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THE SIMULTANEOUS ANALYSIS OF
URANIUM AND NITRATE

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THE SIMULTANEOUS ANALYSIS OF URANIUM AND NITRATE

D. T. Bostick

ABSTRACT

A direct spectrophotometric method has been developed for the determination of 20-200 g/l of uranium in the presence of 3-5 M nitric acid. A dual-wavelength analysis is used to eliminate the enhancing effect of nitrate ion on the uranium visible spectra. The precision and accuracy of the simultaneous analysis of uranium and nitrate were compared using combinations of the four uranium wavelength maxima, occurring at 426, 416, 403 and 359 nm. Calculations based on 426 and 416 nm data yielded the most accurate results. The calculated relative standard deviation of uranium and nitrate concentrations was 5.4% and 15.5%, respectively. The photometric procedure is slightly affected by temperature; an increase of one degree centigrade results in a 0.2 g/l overestimation of uranium concentration. Because the method is non-destructive, it is directly applicable to the continuous in-line analysis of dissolved uranium in aqueous fuel reprocessing streams.

1. INTRODUCTION

Accurate in-line analysis of uranium in process streams is essential for real time (continuous) process control. Real time process control can enhance plant operations by providing: 1) continuous processing to achieve greater production throughput; 2) a higher quality product with reduced losses and rework through continuous process optimization; and 3) a greater degree of process safety which is achievable through material

balance control and better operator awareness because of real time analysis. Present in-line uranium monitors are based on the direct colorimetric measurement of the uranyl ion at 416 nm. The in-line monitors generally incorporate a dual-beam optical system to reduce errors resulting from sensor cell window fouling and sample turbidity (1-4). However, these uranium monitors are subject to errors as great as 15-20% due to variations in nitric acid concentration and temperature, in addition to turbidity (2). Bhargava et al. (5) investigated the observed variability in uranium analysis and found the absorption of uranium to be linearly proportional to nitric acid concentration. Erickson and Slansky (6) also noted this linear relationship and suggested that uranium and nitric acid might be simultaneously analyzed using a multi-wavelength approach. However, their subsequent uranium monitor did not incorporate this proposal.

This report further investigates the influence of nitric acid on the uranium absorption spectra. A dual-wavelength procedure for uranium was developed based on these results. The modified photometric method improves the accuracy of the existing in-line uranium monitors by compensating for fluctuations in nitric acid concentration and temperature. The improved accuracy is demonstrated over a wide nitrate concentration range. An error analysis of the procedure is presented.

2. EXPERIMENTAL

Uranium standards were prepared from serial dilutions of a 520.1 g/l depleted uranium standard in 0.001 M nitric acid. The acidity of the standards was adjusted by the addition of appropriate volumes of reagent grade, concentrated nitric acid. Solid sodium nitrate was

used to determine the effect of nitrate ion on the uranium spectrum. Dilutions of 70% perchloric acid were used to study the affect of hydrogen ion concentration.

Photometric measurements were made using a Cary Model 14 recording spectrophotometer and 0.1 cm quartz cell. Samples were analyzed vs. a water blank. A Beckman T_M Analyzer and DB-G spectrophotometer were used to record the absorbance change of an 104.1 g/l uranium standard as the sample temperature was linearly increased from 50 to 80°C at 2°C/min. The thermistor of the T_M analyzer was calibrated prior to the temperature study.

3. RESULTS AND DISCUSSION

Typical output streams from the Purex fuel recycling process contain from 20-200 g/l uranium, in addition to approximately 4 M nitric acid and 1 M nitrate. The nitric acid and nitrate concentrations may fluctuate within one molar unit of these values. Visible scans of uranium standards containing varying concentrations of acid and nitrate were evaluated in order to develop a uranium monitor which could accurately operate under these variable process stream conditions.

3.1 Effect of Nitric Acid, Nitrate, and Hydrogen Ion on the Uranium Spectra

The visible uranium spectrum contains four major absorption maxima, occurring at 426, 416, 403, and 359 nm (Figure 1). Calibration curves, obtained at constant nitric acid and nitrate concentrations, are linear with uranium concentration at each of these wavelengths (Figure 2). The

