
Continuous Analysis for Vanadium in LOMI Decontamination

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Omni Tech International, Ltd.

Prepared for
U.S. Nuclear Regulatory Commission

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ABSTRACT

Methods were investigated for the determination of vanadium ions in aqueous solutions used in the LOMI (Low Oxidation-state Metal Ion) process for the chemical decontamination of piping systems in nuclear power plants. In the LOMI process, a dilute solution of vanadous formate and picolinic acid is circulated at elevated temperature in the system to be cleaned. 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 renders them soluble, so they can later be removed by ion exchange. The progress of the LOMI is followed by laboratory analysis of samples of the circulating fluid for metal ions and radioactivity. When the values stop increasing, the decontamination is terminated. At present, it cannot be determined if the values are no longer changing because all of the scale has been removed or because of vanadous ion depletion. It is believed that on-line vanadous ion analysis may lead to improvements in the process.

It was found that the complex formed by V(II) with picolinic acid could be used for colorimetric analysis for V(II) in the concentration range used in the LOMI process. Those findings were used to develop an on-line colorimeter for continuously monitoring V(II) concentration in LOMI solutions. It performed very well in laboratory simulations. However, when evaluated in the field it was found to be subject to excessive interference by colored materials which were present in the circulating solution.

A titrimetric method was investigated in which V(II) was titrated with ferric iron using potentiometric electrodes to follow the course of the reaction. Laboratory experiments showed that the method was specific to V(II), and was free of interference from other materials which are normally present. An on-line titrimer using that approach was assembled, tested in the laboratory under simulated LOMI conditions, and was successfully evaluated in the field during a LOMI decontamination.

TABLE OF CONTENTS

	Page
Abstract	iii
Table of Contents	v
Foreword	vii
Acknowledgments	viii
Introduction	1
Part I - Spectroscopic Method	
Introduction	3
Experimental Procedures	3
Results and Discussion	5
Part II - Titrimetric Method	
Introduction	7
Experimental Procedures	7
Instrument Description	9
Results and Discussion	11
Conclusions	20
References	20
Appendices	
A Determination of Vanadium Ion Concentration by Continuous Colorimeter	22
B Determination of Vanadium Ion Concentration by Automatic Titrimeter	25

TABLE OF CONTENTS (continued)

Figures

1	Colorimeter Details	6
2	Titration Apparatus	14
3	ORP Titration of Vanadous and Vanadic Ion	14
4	Electrode Lag and Mixing Noise	15
5	Electrode Response at Low pH	15
6	Titrimeter Major Components Layout	16
7	Representative Titration Curves	17
8	Titrimeter Evaluation	18
9	Brunswick-2 LOMI On-line Vanadium Analysis	19

Tables

1	Titrimeter Test Results	12
2	Brunswick-2 LOMI	13

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 topical 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 Analysis of Vanadous and Vanadic Ions project was selected because it met these criteria. Under this project, methods for real-time, on-line analysis of vanadium ion concentrations during LOMI chemical decontamination of piping in nuclear power plants were developed. The on-line colorimeter developed for this project did not perform well in the field due to excessive interference by colored materials in solution. The automatic titrimetric method developed for this project performed well in the laboratory and the field during a LOMI chemical decontamination based on the ferric ion concentration in solution.

NUREG/CR-6494 is not a substitute for a regulation, and compliance is not required. The approach and method described in this NUREG are provided for information only. Publication of this report does not necessarily constitute NRC approval or agreement with the information contained therein.



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INTRODUCTION

One of the methods used by nuclear power plants to reduce radiation fields is chemical decontamination. Over time metal oxide films containing cobalt-60 and other radioisotopes develop on the interior surfaces of stainless steel piping and equipment in these plants. As the radiation fields increase, they limit the allowable time for exposure by operating and maintenance personnel. The decontamination is performed by contractors, typically during a fuel outage. One of the chemical decontamination processes which has been used successfully for a number of years is the LOMI (Low Oxidation-state Metal Ion) process (Ref. 1,2). In that process vanadous ion (+2 oxidation state) is used with a chelating agent to remove the metal oxide deposits.

In the LOMI process, a dilute aqueous solution containing a mixture of vanadous formate and picolinic acid is circulated through the system which is to be chemically decontaminated. The vanadous ion, which is a powerful reducing agent, causes the oxide films to loosen. The picolinic acid converts the metal ions to soluble chelates (Ref. 2). At the completion of the process, the chelates of iron, nickel, and the other metals present are removed from the cleaning solution by means of ion exchange resins. The ion exchange resins are transported in shielded casks to low-level radioactive disposal sites.

During a decontamination samples are taken periodically for laboratory determination of radioisotope and metal concentrations. When those values reach a point where they are no longer increasing, the decontamination is terminated. The present technology can not be used during the decontamination to determine whether the values are no longer increasing because the metal oxide film removal is complete or because of loss of the reducing agent, the vanadous ion. If the vanadous ion concentration 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 this research project to determine the feasibility of performing on-line analysis for V(II) while the decontamination is being carried out.

Clark (Ref. 3) reviewed the older gravimetric, volumetric and colorimetric methods for the determination of vanadium. In the method that is used in production of vanadous formate, V(II) is titrated with aqueous potassium permanganate solution (Ref. 4). Total vanadium is determined by reduction of all vanadium present to V(II) by means of a Jones reductor, followed by permanganate titration (Ref. 5). While excellent for concentrations in the range of interest in the manufacture of vanadous formate, none of those methods appeared to be adaptable for use in a continuous monitor to be used at concentrations in the range 0 - 0.010 M, as used in the LOMI process.

The spectra of vanadous and vanadic ions have been investigated (Ref. 6, 7, 8). Upon the addition of picolinic acid, dilute V(II) formate solution exhibits an intense purple color, suggesting that colorimetric measurements might be usable for the analysis. In the EPRI Fifth Workshop on Chemical Decontamination (Charlotte, 1993) data were presented on continuous analysis of vanadous formate-picolinic acid complex by means of a colorimetric method (Ref. 9).

PART I of the present report covers work performed to utilize a colorimetric method for on-line V(II) analysis. In **PART II** the work which was performed to develop a titrimetric instrument is described.

MATERIALS

The V(II) was obtained as a commercial preparation from Vantek Corporation (Midland, MI) as vanadous formate solution, approximately 0.25 M, containing excess formic acid at a concentration of approximately 0.23 M.

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

The chemicals were prepared as stock solutions which were stored in argon-purged glass bottles. To reduce the loss of V(II) due to the intrusion of atmospheric oxygen, transfers were made by means of pre-purged hypodermic syringes, and all vessels were purged by means of a continuous flow of argon. Quantitative transfers of V(II) solutions were performed gravimetrically, using a value of 1.01 g/ml for the density of the 0.25 M starting material. Dilute V(II) solutions were analyzed by redox titration with standard 0.1 M ferric ammonium sulfate using electrometric determination of the end point.

