References 6, 7). Upon the addition of picolinic acid (Pic), dilute V(II) formate solution exhibits an intense purple color, suggesting that colorimetric measurements might be usable for the analysis and that the molar absorbance might be large. Since the concentrations which are present during the manufacture of vanadous formate were expected to be too strongly absorbing to permit direct transmittance determination, it was decided to evaluate a reflection technique as a means of securing a sufficiently short path length. The alternative would be the use of dilution, which would be acceptable for laboratory use, but would severely complicate the design of an on-line analyzer. The cell which was chosen was one used for FMIR (an acronym for *frustrated multiple internal reflectance*) in which the light beam undergoes multiple reflections at the interface between a suitable prism and the solution being examined (Ref. 8).

APPARATUS AND MATERIALS

The ultraviolet-visible wavelength spectra were obtained through the use of a Carey Model 118 double-beam spectrophotometer (Carey Instruments, Richmond, CA) with ultraviolet and incandescent light sources and photomultiplier detector. Scans were conducted at 1 nm/sec with a chart display of 100 nm/inch and a 0 - 1 linear absorbance scale.

For work at the smallest concentrations, standard rectangular silica cells with 10 mm path length were employed; the cells held approximately 3 ml. Where a shorter path length was needed, International Crystal (Garfield, NJ) Type 21 glass cells with a 1 mm path were employed.

The infrared data were gathered through the use of a Nicolet Instrument Company (Madison, WI) Model DX Fourier-transform (FTIR) instrument. For each sample 20 scans were collected at a resolution of 4 wavenumbers. The infrared scans and some visible wavelength measurements were conducted using an Harrick Scientific Corp (Ossining, NY) Model PLC-9 prism liquid cell with a zinc selenide prism.

The V(II) was obtained as a commercial preparation from VF Sales (Midland, MI) as vanadous formate solution, approximately 0.25 M,

containing excess formic acid at approximately 0.23 M. All vanadium compound solutions with concentrations greater than 200 millimolar were analyzed by redox titration (Ref. 4).

Picolinic acid (2-pyridinecarboxylic acid (CAS 98-98-6) assaying 98.5% was obtained from Nepera, Inc., Harriman, NY 10926. The other chemicals used were standard laboratory-grade reagents.

The chemicals were prepared as stock solutions which were stored in a nitrogen-purged glove box in which dilutions were performed and the spectrometer cells were filled. To reduce the possibility of loss of V(II) due to the intrusion of atmospheric oxygen, the V(II) was added immediately before the spectrophotometric observations were performed.

DISCUSSION OF RESULTS

I. Reflectance Infrared and Visible Spectroscopy

A. Infrared Region

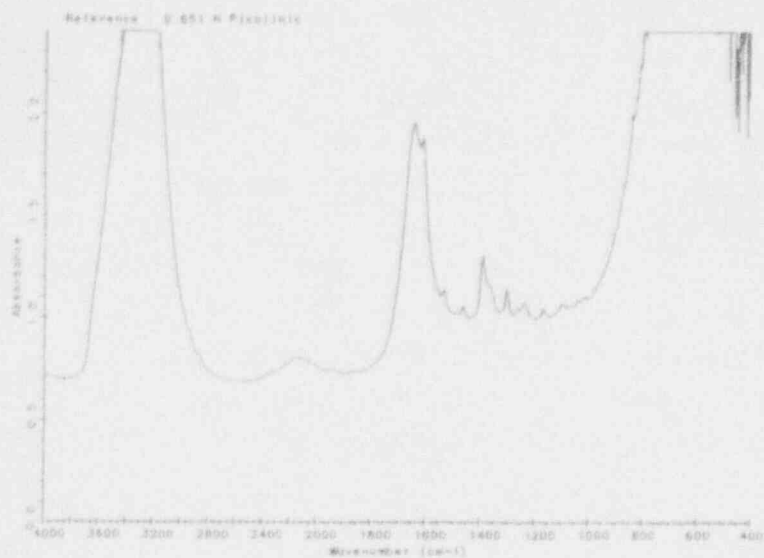
FMIR spectra were gathered on solutions 0.217 M in V(II), picolinic acid, and the vanadous picolinate complex at 400 - 4,000 wavenumbers (Figure 1). The infrared spectra showed absorbance due to water, formic acid and picolinic acid. No features were recognized which could be specifically attributed to interaction between the vanadium and the other components which were present.

B. Visible Region

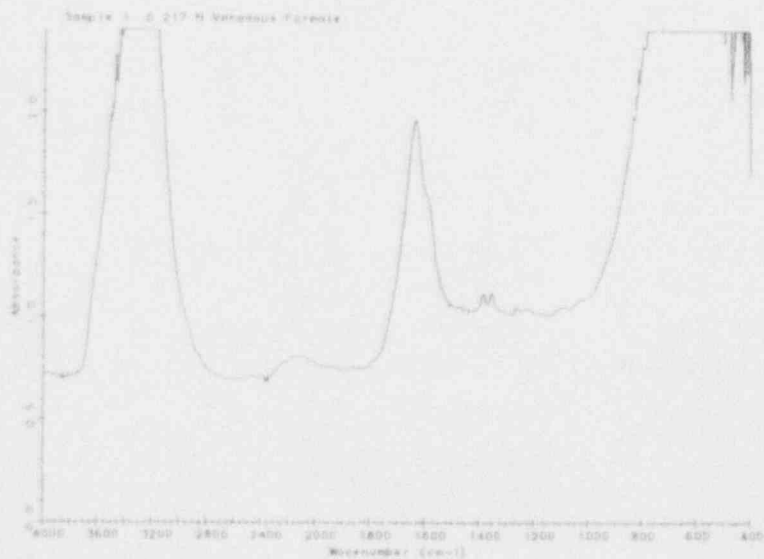
Measurements in the visible region were unsuccessfully attempted on the vanadous picolinate complex. There was a strong background absorbance which varied from 0.45 near 300 nm to 0.3 at 700 nm which had as its source the yellowish color of the zinc selenide optical element. Any absorbance which may have resulted from the complex was not observed.