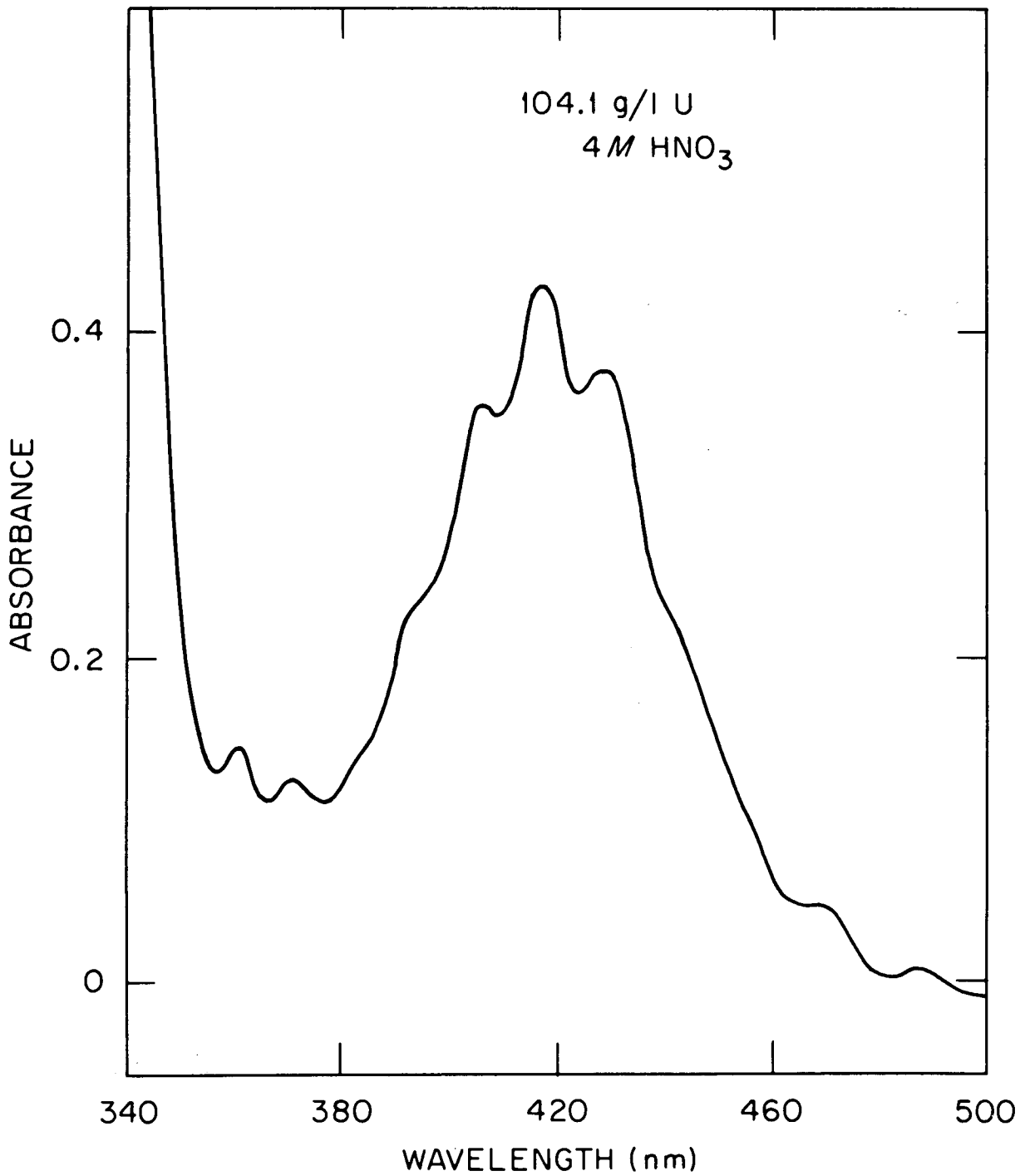


Figure 1. Uranium Visible Spectra

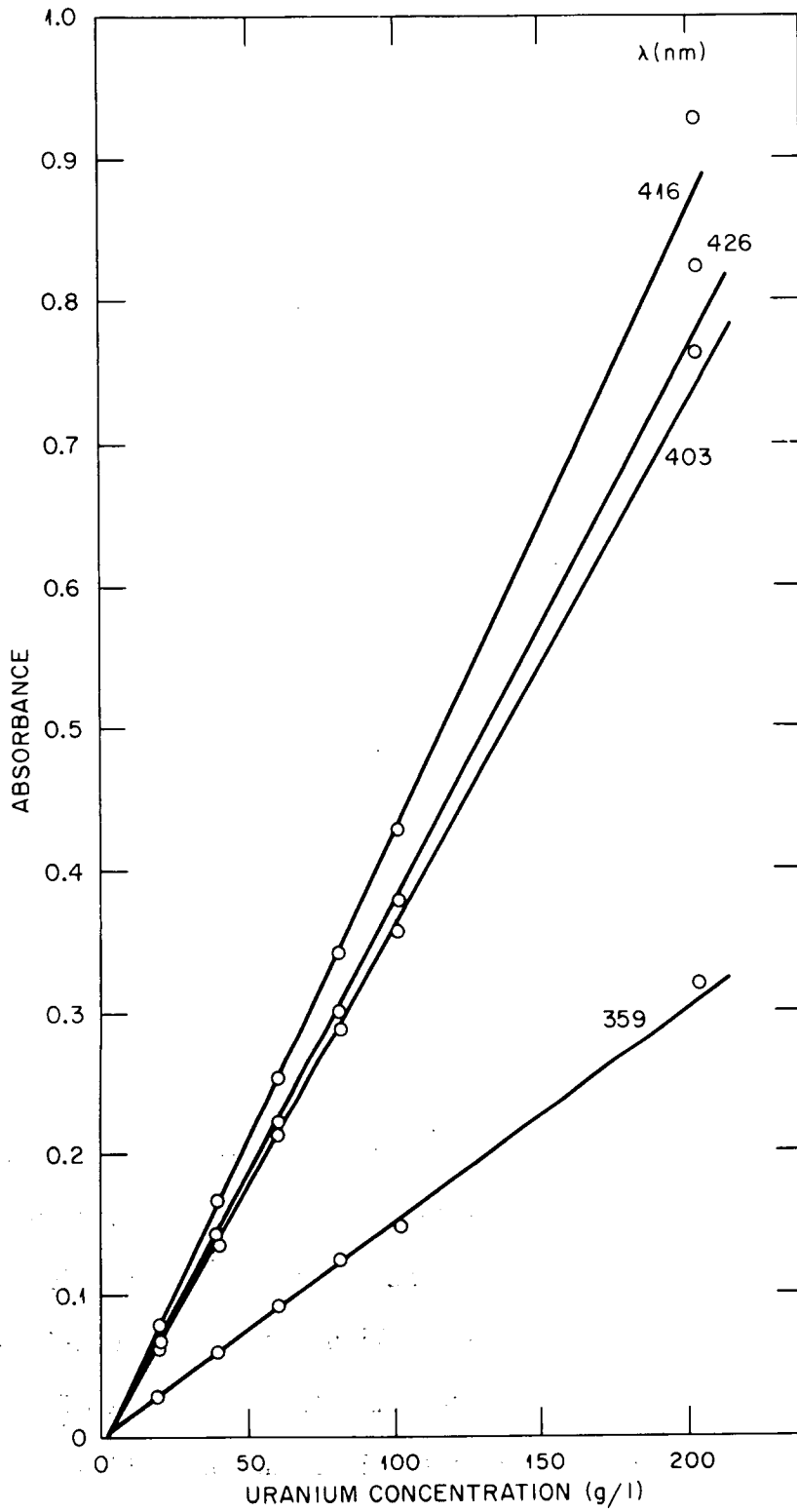


Figure 2. Uranium Calibration Curves at Constant Nitrate Concentration

416 nm absorption line possesses the greatest sensitivity, whereas the 359 nm line exhibits a sensitivity which is only one-third of this value.

The visible spectra of uranium change significantly as the concentration of nitric acid is increased. Figure 3 illustrates spectra in which uranium concentration is held constant and nitric acid is increased from 2 to 6 M. The absorption at all wavelengths increases with nitric acid concentration. The 403, 426, and 416 nm uranium triplet becomes less defined, as the 426 nm line broadens into a shoulder. As discussed previously, the absorption at the wavelength maxima is linearly proportional to nitric acid concentration (Figure 4). The 426 nm line appears to be most affected by nitric acid.

It becomes obvious from Figures 3 and 4 that uranium analysis, based solely on the absorption measurement at 416 nm, is considerably influenced by the fluctuations in nitric acid concentration as commonly encountered in the reprocessing streams. However, since the relationship between nitric acid and uranium absorbance is linearly predictable, a means is available to compensate for the elevation in uranium absorption caused by nitric acid.