Part I Spectroscopic Method

INTRODUCTION

The spectra obtained in the initial study (Ref. 10) show that the absorbance of V(II) complexed with picolinic acid is linear with vanadous ion concentration in the range 0 to 0.0111 moles/liter (0 - 11.1 mM) at wavelengths in the range of 575 - 630 nm. The results also show that the picolinate/vanadous ion ratio affects the absorbance. The absorbance reaches a maximum when the picolinate to vanadous molar ratio is equal to, or larger, than 6/1. There is also a pH effect on the spectral curve shapes. To minimize those effects, in this work provision was made to have present an excess of picolinic acid (at least 6/1) and to maintain the sample and reagent pH values to 4.5, a value which is congruent with that employed in LOMI process.

The prior work showed that interference by iron or nickel at the metal ion concentrations realized in LOMI decontaminations would be negligible at 630 nm.

EXPERIMENTAL PROCEDURES

A colorimeter was constructed for which the key elements of the fluid system were as shown in Figure 1. Samples entered at connector C1 and left the instrument through connector C5. A metering pump, P1, provided the desired sample flow rate of 3-4 milliliters per minute. A second metering pump, P2, added sodium picolinate solution from nitrogen-purged container D1 at a rate chosen to achieve the desired picolinate/vanadium ratio. The mixture passed through a flow-through optical cell, XX, and left the measurement path through check valve CV2. The sample and reagent streams flowed through 5-micron sintered metal filters, F1 and F2. A by-pass consisting of valve V1 and a flow meter, R1, was provided to achieve a total flow rate of approximately 30 milliliters/minute to minimize lag time in the process sample line. The flow-through optical cell (Ref. 11) employed a unique light pipe design to conduct light into and out of the cell which made it possible to make fine adjustments in the approximately 1 mm. path length.

A light-emitting diode with a spectral maximum at 630 nm was used as the source, along with a 630 nm plastic filter. Operational amplifier circuits accepted the output of a silicon photodiode and converted its output current into a voltage signal which was linear over the range 0-2 absorbance units. The absorbance signal was led to a digital recorder which was provided with a means of

downloading data for computer processing. The digital recorder and other electronic components were mounted on a panel placed immediately above the fluid components, so that any potential leaks, e.g. from the pumps, would not impinge on them. The colorimeter was contained in a NEMA Style 4X instrument cabinet with dimensions 76 X 61 X 18 cm. (30 X 24 X 7 inches) made of glass fiber-reinforced polyester. The cabinet was mounted on a welded, rectangular tubular stainless steel stand with base dimensions of 61 X 66 cm. (24 X 26 inches) and height of 165 cm. (65 inches) (Figure 1).

In operation, nitrogen at a gauge pressure of 69 kPa (10 psi) was connected to reservoir D1 (Figure 1). D1 was loaded with 500 ml of 0.155 M picolinic acid solution which had been adjusted to 4.5 pH using sodium hydroxide. The reagent pump, P2, was adjusted for a rate of 1.0 ml./min.. The sample pump, P1, was set to 4.0 ml./min.

The instrument was tested with both static and flowing samples. Because of the reactivity of dilute vanadous picolinate solutions to minor air leaks, it was found desirable to utilize a secondary standard in performing some of the testing and in verifying instrument performance, both in the laboratory and in the field. The secondary standard chosen was Blue Food Color No. 5210007087 (McCormick & Co., Hunt Valley, MD). Solutions of the dye in the range of 0-1% (v/v) were comparable in general spectral character and in absorbance to vanadous picolinate at the concentrations used in LOMI (0-10 millimolar). The absorbances of the vanadous complex and of the secondary standard were linear with concentration. Tests conducted over extended periods showed that the dye was adequately stable to be used as a secondary standard for verifying proper instrument operation and calibration.

The completed photometric instrument was tested in the laboratory using simulated LOMI solutions to verify its operation. It was then evaluated during a LOMI decontamination conducted by Vectra Corporation (now PN Services) at the J. A. Fitzpatrick plant in Oswego, New York on December 26-27, 1994. The instrument was positioned immediately outside a temporary radiation barrier which had been erected by the contractor. The calibration was first checked by means of the secondary standard solution. The instrument was then connected by means of approximately 6.1 m. (20 feet) of 0.635 cm. (1/4-inch) thick-wall stainless steel tubing to the piping system in which the LOMI was to be performed. The instrument was operated following the procedure presented in Appendix A.

RESULTS AND DISCUSSION

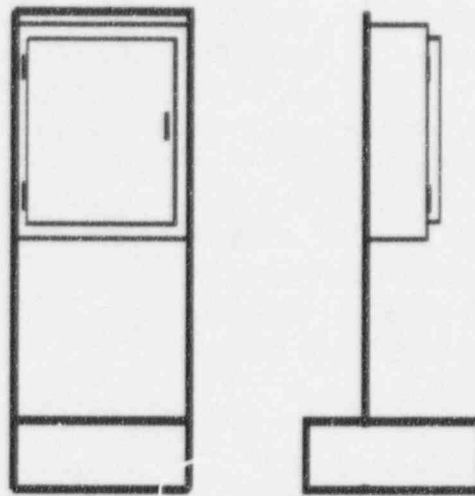
In the plant trial the concentration readings obtained were lower than expected based on the number of 55-gallon drums of vanadous formate solution which were added to the system. Based on estimates of the system volume, each drum was expected to contribute a V(II) concentration of 0.000586 moles/liter. After the contractor had introduced 8 drums of vanadous formate solution the V(II) concentration was expected to be 0.0047 M (equal to 4.7 millimolar), assuming good mixing and no loss of vanadous ion concentration in this early stage of circulation. The colorimeter measured a value of 0.29 mM. Investigation showed that the extremely small reading was the result of the choice of sampling point, where the flow was inadequate.

After the sampling point was connected to a better location, the colorimeter reading immediately rose to 3.3 mM. The reading reached a maximum value of 3.7 mM just before the LOMI was terminated by the contractor. Visual observation of the bypass flow meter showed its contents to be black in color, unlike the purple color of the vanadous picolinate complex.