FIGURE 1

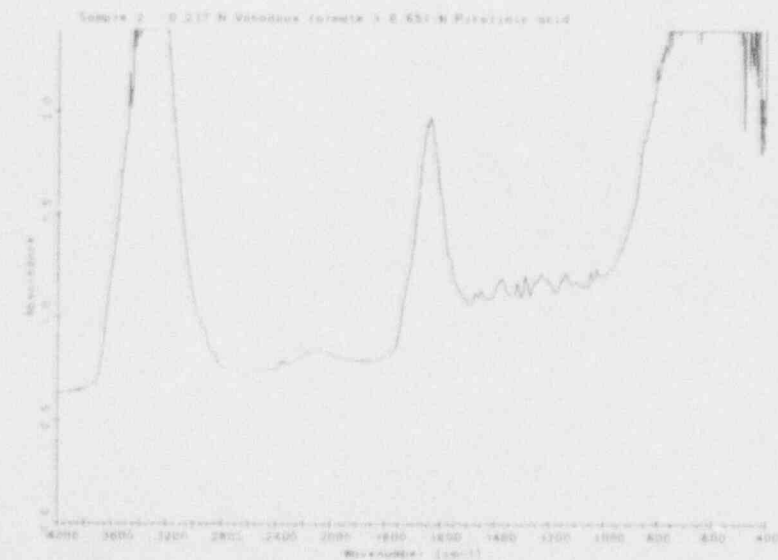
REFLECTIVE INFRARED SPECTRA



Reference
0.651 N Picolinic Acid



Sample 1
0.217 N Vanadous Formate



Sample 2
0.217 N Vanadous Formate
+
0.651 N Picolinic Acid

II. Transmission Spectroscopy

A. Monitoring Production of V(II)

The transmission spectra of vanadium formate solutions in which the metal was in the +2, +3, and +4 oxidation states showed dramatic differences. A 0.217 M V(II) solution was a dark purple with $\lambda_{\text{max}} = 565$ nm. A 0.22 M V(III) solution was green, with purple tints, while a 0.22 M V(IV) solution was blue. The spectra which were obtained are shown in Figure 2. At approximately 750 nm, a distinct pattern of changes in absorption could be followed for the 3 species. The absorbance is too large for solutions in that concentration range to be usable without dilution. Further investigation of the use of the reflectance technique would be warranted if a suitable prism were selected which might be free from the interference discussed in Section I.B, above.

B. Monitoring V(II) at LOMI Concentration

The spectra presented in Figure 3 show the absorbance of V(II) in a 1:3 molar ratio with picolinic acid for vanadium concentrations of 0.00111 to 0.0111 moles/liter (1.11 - 11.1 mM) at 1 mm path length. The corresponding numerical data are presented in Table 1, while the absorbance is graphed as a function of concentration for a wavelength of 675 nm in Figure 4. The line drawn through the origin shows the absorbance expected based on the upper data points. The absorbance follows a linear dependence on concentration, in accord with theory, except at low absorbance values.

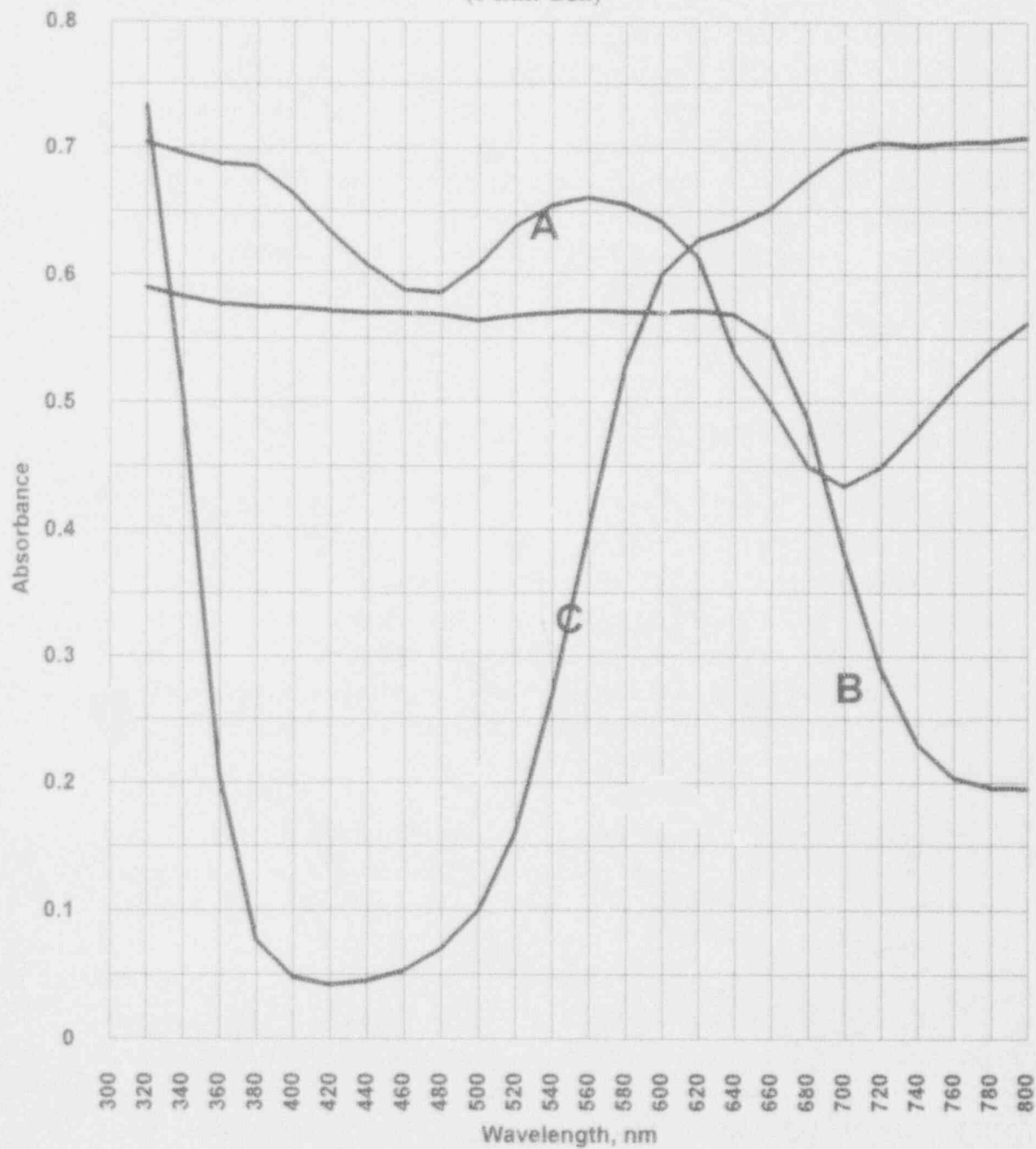
Figure 5 shows the spectra resulting from a 9/1 molar ratio of picolinic acid to V(II) at 1 mm path length. The already complex spectra which were observed at a 3/1 Pic/V(II) ratio (Figure 3) have become broadened toward longer wavelengths.