To evaluate the effect of nitric acid, scans of uranium were made in the presence of i) 2 M nitrate and ii) 2 M hydrogen ion and were compared to that obtained in the presence of 2 M nitric acid. Figure 5 represents a composite of the scans, all of which were obtained in the presence of equal quantities of uranium. In the absence of hydrogen ion, the uranium spectrum consists of a single broad absorption band; broad uranium absorption is greatly suppressed and the characteristic uranyl triplet emerges in the presence of hydrogen ion. If nitrate is

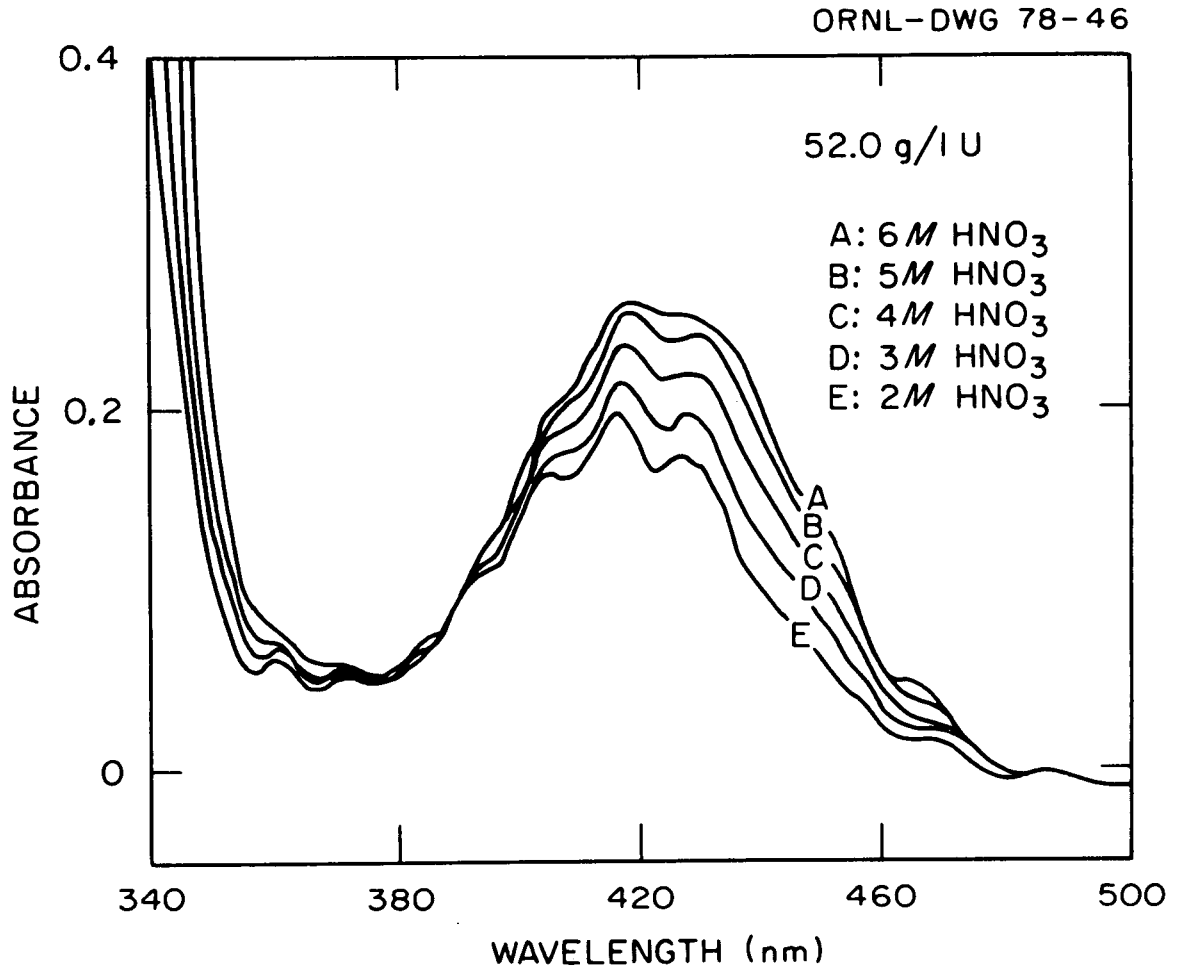


Figure 3. Uranium Visible Spectra at Varying Nitric Acid Concentration

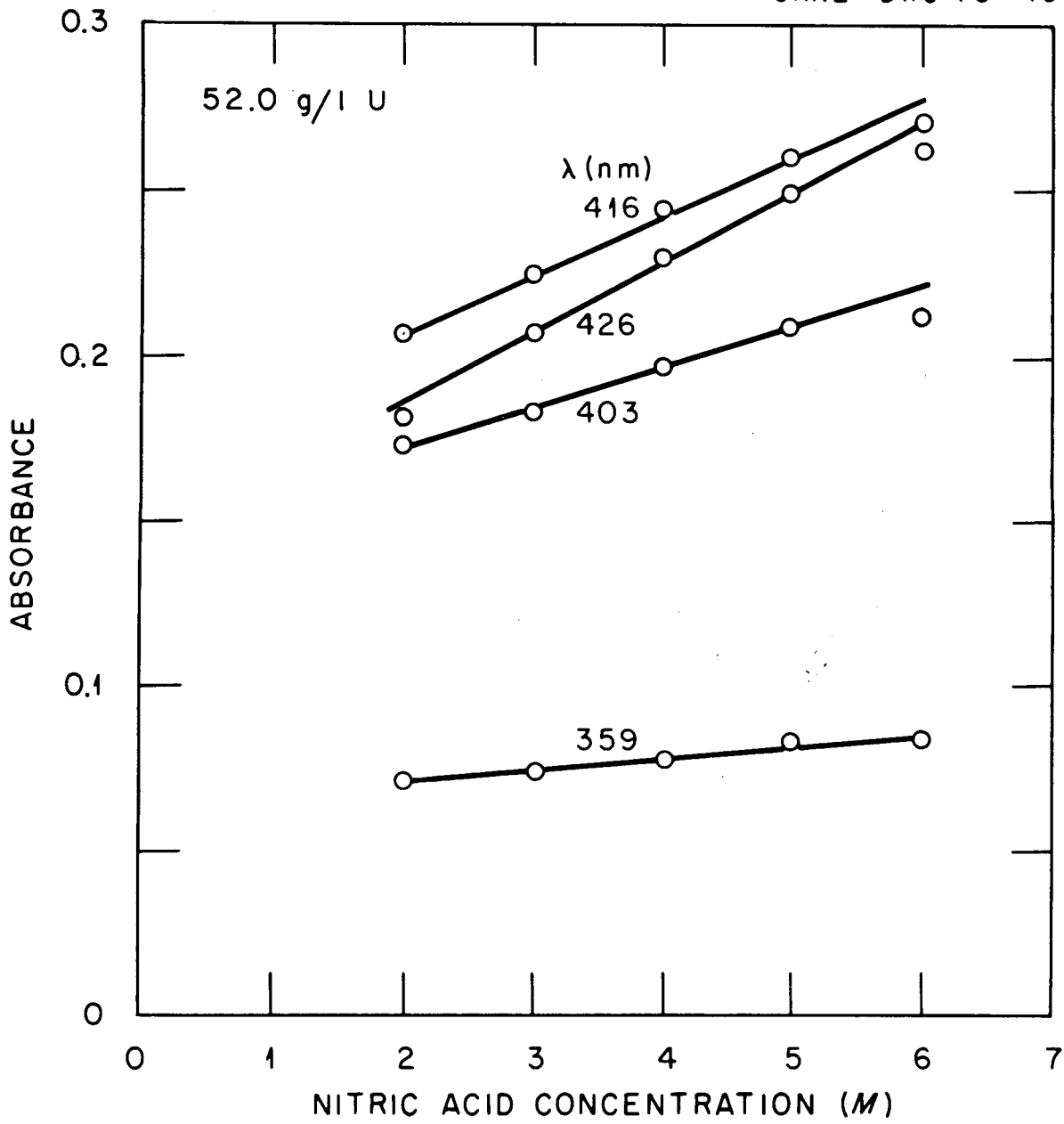


Figure 4. Effect of Nitric Acid on Uranium Absorption

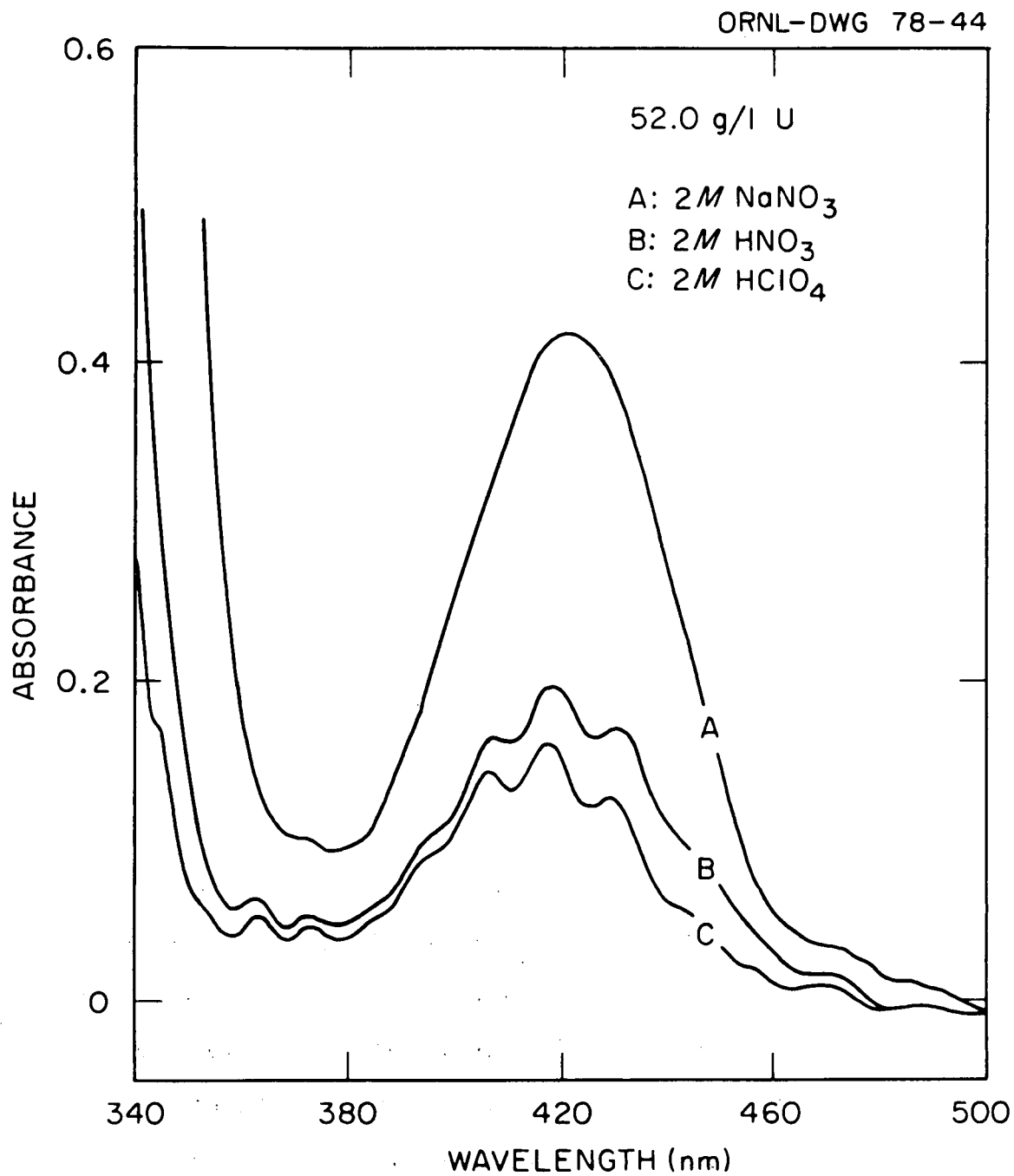


Figure 5. Uranium Spectra in the Presence of Nitrate, Perchloric Acid and Nitric Acid

additionally present, as with nitric acid, the uranyl extinction coefficients increase. The scans suggested that further studies must be performed in the presence of at least a minimum amount of hydrogen ion in order to observe the behavior of the uranyl absorption triplet.

The relationship between nitrate and uranyl absorption was thus studied in the presence of 2 M HNO_3 . Solid sodium nitrate was then added to the acidified 52 g/l U samples to adjust the total nitrate concentration within a 2-6 molar range. At constant hydrogen ion concentration, the uranium absorption linearly increases with total nitrate concentration at each of the wavelength maxima (Figure 6). The slopes of the curves obtained with varying nitrate were found to be identical to those obtained with varying nitric acid. This behavior indicates that the elevation in uranyl absorption is primarily due to the presence of nitrate rather than hydrogen ion.

This conclusion was confirmed by analyzing a series of samples in which uranium and nitrate concentrations were held constant and hydrogen ion was varied. The samples contained 52 g/l U, 2 M HNO_3 and appropriate volumes of 70% perchloric acid to adjust the hydrogen ion concentration to within a 2-6 molar range. As observed in Figure 7, the results are slightly curvilinear for all but the 359 nm data. In actual process streams the acid concentration will only vary between 3-5 molar. Therefore, the accuracy of the uranium monitor should not be significantly altered by the slight absorbance changes which occur within this acidity range.