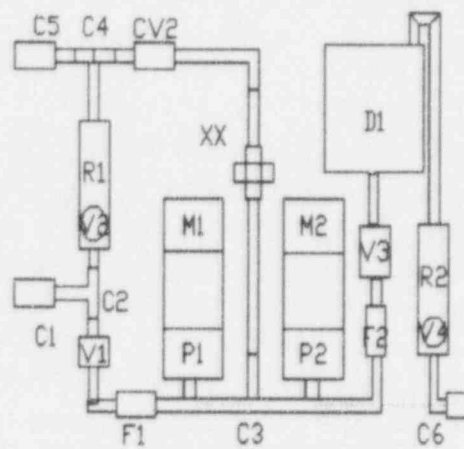
Throughout the field trial the instrument's fluid, optical, and electronic systems performed very well. However, the presence of such a large residual light absorbance rendered the readings unusable for the intended purpose. Subsequently, anecdotal data were obtained that residual color following completion of the desired reactions is highly variable and is the rule, rather than the exception.

The JAF Chemistry Department, which decontaminated the instrument for release from the plant, found that the sintered metal sample line filter (F1 in Figure 1) was markedly contaminated with radioisotopes. The presence of filterable material and the black residual color of the sample stream suggest that very finely divided iron or mixed-metal oxides may be the source of the unwanted absorbance. Such an hypothesis would fit the reported variability of the residual color since the presence or absence of suspended solids would be dependent on so many factors. Any such particulate material would ultimately be filtered by the ion exchange beds during the radioactivity removal step and would not remain in the circulating stream. At this time, there has been no further investigation to test that hypothesis.

Figure 1 - Colorimeter Details



Stand with Colorimeter



Colorimeter Fluid System

Part II Titrimetric Method

INTRODUCTION

The titration method which is used for quality control in the production of vanadous formate solution is time-consuming and utilizes multiple titrations with visual end point determinations (Ref. 4). The procedure did not appear to be well suited for automation. The LOMI vanadium concentration is on the order of 50-fold smaller. Also, the field experience with the photometric instrument showed that optical detection of the end point might be subject to interference, as discussed above. In view of the strength of the vanadous picolinate complex as a reducing agent, investigation of a titration method followed by means of oxidation-reduction (ORP) measurements appeared to be warranted (Ref. 12). The research performed to develop such a method is presented below. The work was discussed in a paper which was presented at the EPRI Radiation Field Control conference in November, 1995 (Ref. 13).

EXPERIMENTAL PROCEDURES

Laboratory experiments were carried out in the apparatus shown in Figure 2. The cylindrical titration vessel of about 100 ml volume was fabricated from transparent acrylic plastic. Small polypropylene tubing fittings were used to admit a platinum ORP electrode, a silver-silver chloride reference electrode, an argon purge, a pH probe, and to provide openings for entry and removal of samples. Water, picolinic acid solution and other reagents required were added to the acrylic cell and were freed of dissolved oxygen by means of the flow of argon. Samples derived from commercial vanadous formate solution were weighed and transferred into the titration cell under oxygen-free conditions by means of pre-purged hypodermic syringes. The cell contents were stirred by means of the inert gas flow.

Ferric ammonium sulfate solution (0.1 M) was supplied from storage bottle D1 by means of a calibrated small positive displacement pump, P1. The valves which are shown in Figure 2 were useful in washing and draining the cell. Titration curves were obtained by recording the measured ORP (oxidation-reduction potential) between the platinum and reference electrodes by means of an high input impedance digital voltmeter. The quantity of titrant delivered was

derived from the running time of the pre-calibrated titrant pump. The ORP was recorded as a function of reagent pumping time using a personal computer which was equipped with an analog to digital converter. The recorded data were subsequently converted into tabular and graphic form.

The use of oxidation-reduction potential (ORP) measurements in a redox titration is illustrated in Figure 3 which shows the results obtained from the manual titration of an 0.06 M solution of vanadous formate which was 0.3 M in sodium picolinate at 4.5 pH using 0.02M ferric ion solution. The ORP electrodes used were platinum and silver-silver chloride. The graph exhibits two regions of rapidly increasing ORP. The first rise is associated with oxidation of the vanadium from the +2 oxidation state to the +3 state. That reaction is the same as the predominant reaction in the LOMI decontamination, itself. As shown by the second rise in ORP, under the conditions used, the ferric ion can further oxidize the vanadium to the +4 oxidation state where it will be in the form of the vanadyl ion. The total volume of titrant required to reach the end point of the second reaction will be twice the volume of titrant needed for the first end point, provided no V(III) is present initially. That proved to be the case.

The samples which were first investigated ranged from 0 to 0.010 M in vanadous formate (VF) concentration and contained picolinic acid at molar ratios in the range 0 - 9 relative to the V(II). Manual titrations employing stepwise addition of the titrant such as the one shown in Figure 3 gave results in accord with the expected values calculated from the concentrations of the vanadous formate stock solutions from which they were prepared.

However, when the reagent pump was employed to add the ferric reagent, the ORP titration curves initially exhibited two defects which were troublesome in designing an automatic instrument. The recorded ORP readings exhibited large noise pulses. Those were traced to concentration gradients resulting from poor mixing of the ferric reagent by the inert gas flow which stirred the cell contents. The noise pulses were eliminated by adding a magnetic stirrer and raising the entry point of the argon purge to a position above the level of the liquid contents of the cell.

The second defect appeared to be the result of a slow reaction between vanadium picolinate and the ferric reagent. The titration curves departed from the theoretical S-shape, and the apparent end points were subject to shifts which seemed to depend on the reagent concentration, on the rate of addition, and on the picolinic/vanadium molar ratio. Under some conditions there were no breaks in the ORP curves at all. Typical results are illustrated in Figure 4.

Since the titration vessel was transparent, it was possible to see the change from the original intense purple color of the vanadous picolinate complex to the pale green color of the V(III) complex. As demonstrated in Figure 4, the visual end point sometimes occurred at a volume of titrant less than that required to reach the rise in the ORP. It is the rapid increase in the ORP which is expected to define the end point of the titration. Those effects are attributable to slow electrode response, rather than slow reaction between the ferric titrant and the vanadium complex. The oxidation reaction proceeds rapidly, as evidenced by the color change, while the ORP values lagged behind.

That was confirmed in the course of investigating the response of the system to the hydrogen ion concentration. Initially the titrations were performed at 4.5 pH, the nominal value expected in the sample stream. However it soon became clear that an increase in acidity greatly increased the ORP electrode response rate.

Figure 5 illustrates the effect of using a pH less than one. The graph shows the titration curves of 3 samples which contained 0.003, 0.006 and 0.009 mole/liter vanadous formate, respectively. At 0.7 pH the ORP titration curves responded rapidly upon addition of the titrant, and their volumes at the end points were as predicted. It was visually confirmed that the color changes occurred at the ORP end points. In addition, lower pH suppressed the vanadic to vanadyl oxidation. At low pH the titration curves exhibited only the desired V(II) to V(III) oxidation.