Changes in absorbance of 0.005 M V(II) as the picolinic acid ratio was varied are shown in Figure 6. For this vanadium concentration, which is in the LOMI process range, the average absorbance at 565-575 nm increases with increasing picolinic acid concentration until a 6/1 ratio is reached. The inference is that the complex requires 6 picolinic acid molecules for each vanadous ion. Other metal ions which may be present may also consume

Figure 2

Spectra of 0.2M Vanadium Formate Solutions

(1 mm Cell)

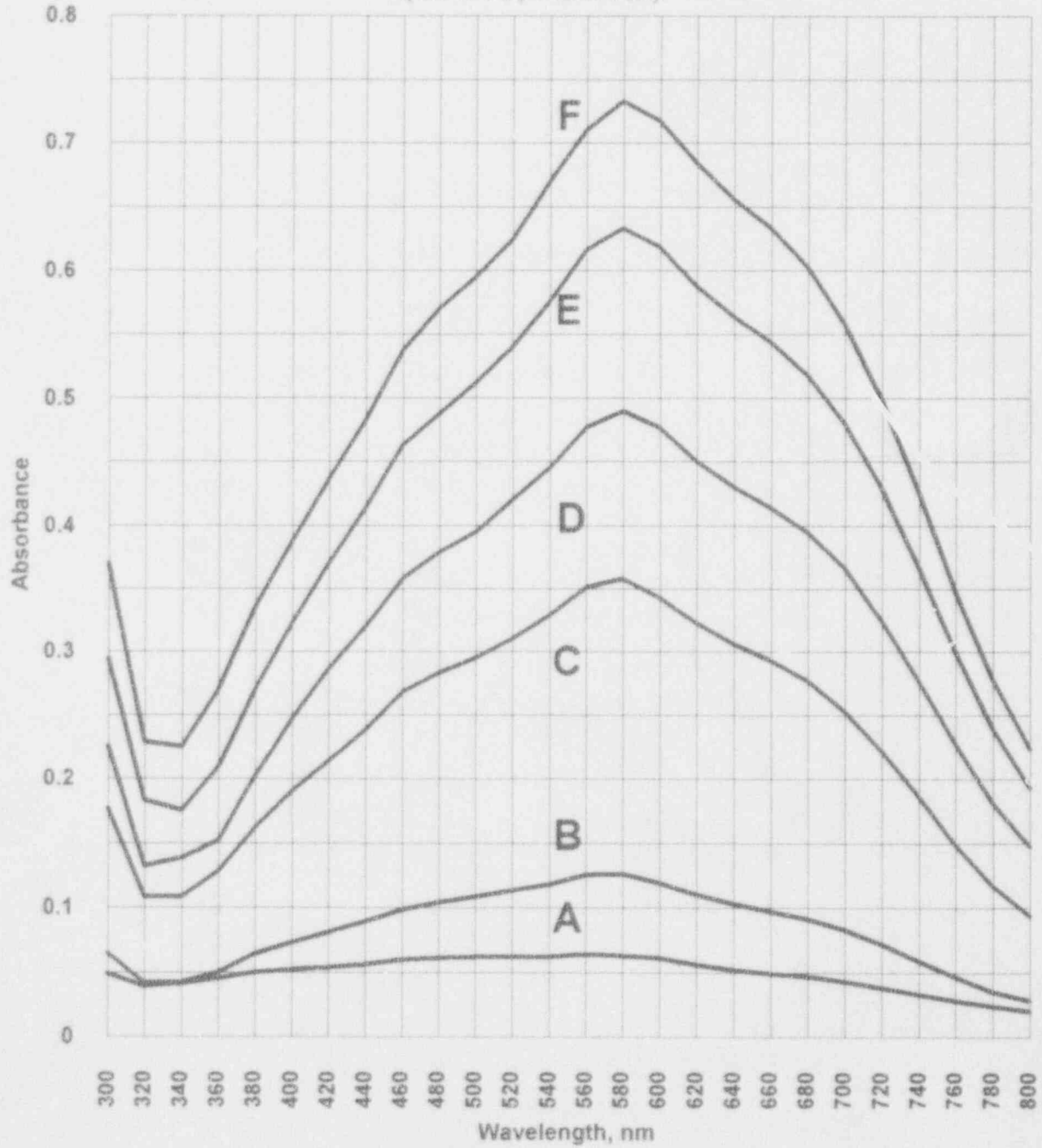


Vanadium Oxidation State: A II B III C IV

Figure 3

Spectra of Vanadous Formate/Picolinic Acid Solutions

(V/Pic 1:3, 1 mm Cell)



Vanadium Concentration, mM: A 1.11 B 2.22 C 5.55 D 6.66 E 8.88 F 11.1

Table 1

Absorbance of V(II) Formate/Picolinic Acid
(1:3 V/Pic Ratio)

V(II) Concn mM	Absorbance Values at Indicated Wavelengths							
	575 nm		625 nm		675 nm		725 nm	
	Value	Avg	Value	Avg	Value	Avg	Value	Avg
1.11	0.101		0.082		0.068		0.046	
	0.099		0.081		0.066		0.048	
	0.093	0.098	0.076	0.080	0.063	0.066	0.045	0.046
2.22	0.281		0.239		0.206		0.152	
	0.283		0.246		0.214		0.164	
	0.282	0.282	0.242	0.242	0.209	0.210	0.157	0.158
5.55	0.817		0.726		0.642		0.483	
	0.822		0.741		0.656		0.511	
	0.821	0.820	0.732	0.733	0.650	0.649	0.502	0.499
6.66	1.058		0.959		0.858		0.658	
	1.064		0.971		0.874		0.686	
	1.058	1.060	0.959	0.963	0.855	0.862	0.670	0.671
8.88	1.354		1.246		1.128		0.879	
	1.353		1.250		1.132		0.894	
	1.355	1.354	1.248	1.248	1.130	1.130	0.887	0.887
11.1	1.736		1.607		1.461		1.151	
	1.738		1.618		1.473		1.173	
	1.737	1.737	1.609	1.611	1.463	1.466	1.154	1.159
Correlation coefficient	0.9993		0.9993		0.9993		0.9990	

Figure 4

Absorbance of Vanadous Formate/Picolinic Acid Solutions

(V/Pic 1:3, 1 mm Cell)