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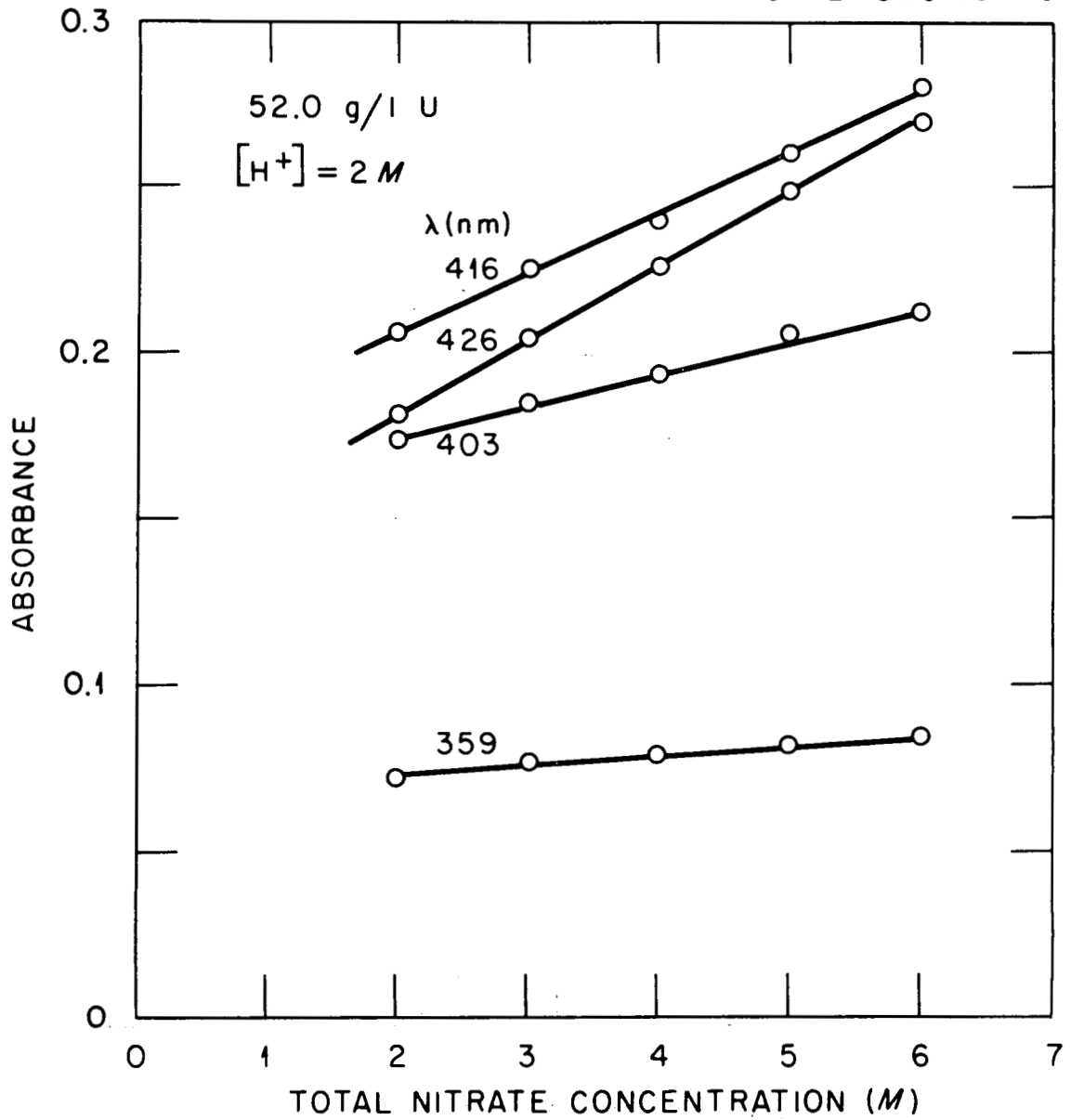