The increased rapidity of electrode response was accompanied by the increase in the noise component of the redox potential which is evident in Figure 5. Since plans for the on-line instrument design called for detection of the end point by choosing a suitable fixed end point ORP value, it became essential to reduce the ORP noise which could lead to false triggering and poor reproducibility. The data showed that the remaining ORP fluctuations were produced by the strokes of the positive displacement pump which was being used to add ferric reagent. Changing to a peristaltic pump made the flow more uniform and eliminated the problem.

INSTRUMENT DESCRIPTION

An automatic titrimer was constructed utilizing the findings discussed above. It is housed in an instrument cabinet and on a stand similar to those shown in Figure 1. The cabinet housing the titrimer has dimensions of 30 X 24 X 10 inches. The identities and layout of the major components is given in Figure 6, to which reference is made in the description which follows. The instrument operating procedure is presented in Appendix B.

The titrimeter operates on 120 volt, 60 cycle, single phase power with switch and fuse located on the control panel. Time-programmed operation of the pumps and solenoid drain valve is governed by an Allen-Bradley Model 1000 programmable logic controller. The titration cell is similar to the one described previously (Figure 2), except provision is made for removal of the cell top and for a lower portion which can accommodate an 1-inch diameter, cross-shaped, Teflon-coated magnetic stirring bar. The stirring bar is operated by means of a permanent magnet which is turned by a 30 rpm miniature gearmotor. An inert gas line is provided for purging the cell to prevent ingress of air. Internal fluid connections within the titrimeter are made with 1/8-inch polypropylene tubing and polypropylene tubing fittings. If portions of the sample loop become contaminated during use, the affected portions of the sample path can be disassembled and consigned to solid waste with only a small cost for replacement of the discarded parts.

The sample, acid, and reagent are supplied by peristaltic pumps (Cole-Parmer Instrument Company, Chicago, IL) in which the quantity of fluid pumped is governed by the pump size, elastomer tubing size, and rotation rate. The logic controller timing and Pump 1 rate are set to introduce 25 ml. of sample solution into the titration cell. Pump 2 operates at the same time to provide 1 ml. of 8% (v/v) sulfuric acid for pH control from a polyethylene bottle placed within the instrument cabinet. Following sample and acid introduction, Pump 3 is turned on to add 0.1 M ferric ammonium sulfate solution at the rate of 0.625 ml./min. as the titration reagent, also from a plastic supply bottle. It is the running time of Pump 3 which is measured to establish the quantity of titrant consumed in each titration. The cycle time of the analysis is 6 minutes which includes cell drain time, sample and acid introduction, and titration. The cell contents drain into a waste bottle which is placed beneath the instrument. The volume of waste accumulated is approximately 300 ml./hr.

The potential difference of the ORP electrodes is measured by means of a digital controller with adjustable set points. When the ORP reaches the desired value, a relay contact in the ORP controller stops the reagent pump. The mode control panel provides a switch which selects whether the digital recorder records the entire titration curve or whether it records only the running time of the reagent pump.

RESULTS AND DISCUSSION

The improvements effected by the reduction in pH and by more uniform reagent flow are evident in Figure 7, which shows the results obtained in the automatic, continuous titration of a number of samples by means of the completed titrimeter. This sample series contained V(II) at concentrations which ranged from 0.3 to 7.8 millimoles/liter. The titrations were performed at pH values in the range 0.6-0.8 using 0.1M ferric solution added at the rate of 0.625 ml/min. The 3 ml volume mark on the abscissa represents 4.8 minutes of reagent pumping time. The picolinate/vanadium ratios, shown on the graph adjacent to each curve, ranged from 2/1 to 28/1 and were not critical. There was no evidence of onset of a second stage of reaction of the V(III) to produce V(IV).

Displacement of the ORP curves at small V(II) concentrations to more positive values presents a problem in selecting a suitable detection level for halting the reagent pump. For the titrations shown in Figure 7, a value of -100 mv was chosen. At V(II) concentrations less than 1 mM, that choice results in an analytical error of approximately -15% of the amount present. That is equivalent to an uncertainty of 0.15 mM. The data for the lowest concentration (leftmost curve in Figure 7) indicate that the end point was reached within a few seconds of the beginning of titrant flow, leading to an estimate for the lower limit of detection of 0.15 mM V(II).

The numeric results from that series of simulations are presented in Table 1 and in Figure 8. The titration curves for samples with pH values in the range 1.3 - 4.3 exhibited poor shapes, making it difficult to determine the end points. At $\text{pH} < 1$, they were excellent. Figure 8 shows that the instrument calibration is linear, with a slight bias toward low values at the smallest concentrations for the reason discussed above.

The completed titrimeter was evaluated at the Brunswick-2 plant of the Carolina Power and Light Company in February, 1996, following the operational procedure given in Appendix B. The contractor, PN Services, performed an NP-LOMI-NP-LOMI decontamination of the suction side of the recirculation system. The titrimeter was successfully employed to monitor vanadous ion concentrations during the second LOMI from the initial concentration of 4.5 millimolar to the last analysis of 0.03 millimolar, after which the LOMI step was terminated. The data which were secured during the plant evaluation are presented in Table 2 and in Figure 9. The low initial reading is due to incomplete mixing in the piping system. Several momentary increases in V(II) concentration evident in the data coincided in time with changes which the contractor made in circulation in the piping system. The concentration values and their decrease with treatment time are completely in accord with expectations.

Table 1
Titrimeter Test Results

Run No.	V(II) Added mmole	Pic/V Ratio	pH	V(II) Found mmole	Comments
951017A	0.133	6.7	0.8	0.12	
951017B	0.15	6.0	4.3	~0.14	Poor curve
951017C	0.18	0.0	0.8	0.18	
951017D	0.12	0.0	1.3	0.12	Poor curve
951017E	0.091	19.8	0.9	0.08	
951017F	0.15	6.0	0.8	0.15	
951017G	0.19	4.7	0.7	0.18	
951018A	0.209	9.6	0.9	0.195	
951018B	0.254	2.0	0.7	0.19	
951018C	0.202	0.0	0.6	0.19	
951018D	0.226	4.0	2.2	0.24	Poor curve
951018E	0.098	10.2	0.7	0.085	
951018F	0.036	27.8	0.7	0.032	
951018G	0.028	8.7	0.6	0.021	
951018H	0.009	28.0	0.7	<0.002	

TABLE 2
BRUNSWICK-2 LOMI

February 18, 1996

<u>Time</u>	<u>Titration Time, sec</u>	<u>V(II) Conc., mM/L</u>
0225	74	2.22
0245	146	4.38
0255	145	4.35
0305	141	4.23
0315	143	4.29
0325	135	4.05
0330	136	4.08
0340	117	3.51
0348	100	3.00
0355	103	3.09
0410	72	2.16
0420	39	1.17
0435	41	1.23
0445	24	0.72
0457	18	0.54
0513	12	0.36
0528	11	0.33