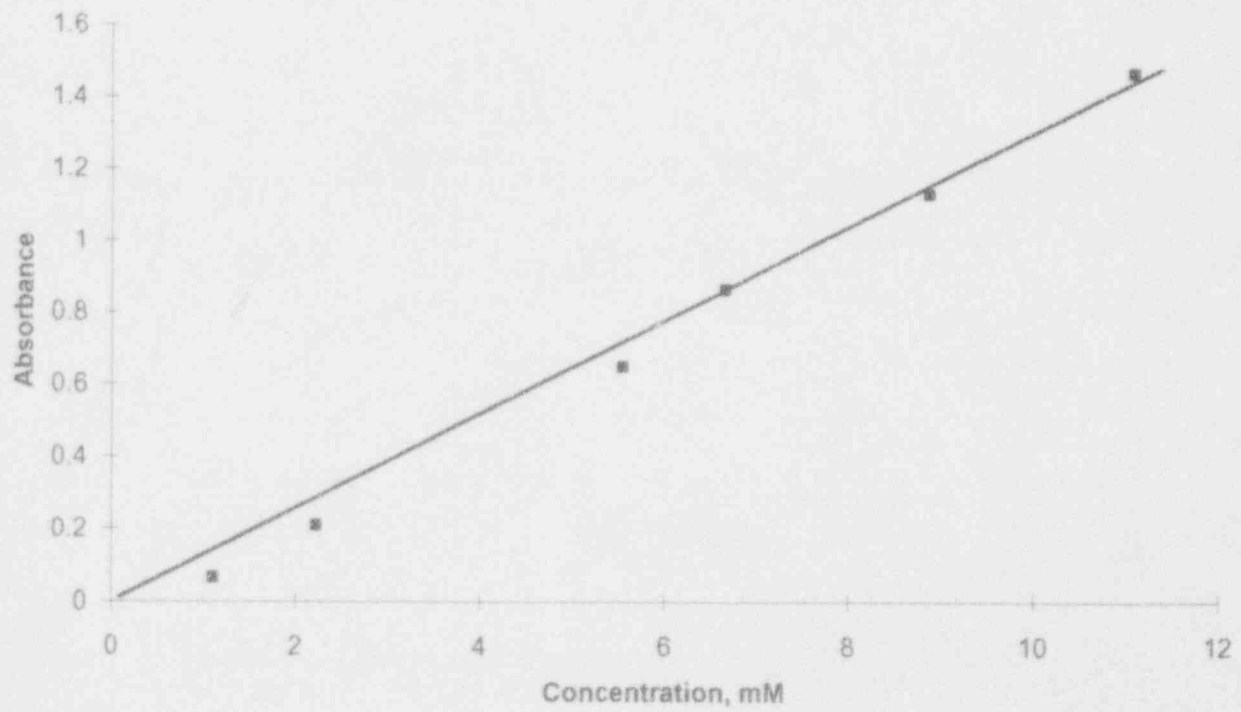
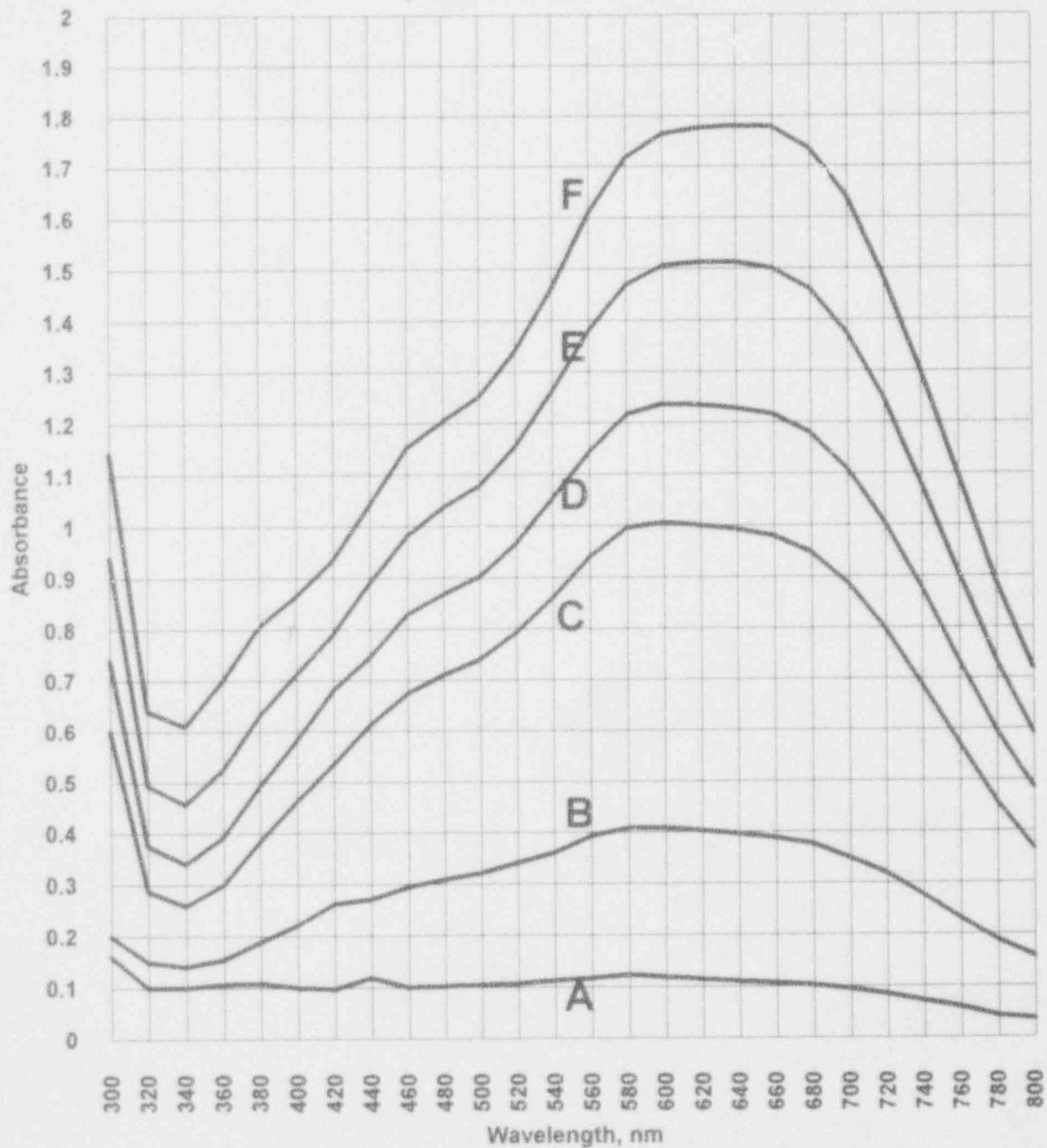


Figure 5

Spectra of Vanadous Formate/Picolinic Acid Solutions

(V/Pic 1:9, 1 mm Cell)