Figure 6. Effect of Nitrate on Uranium Absorbance

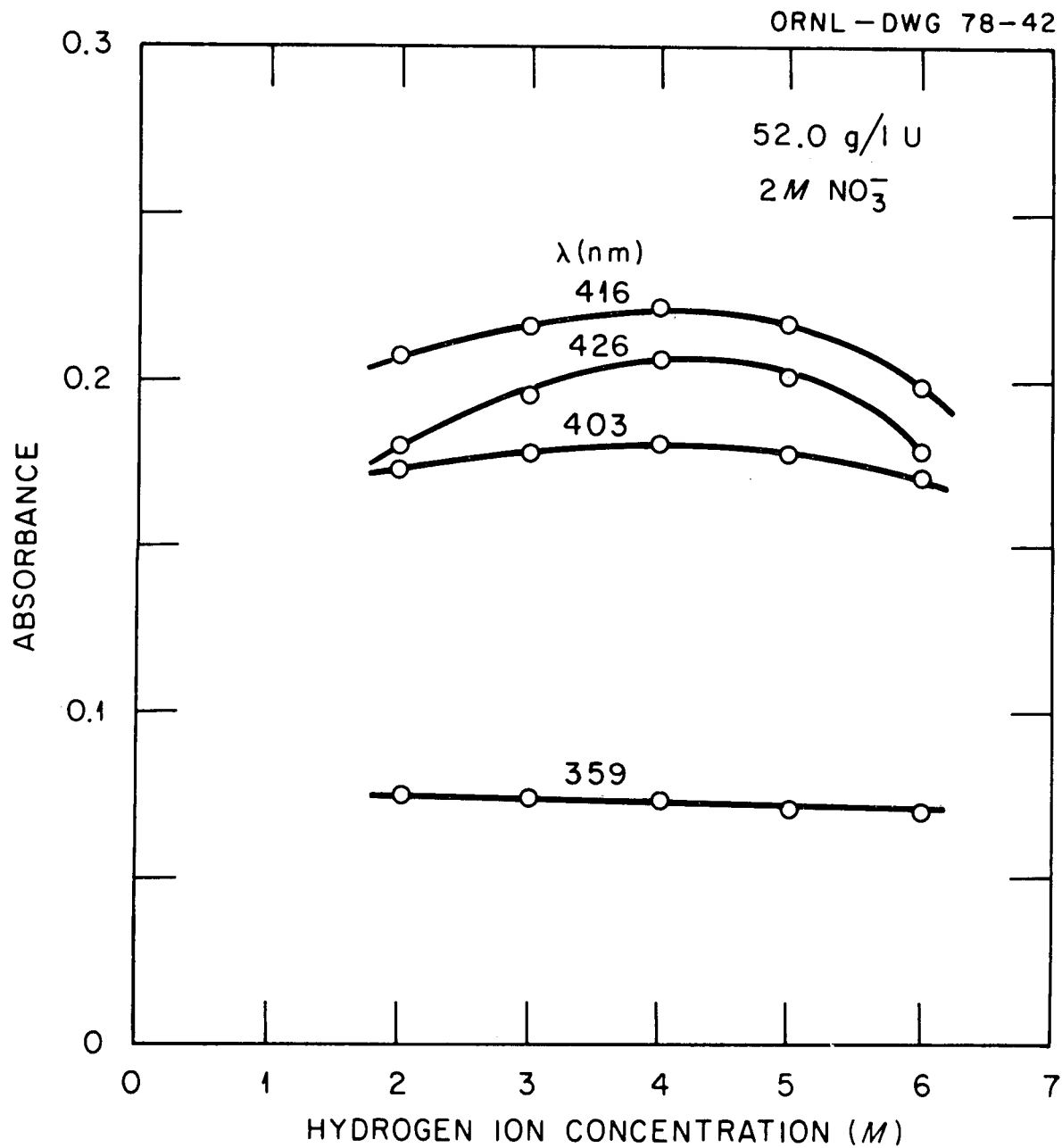


Figure 7. Effect of Hydrogen Ion on Uranium Absorbance

3.2 Derivation of the Uranium Calibration Equation

The relationship between nitrate and uranyl absorption was additionally investigated as a function of uranium concentration. A series of uranium standards was prepared in varying concentrations of nitrate. The uranyl absorption at 416 nm is plotted vs. nitrate concentration in Figure 8 for each of the five sets of uranium standards. The graph demonstrates that uranyl absorbance is linear with nitrate throughout the uranium concentration range. This relationship at a given uranium concentration can be expressed in the following equation:

$$A_{416} = \frac{d(A_{416})}{d[NO_3^-]} \times [NO_3^-] + A_{416}^{\circ} \quad (1)$$

where A_{416} is the uranyl absorbance at the 416 nm maxima, $d(A_{416})/d[NO_3^-]$ is the slope of the curve, and A_{416}° is the absorbance of the uranium standard extrapolated to zero nitrate concentration. The intercept (A_{416}°) has been extrapolated from the data since the uranyl triplet does not exist without a minimum amount of hydrogen ion in the sample. Data were also obtained at the remaining uranyl wavelength maxima and also demonstrated a linear relationship with nitrate similar to that in Figure 8. Analogous equations similar to the above can also be written for each set of uranium standards at each wavelength.

The uranium concentration appears to influence the magnitude of both $d(A_{416})/d[NO_3^-]$ and A_{416}° values as seen in Figure 8. The exact proportionality can be evaluated by plotting $d(A_{416})/d[NO_3^-]$ and A_{416}° vs. the uranium concentration. The relationship between $d(A_{416})/d[NO_3^-]$ and uranium concentration is illustrated in Figure 9. Similar data are

$$A_{\lambda} = \frac{d(A_{\lambda})}{d[\text{NO}_3^-]} \times [\text{NO}_3^-] + A_{\lambda}^0$$