Figure 2 - Titration Apparatus

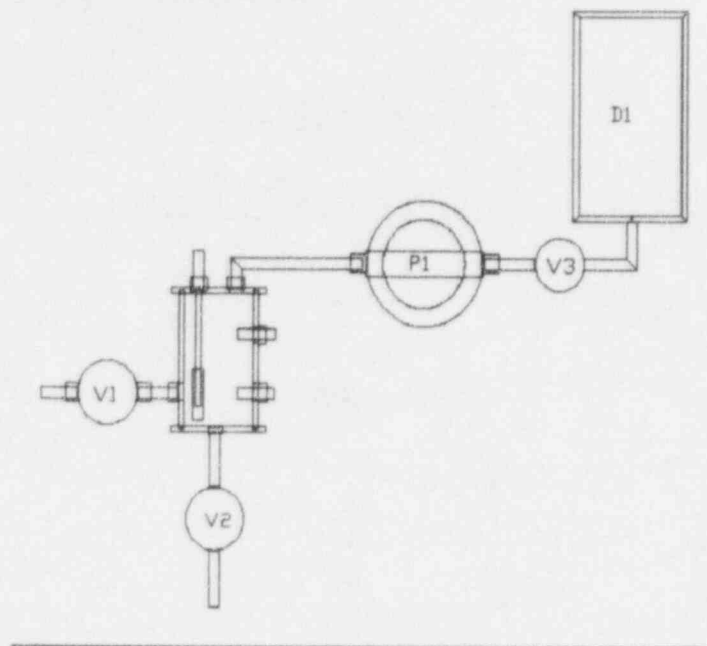


Figure 3 - ORP Titration of Vanadous and Vanadic Ion

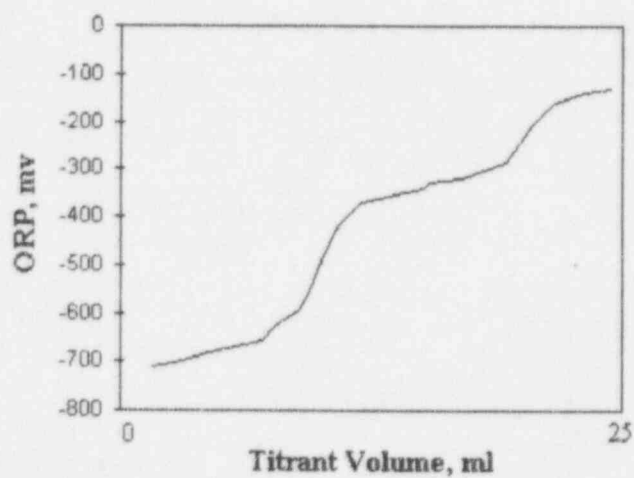


Figure 4 - Electrode Lag and Mixing Noise

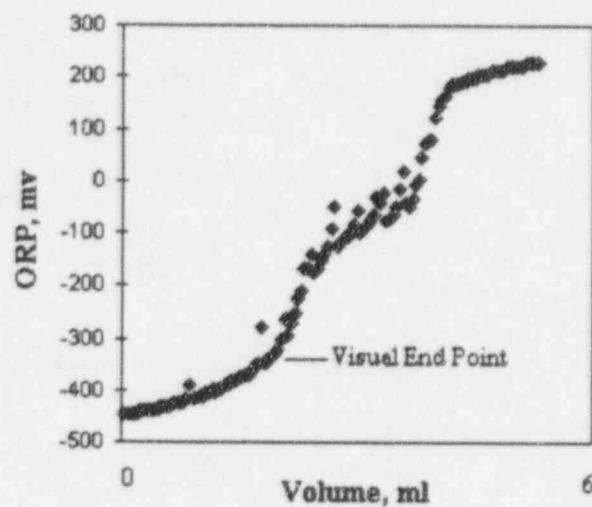
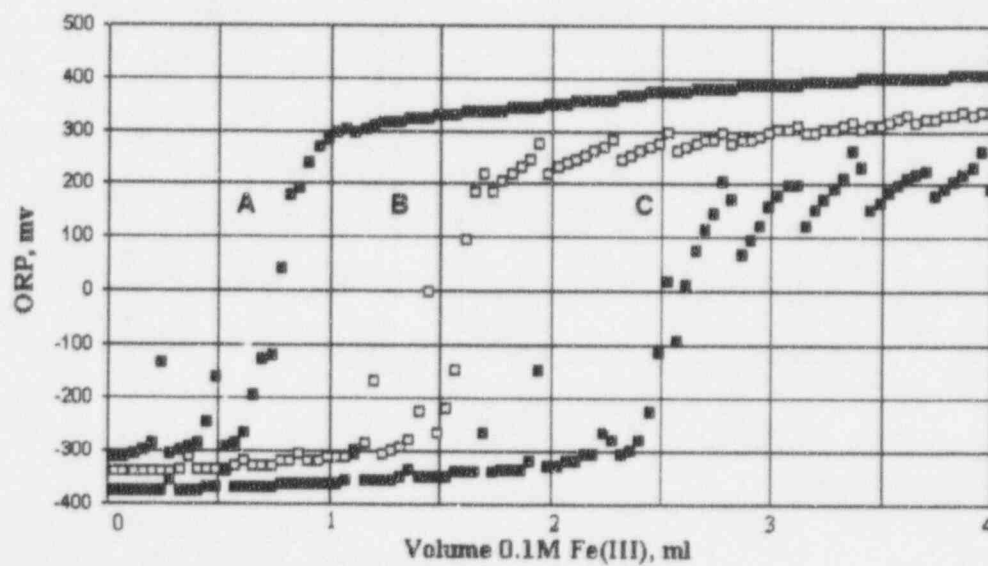