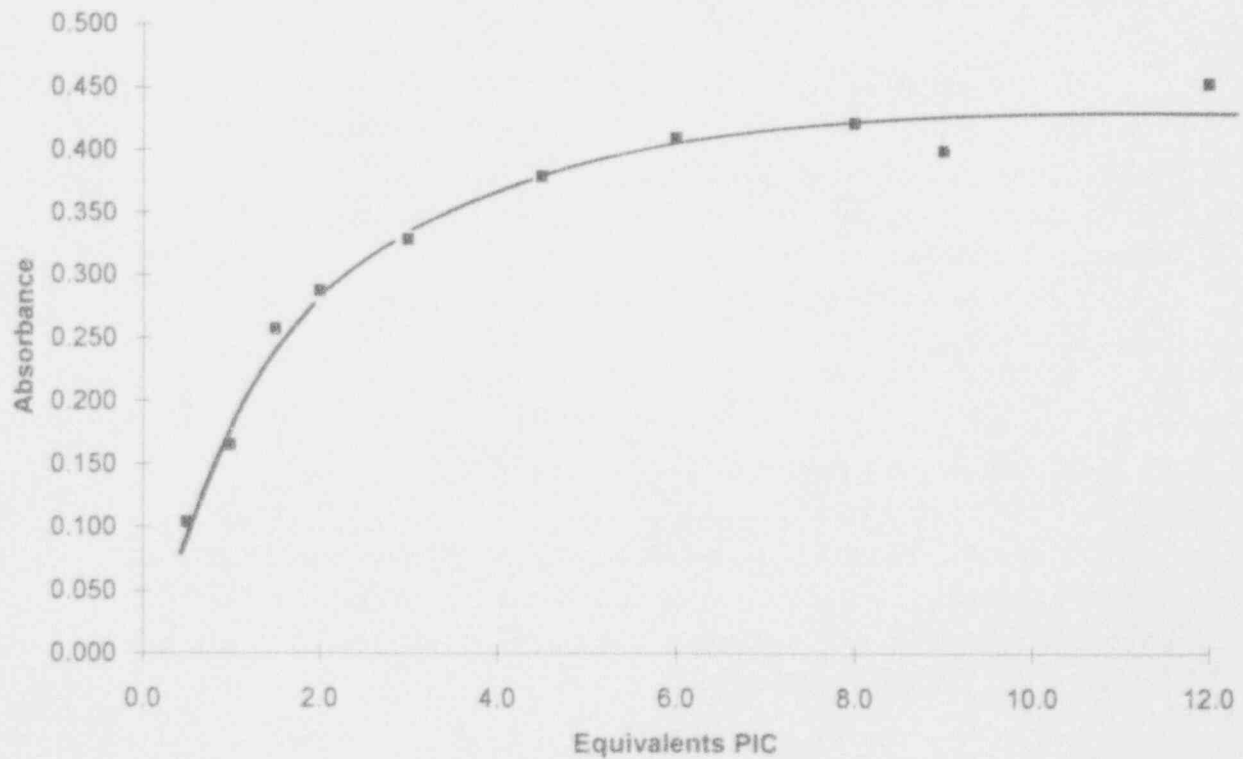


Vanadium Concentration, mM: A 1.11 B 2.22 C 5.55 D 6.66 E 8.88 F 11.1

Figure 6

Effect of V(II)/Picolinic Acid Ratio on Absorbance

(Averages of All Runs, 565-575 nm, 1 mm Cell)



picolinic acid, thereby depriving the vanadous complex to a degree dependent on the relative dissociation constants of the complexes and on the relative concentrations. As a consequence, it may be necessary to have present a large excess of picolinic acid in order to perform the V(II) analysis accurately.

Observation of the solution pH showed that it decreased as the picolinic acid concentration was increased. (See Table 2 and Figure 7.) The decrease in pH was accompanied by a shift in the wavelength of maximum absorbance (Figure 8). These effects, which require further investigation, will have to be taken into consideration in designing an on-stream analyzer. It may become necessary to both (1) provide an excess of picolinic acid and (2) control the pH of the sample solution to a constant value.

The potential for interference by iron and nickel was evaluated by separately examining 0.005 M Fe(II), Fe(III), and Ni(II) solutions with a 3/1 ratio of picolinic acid present. Their spectra are shown in Figure 9. The maximum concentrations experienced in the LOMI work described in Reference 1 may be calculated to be 0.009 M iron and 0.002 M nickel. The spectra show for wavelengths above 550 nm, the interference will be negligible.

CONCLUSIONS AND RECOMMENDATIONS

This work shows that it is feasible to follow V(II) concentration in a LOMI decontamination spectrophotometrically. The results show that it will be feasible to develop a continuous monitoring instrument which can be used on-line during LOMI decontaminations.

At concentrations which are typical of LOMI decontaminations, iron and nickel pose no interference to the V(II) analysis, except indirectly, by reducing the concentration of picolinic acid available to form the V(II) complex. Because the iron and nickel, as well as other metallic ions which might be present, can consume picolinic acid, it may be necessary to add a large excess of picolinic acid to the analytical sample. It may be necessary to insure that the pH of the analyte is maintained at a constant value in order to avoid affecting the V(II) complex concentration.

The reflectance method using a prism cell was not suitable for measurement of vanadium species in the infrared spectral region, although it could be useful for measuring the concentrations of organic compounds which may be present in the aqueous medium. The potential of a suitable prism cell for analysis on the visible spectral region should be further evaluated.

Table 2

Wavelength Shifts for V(II)/Pic Complex

V(II) Concn mM	Wavelength of Maximum Absorbance					
	pH	nm	pH	nm	pH	nm
1.11	3.37	564	3.30	572	3.27	580
2.22	3.18	570	3.07	582	3.02	585
5.55	3.03	576	2.88	590	2.82	595
6.66	2.96	578	2.82	593	2.78	600
8.88	2.93	579	2.77	598	2.71	610
11.10	2.87	580	2.74	600	2.68	650

Figure 7

pH of Vanadous Formate/Picolinic Acid Solutions

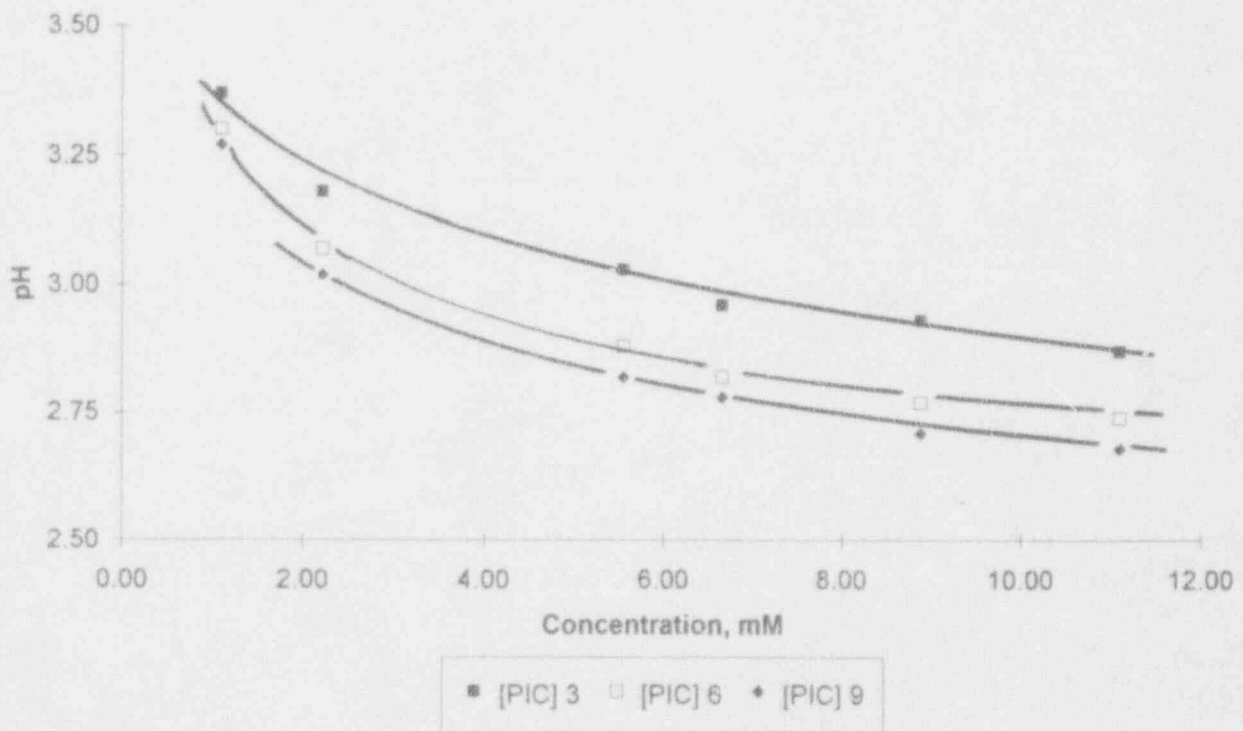


Figure 8