Figure 5 - Electrode Response at Low pH



Vanadium concentration: A 0.003M B 0.006M C 0.009M

Figure 6 - Titrimeter Major Component Layout

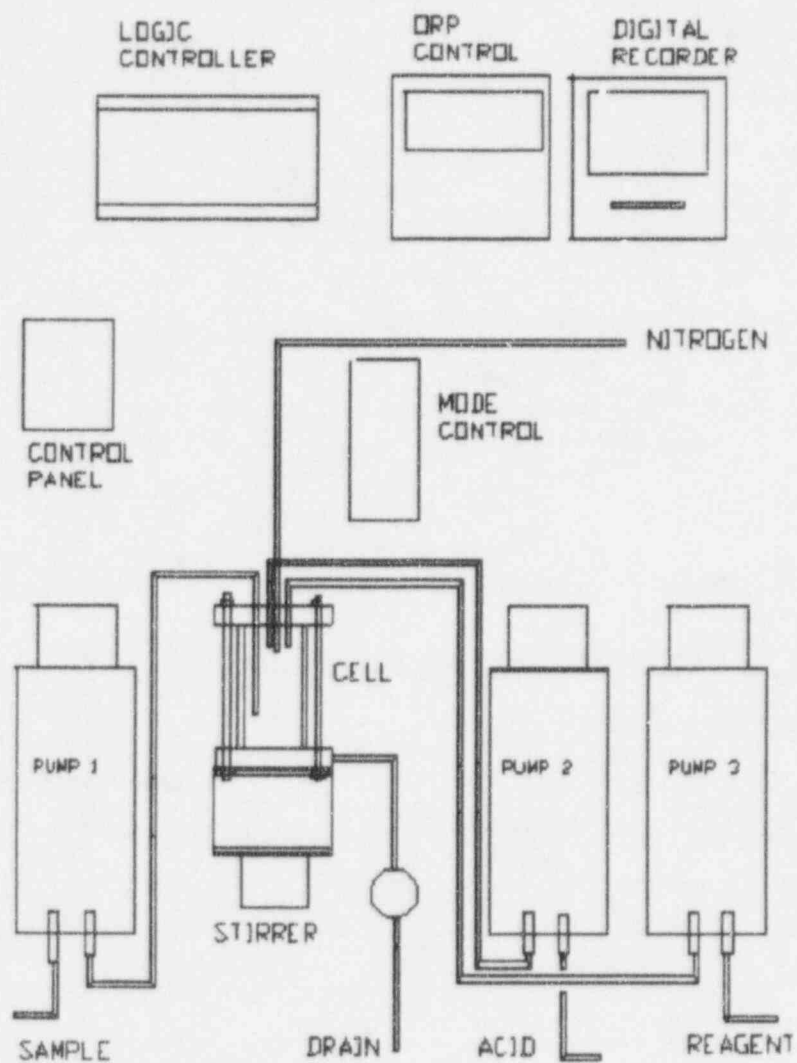
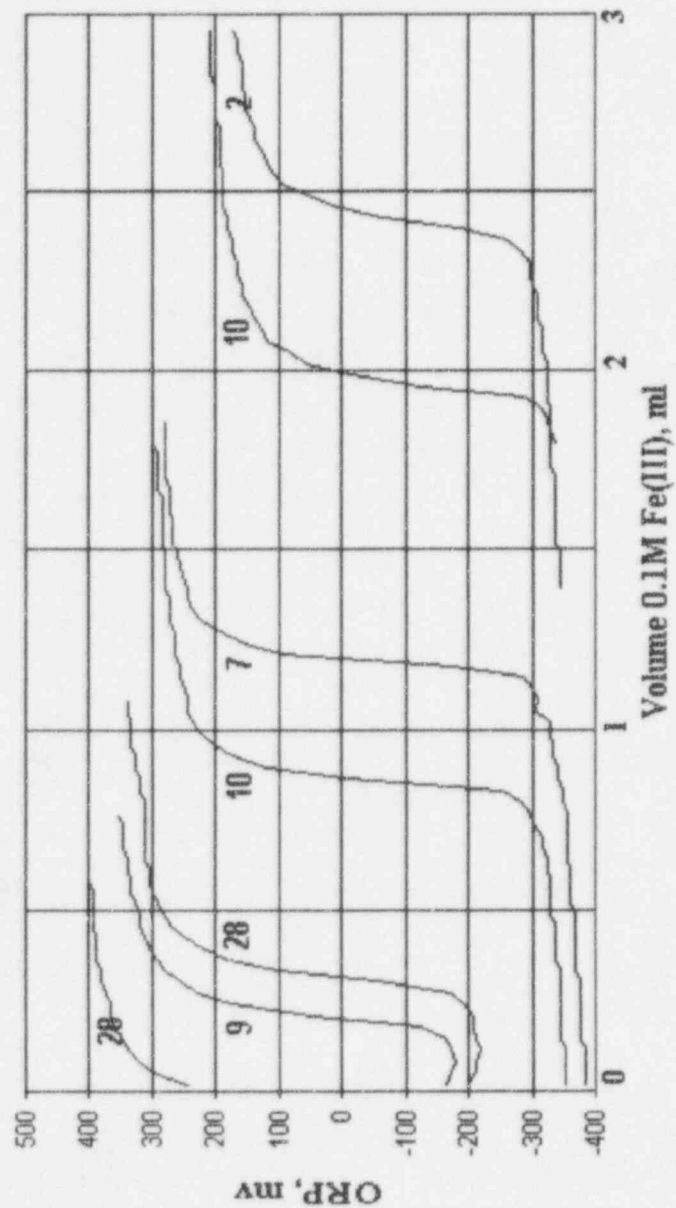