Wavelength Shifts Accompanying pH Changes

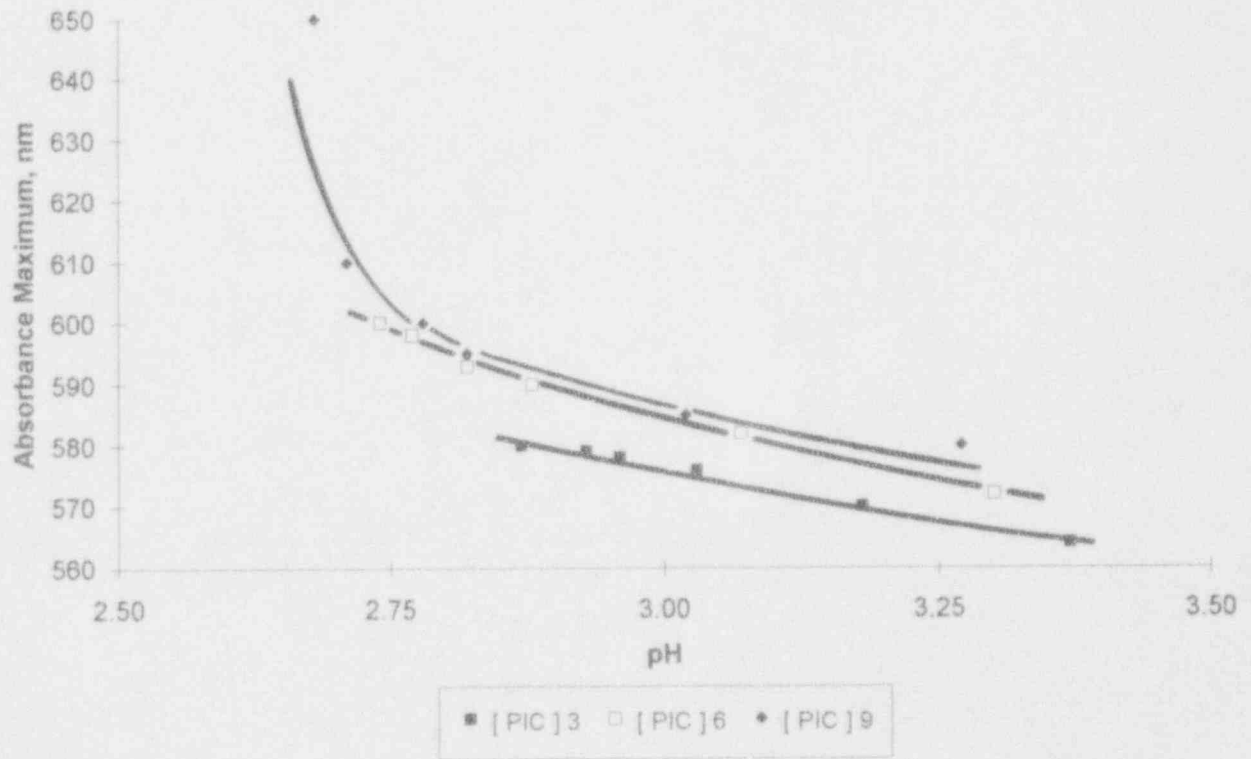
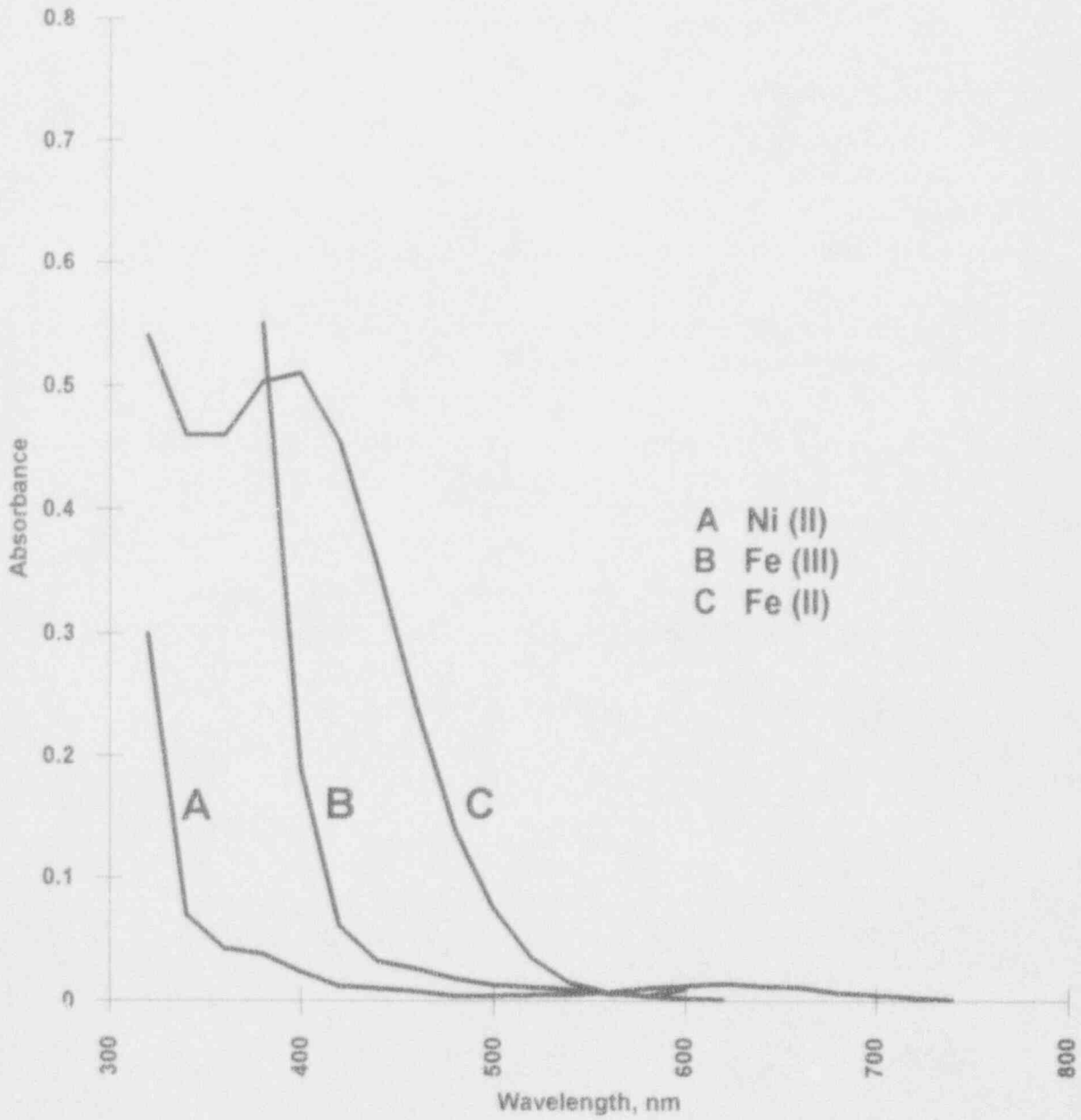


Figure 9

Spectra of Potential Interfering Ions

(0.005M, 10 mm)



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10. SUPPLEMENTARY NOTES

11. ABSTRACT *(200 words or less)*

Spectroscopic methods were investigated for the determination of vanadium ions in aqueous solutions arising in the production of vanadium (II) formate and its use in the LOMI (Low Oxidation-state Metal Ion) process for the chemical decontamination of systems in nuclear power plants.

In the LOMI process, a dilute solution of vanadous formate and picolinic acid is used. The vanadous formate reduces metal oxides in the scale on the equipment, causing the scale to break up and become suspended. The picolinic acid chelates these materials and makes them soluble. During the decontamination the progress is followed by analyses of the metal ions and of the radioactivity. When the values stop increasing, the decontamination is terminated. At present, it cannot be determined if the values are no longer changing due to all the scale being removed or due to the vanadous ion being spent.

Infrared and ultraviolet-visible analysis were investigated as the means of analyzing for vanadium species. It was found that the complex formed by V(II) with picolinic acid could be used for colorimetric analysis for V(II) in the range of 0 - 0.011 moles/liter, which encompasses the concentration range used in the LOMI process. The findings will be used to develop an on-line instrument for continuously monitoring V(II) during decontamination.

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Vanadium formate
Vanadium analysis
Continuous analysis
Decontamination

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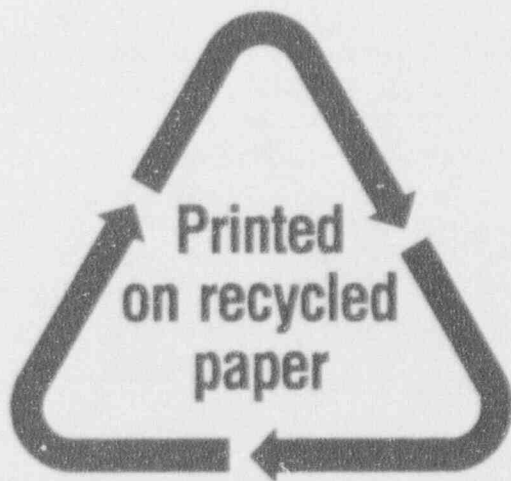
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