Figure 7 - Representative Titration Curves



Picolinate/Vanadous Ratios Shown Adjacent to Curves

Figure 8 - Titrimeter Evaluation

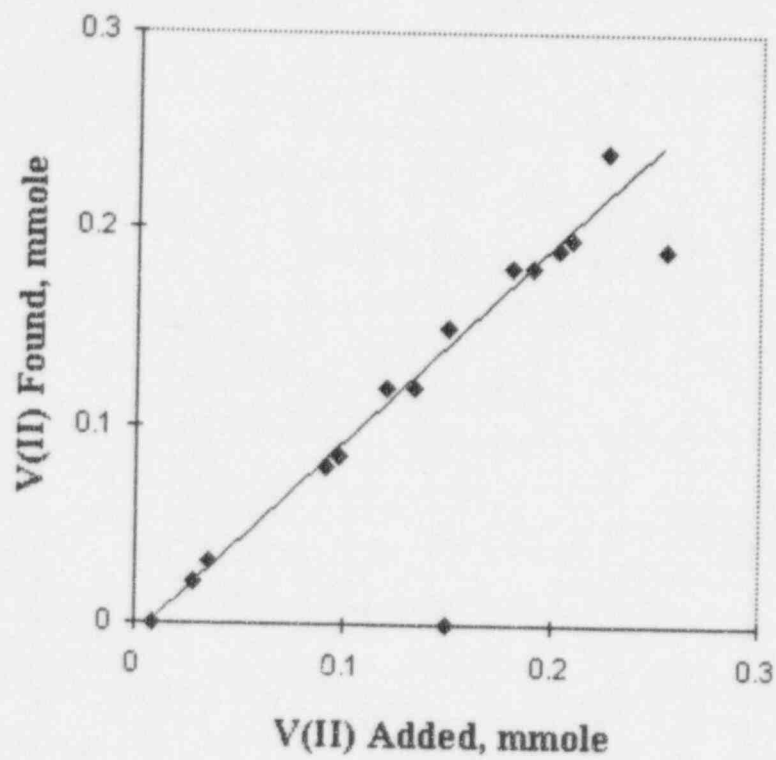
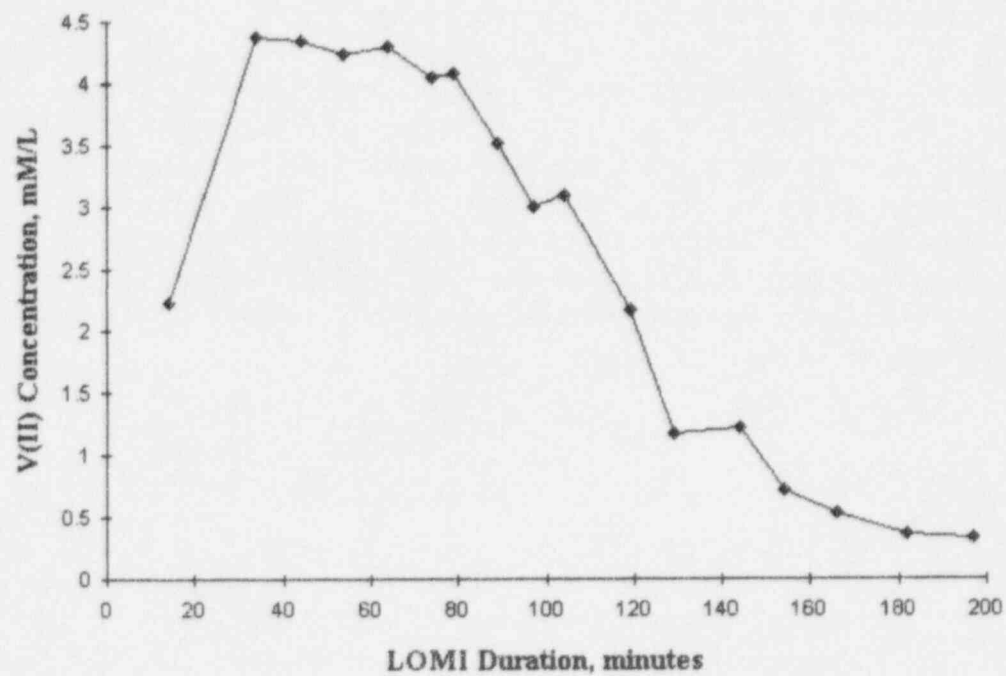


Figure 9 - Brunswick-2 LOMI On-line Vanadium Analysis



CONCLUSIONS

The colorimetric technique utilizing the absorption of light by the vanadous picolinate complex is very sensitive and convenient to implement in an on-line instrument. However, it was found that there is the possibility that a variable and unpredictable quantity of light absorbing material may be present during or after the decontamination. As a result, the colorimetric method is poorly suited for on-line analysis of V(II) during LOMI decontamination.

The titrimetric method works very well and provides excellent sensitivity and accuracy. The use of low pH provides two benefits. It greatly reduces the ORP electrode response time, making it possible to perform the titrations rapidly. It also suppresses the oxidation of V(III) to V(IV), thereby providing an unambiguous result and permitting more latitude in the instrument design. The repetitive, rather than continuous, nature of the titration analysis was not an important factor since the cycle time of several minutes was much shorter than the duration of the LOMI procedure.

REFERENCES

1. D. Bradbury, M.E. Pick, M.G. Segal, R.M. Sellers, T. Swan, N.R. Large, and J. Monahan, "Experience of Plant Decontamination with LOMI Reagents", in *Water Chemistry of Nuclear Reactor Systems*, British Nuclear Energy Society, London, Vol 3, p.203, 1980.
2. M.G. Segal and R.M. Sellers, *J. Chem. Soc. Faraday I*, p.1149, 1982.
3. R.J.H. Clark, *The Chemistry of Titanium and Vanadium*, Elsevier Publishing Company, New York, NY, 1968.
4. *Chemical Analysis of Vanadous Formate, Method 1-053*, Monarch Analytical Laboratories, Inc., P.O. Box 2990, Toledo, OH, 1992.
5. I.M. Kolthoff and R. Belcher, *Volumetric Analysis*, Interscience Publishers, Inc., New York, NY, Volume 3, 1957.
6. S.C. Furman and C.S. Garner, "Absorption Spectra of Vanadium (III) and Vanadium (IV) Ions in Complexing and Non-complexing Media", *J. Am. Chem. Soc.*, 72, p.1785, 1950.

7. T.W. Newton and F.B. Baker, "The Kinetics of the Reaction between Vanadium (II) and Vanadium (IV)", *J. Phys. Chem.*, 68, p.228, 1964.
8. N. Harrick, M. Milosevic, and S. Berets, *Appl. Spectrosc.*, 45, p.944, 1991.
9. J. V. Bishop, S. Kottle and R. A. Stowe, "Analytical Methods for Vanadous Formate", Fifth EPRI Workshop on Chemical Decontamination, Charlotte, NC, June, 1993.
10. J. V. Bishop, R. A. Dutcher, M. S. Fisher, S. Kottle and R. A. Stowe, "Continuous Spectrographic Analysis of Vanadous and Vanadic Ions", Omni Tech International, Ltd., U. S. Nuclear Regulatory Commission Report NUREG CR-6047, October, 1993.
11. J. L. Smee and D. Bradbury, "Low Picolinate LOMI - Update", Fifth EPRI Workshop on Chemical Decontamination, Charlotte, NC, June, 1993.
12. Sherman Kottle, John V. Bishop, and Robert A. Stowe, "Vanadium Analysis During LOMI Decontamination", EPRI Radiation Field Control and Chemical Decontamination Conference, Tampa, FL, November, 1995.

APPENDIX A

DETERMINATION OF VANADIUM ION CONCENTRATION BY CONTINUOUS COLORIMETER

1. PURPOSE

On-line monitoring of vanadium (II) concentration during LOMI chemical decontamination.

2. SCOPE

This analytical method is suitable for the continuous, quantitative, colorimetric determination of V(II) at concentrations of 0 - 10 millimolar as a picolinate complex in LOMI solution during decontamination.

3. DEFINITIONS

LOMI - Low oxidation-state metal ion chemical decontamination procedure using vanadous formate and sodium picolinate.

Colorimetric determination - Analysis method which utilizes measurement of the absorption of visible light by a form of the substance to be detected.

4. PREREQUISITES

The solution to be analyzed must be available at up to 15 milliliters/minute at a pressure in the range 5 -100 psig and a temperature in the range of 65 - 85 F. A suitable waste reservoir must be available capable of accepting the instrument effluent stream. If the sample stream is outside the desired temperature limits, an external heat exchanger should be employed to adjust the temperature.

5. PRECAUTIONS

The sample stream and instrument internals must be kept free of oxygen which would consume part or all of the V(II). The use of stainless steel tubing for connections is recommended over the use of plastic or elastomer tubing which may be permeable to atmospheric oxygen. The sample line should be kept short to avoid analysis lag-time.

Proper consideration should be given to the possible radioactive nature of the sample stream. The sample path volume within the instrument is approximately 20 milliliters. At conclusion of use, the sample path should be drained, washed and checked for residual radioactivity by means of a suitable monitor.

8. PROCEDURE

Materials and equipment

Colorimeter - On-stream colorimeter by Lake Service Company, Lake Jackson, TX 77566.

Sodium picolinate reagent - Prepared by adjusting 0.05 molar picolinic acid solution to pH 4.5 by adding sodium hydroxide.

Reference solution - Secondary standard for instrument calibration consisting of 1% v/v aqueous solution of McCormick & Co. blue food color No. 5210007087.

Procedure

	Action
1	Connect sample inlet to source of distilled water. Connect power cable.
2	Connect nitrogen cylinder by means of a 2-stage regulator set for 5 psig outlet pressure.
3	Open the sample valve. Turn on MAIN POWER and SAMPLE PUMP.
4	After warm-up and inert gas purge of at least 15 minutes, set recorder to 0 by means of ZERO control with mode selector in ABSORBANCE position.
5	Add 1 liter (or 1 quart) of sodium picolinate solution pre-purged with nitrogen for at least 15 minutes to reagent reservoir through its filler opening.
6	Turn off SAMPLE PUMP, connect reference solution to sample inlet, and turn on SAMPLE PUMP. When recorder reaches steady reading, adjust SPAN control to achieve a reading equal to the value specified on the reference solution container.
7	Turn off SAMPLE pump, connect sample line from decontamination equipment. Turn on sample pump and commence analysis.

8	With memory card in place in the digital recorder, take data for the desired duration. The reagent reservoir should be refilled after 15 hours of use. Instrument ZERO and SPAN should be rechecked between LOMI runs if required.
9	At the conclusion of use, turn off all pumps, close valves, and disconnect incoming sample and waste lines. Connect the sample inlet to a source of water and connect the waste line to a suitable waste receiver. Open SAMPLE valve and energize the sample pump. Insure that there is enough source pressure that the sample bypass rotameter can also be flushed.
10	Check the instrument for radioactivity. Dilute nitric acid (1:10) may be used to assist in removing any residual activity. Continue cleaning until instrument is acceptable for release by the host plant. The radioactive waste should be handled and disposed of in accordance with host plant procedures.

9. QUALITY ASSURANCE CONSIDERATIONS

Vanadous ion concentration may be read directly from the digital recorder at any time during operation in millimoles/liter. The data may also be saved by downloading to a provided memory card following the procedures given in the recorder operating manual.

Precision and accuracy - Precision and accuracy are expected to be the larger of +/- 5% of reading or 0.1 millimole/liter. The solution being tested must be substantially free of materials with light absorbance in the range 550 - 900 nm other than vanadous picolinate.

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APPENDIX B

DETERMINATION OF VANADIUM ION CONCENTRATION BY AUTOMATIC TITRIMETER

1. PURPOSE

On-line monitoring of vanadium (II) concentration during LOMI chemical decontamination.

2. SCOPE

This analytical method is suitable for the repetitive, quantitative, titrimetric determination of V(II) as a picolinate complex at concentrations of 0 - 10 millimolar in LOMI solution during decontamination.

3. DEFINITIONS

LOMI - Low oxidation-state metal ion chemical decontamination procedure using vanadous formate and sodium picolinate.

Titrimetric determination - Analysis method which utilizes measurement of the quantity of a standard reagent which is required to quantitatively react with the sample.

4. PREREQUISITES

The solution to be analyzed must be available at a pressure in the range 1 - 50 psig and a temperature in the range of 65 - 95 °F. A waste reservoir must be available capable of accepting 25 - 40 milliliter quantities of solution from each analysis by gravity flow.

5. PRECAUTIONS

The sample stream of LOMI solution and the titration cell must be kept free of oxygen which would interfere with the analysis. The purge gas connection should be supplied with inert gas (nitrogen, argon, or helium) at a pressure of 5 - 10 psig. The liquid sample line should be kept short to avoid analysis lag time.

Proper consideration should be given to the possible radioactive nature of the sample stream. At a typical LOMI solution activity of 1 microcurie per milliliter, the instrument will contain less than 50 microcuries of radioactivity at any time.

6. PROCEDURE

Materials and equipment

Analyzer - On-stream titrimeter manufactured by Lake Service Company. Instrument utilizes oxidation-reduction potential (ORP) measurement to detect titration end point.

Titration reagent - 0.1 molar ferric ammonium sulfate solution.

pH control - 10% sulfuric acid solution.

Procedure

	Action
1	Position instrument on stand in area where sample connection is available.
2	Connect power cable to 120 VAC, 1 ph, 15 amp outlet.
3	Connect nitrogen cylinder to instrument by means of a 2-stage regulator set for 5 psig outlet pressure.
4	Turn on main power switch and permit warm-up and inert gas purge to proceed for at least 15 minutes.
5	Connect reagent bottles to Pumps 3 and 4.
6	Connect sample line tubing to instrument. Connect waste line to waste reservoir. Open sample line block valve. Verify that there are no leaking connections.
7	Manually initiate a titration by means of the push button switch to flush sample and reagent lines. Repeat until no air bubbles are visible entering cell.
8	When circulation of the vanadous formate solution is started by the decon operator, begin repetitive analysis.
9	Observe several titration curves on recorder to verify proper operation.
10	At the conclusion of the LOMI, close the sample line shut-off valve and disconnect the tubing.
11	Flush the instrument sample path by running distilled water as the sample. Monitor the cell and Pump 1 for radioactivity and continue to run on water as necessary to meet host plant release standards.
12	Dispose of the instrument waste by returning it to the ion exchange beds.

7. QUALITY ASSURANCE CONSIDERATIONS

Vanadous ion concentration may be estimated from the digital recorder at the completion of any titration cycle. The data may be saved by downloading to a provided memory card following the procedure given in the recorder operating manual.

Precision and accuracy - Precision and accuracy are expected to be the larger of $\pm 5\%$ of reading or 0.1 millimole/liter. No interference is expected from other metals which are normally present.

8. ACKNOWLEDGMENT

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