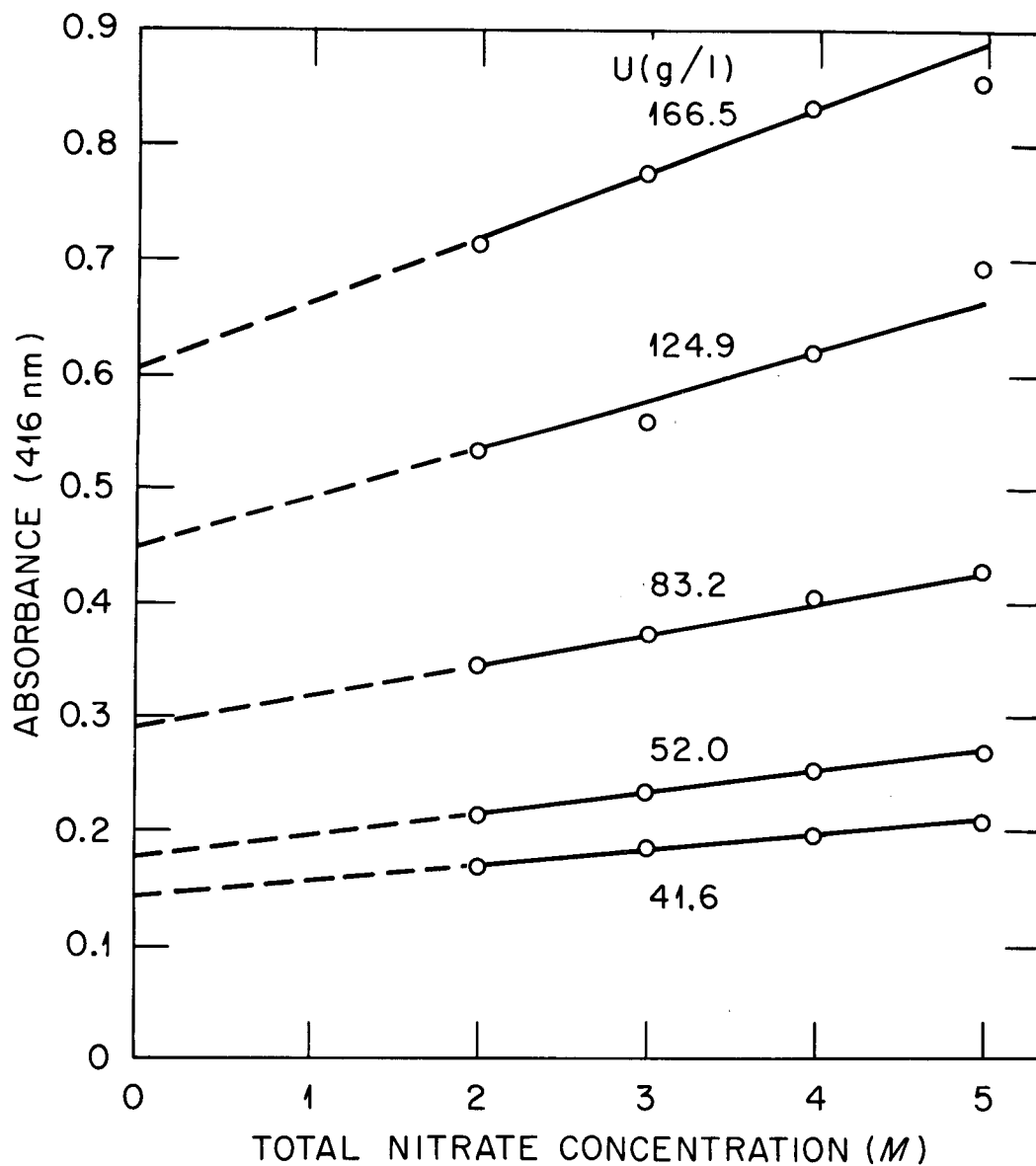


Figure 8. Effect of Nitrate at Various Uranium Concentrations

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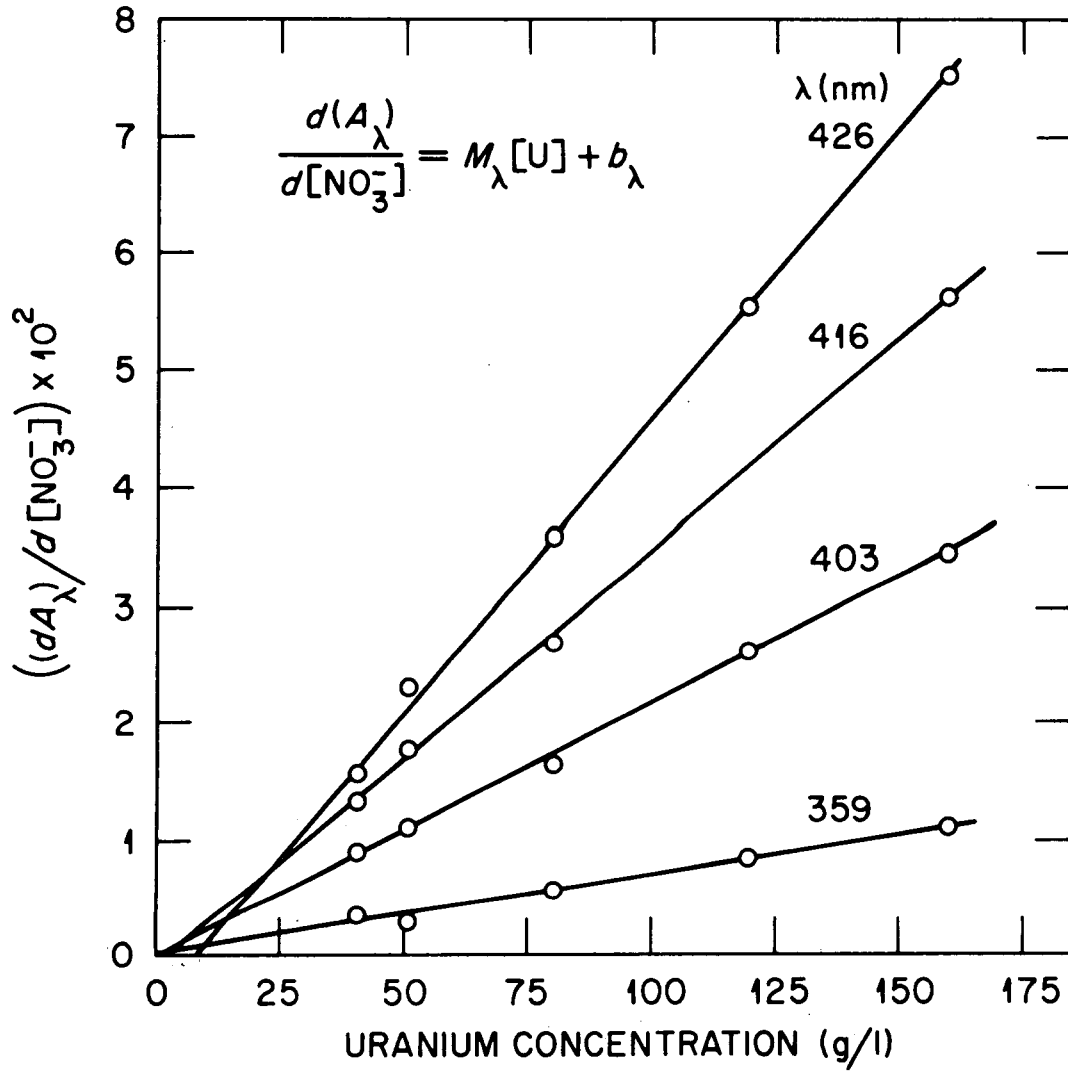


Figure 9. $d(A_\lambda)/d[NO_3^-]$ versus Uranium Concentration

shown for the other wavelengths. The slope of the 416 nm data (Figure 9) can be represented by the proportionality constant, M_{416} , in the following equation:

$$d(A_{416})/d[NO_3^-] = M_{416} [U] + b_{416}. \quad (2)$$

The value, b_{416} , is the intercept of the 416 nm data. Identical relationships can be written in the form of equation 2 for the rest of the uranium wavelengths.

A plot of A_{416}° vs. uranium concentration (Figure 10) permits the computation of the proportionality constant N_{416} such that

$$A_{416}^{\circ} = N_{416} [U] + c_{416}. \quad (3)$$

The parameter, c_{416} , represents a minor correction for a non-zero intercept in Figure 10. Similarly, N_{426} , N_{403} , and N_{359} can also be calculated graphically from the remaining curves presented in Figure 10.

Combining equations 1, 2, and 3 thus completely describes the effect of nitrate ion on uranium absorption at 416 nm:

$$A_{416} = (M_{416} [U] + b_{416}) [NO_3^-] + N_{416} [U] + c_{416}. \quad (4)$$

The quantity $(N_{416} [U] + c_{416})$ represents the absorbance of uranium at zero nitrate concentration and the value $(M_{416} [U] + b_{416}) [NO_3^-]$ represents the elevation in uranyl absorbance due to the nitrate ion. Because the absorbance due to nitrate is only a fraction of the initial uranium absorbance and b_{416} is much smaller than $M_{416} [U]$, the 416 nm calibration equation may thus be simplified to:

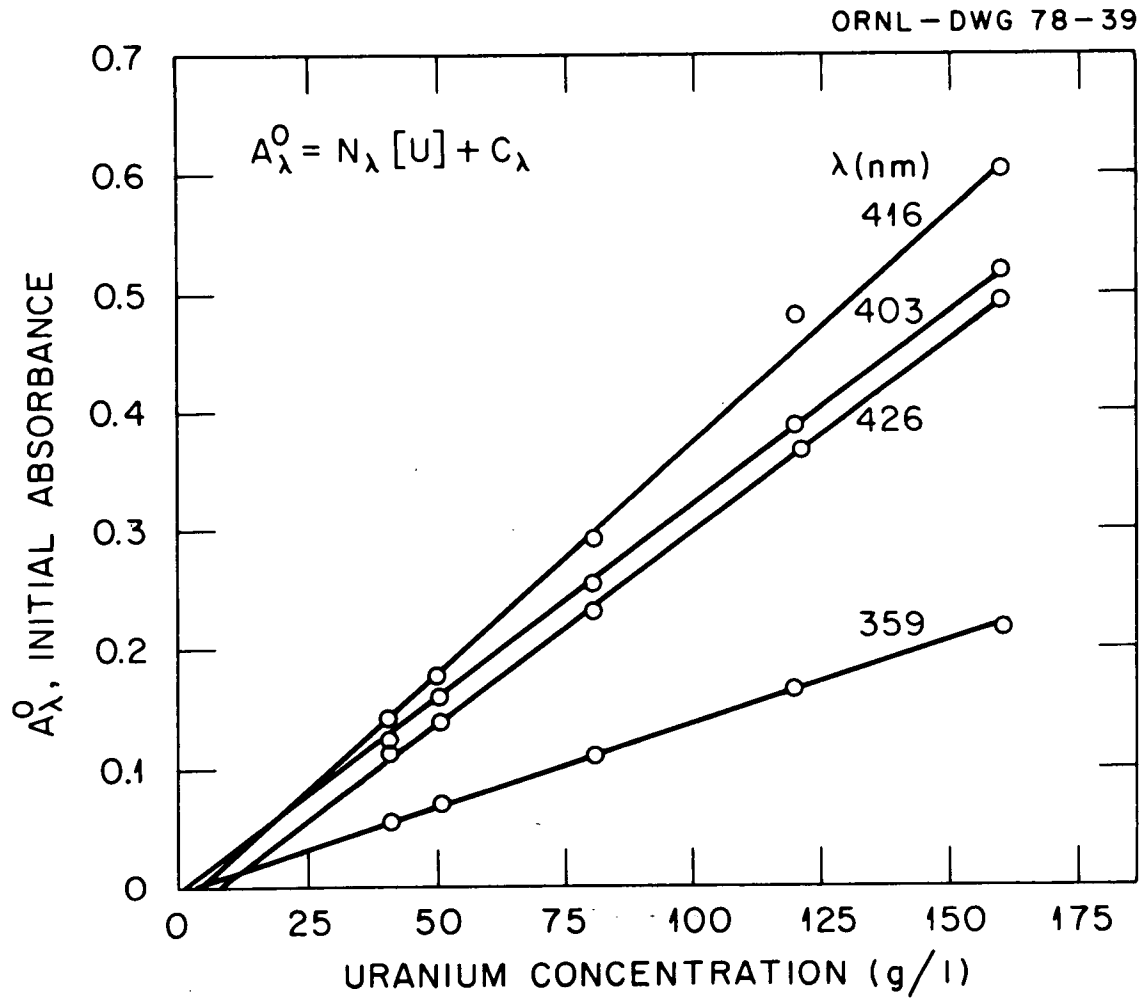


Figure 10. Initial Absorbance (A_{λ}^0) versus Uranium Concentration

$$A_{416} = M_{416} [U] [NO_3^-] + N_{416} [U] + c_{416}, \quad (5)$$

or, in general,

$$A_{\lambda} = M_{\lambda} [U] [NO_3^-] + N_{\lambda} [U] + c_{\lambda}. \quad (6)$$

Table 1 summarizes the uranium calibration equations for each wavelength maxima and includes the numerical values for the associated constants.

3.3 Simultaneous Analysis of Uranium and Nitrate

A simultaneous analysis of uranium and nitrate is possible, since the relationship of uranium and nitrate concentrations is known for at least two wavelengths. The concentrations can be calculated for a particular sample in terms of the absorbance readings taken at any two of the four uranyl maxima by combining two calibration equations:

$$[U] = \frac{M_2(A_1 - c_1) - M_1(A_2 - c_2)}{M_2N_1 - M_1N_2} \quad (7)$$

and

$$[NO_3^-] = \frac{N_2(A_1 - c_1) - N_1(A_2 - c_2)}{M_1(A_2 - c_2) - M_2(A_1 - c_1)}. \quad (8)$$

The subscripts in the above equations represent the respective absorbance readings and constants of the two wavelength maxima. Such a dual-wavelength analysis minimizes the overestimation of uranyl concentration due to nitrate ion. This is achieved by effectively calculating uranium

TABLE 1

Uranium Calibration Equations

$$A_{\lambda} = M_{\lambda} [U] [NO_3^-] + N_{\lambda} [U] + C_{\lambda}$$

$$A_{416} = 3.41 \times 10^{-4} [U] [NO_3^-] + 3.705 \times 10^{-3} [U] - 0.0147$$

$$A_{426} = 4.612 \times 10^{-4} [U] [NO_3^-] + 3.097 \times 10^{-3} [U] - 0.0220$$

$$A_{403} = 2.091 \times 10^{-4} [U] [NO_3^-] + 3.183 \times 10^{-3} [U] - 0.0092$$

$$A_{359} = 6.556 \times 10^{-5} [U] [NO_3^-] + 1.295 \times 10^{-3} [U] + 0.0023$$

concentration based on uranyl absorbance at zero nitrate concentration. The nitrate concentration is calculated from the additional absorbance increment above this initial uranyl absorbance.

The precision and accuracy in the simultaneous analysis of uranium and nitrate were compared using combinations of two of the four maxima. Uranium standards (52 g/l U) containing from 2-4 M HNO_3 and 0-4 M NaNO_3 were analyzed to determine the effect of acid and total nitrate on the calculated uranium concentration. The results are summarized in Table 2. The precision in calculating uranium was found to be best if the analysis was based on either 416 and 426 nm or 426 and 403 nm data. The calculated uranium concentration varies by only 2% when analyzed in the presence of 2-7 molar total nitrate. The accuracy in the analysis is optimal when the calculation is based on the 416 and 426 nm data; uranium analysis based on these two wavelengths is least affected by acid concentration. There is only a 0.3 g/l (0.7%) increase in the calculated uranium concentration for a one molar increase in hydrogen ion concentration. Because the 416 and 426 nm data exhibit the greatest sensitivity for both uranium and nitrate, these wavelengths were selected for use in the uranium monitor.

The accuracy in determining nitrate concentration was also compared at the various wavelength maxima. The results in Table 3 suggest that nitrate analysis is not as accurate or precise as that obtained for uranium. This behavior is to be expected since the absorbance change due to the presence of nitrate is only about 10-20% of that due to uranium. The results seem to be least accurate for high nitrate

Table 2

Calculation of Uranium Concentration in
Varying Nitrate Concentration

| Wavelengths (nm) | Experimental NO ₃ ⁻ , Added as | | Calculated [U]* (g/l) |
|---------------------|---|-----------------------------|--------------------------|
| | [HNO ₃] (M) | [NaNO ₃] (M) | |
| 416 & | 2 | 0-4 | 52.5 ± 4% |
| 426 | 3 | 0-3 | 52.9 ± 1% |
| | 4 | 0-3 | 53.2 ± 1% |
| 416 & | 2 | 0-4 | 51.8 ± 9% |
| 403 | 3 | 0-3 | 55.1 ± 5% |
| | 4 | 0-3 | 56.0 ± 4% |
| 416 & | 2 | 0-4 | 48.2 ± 6% |
| 359 | 3 | 0-3 | 54.6 ± 7% |
| | 4 | 0-3 | 57.5 ± 7% |
| 426 & | 2 | 0-4 | 51.4 ± 1% |
| 403 | 3 | 0-3 | 54.0 ± 2% |
| | 4 | 0-3 | 54.9 ± 2% |
| 426 & | 2 | 0-4 | 49.5 ± 4% |
| 359 | 3 | 0-3 | 54.0 ± 5% |
| | 4 | 0-3 | 56.3 ± 5% |

* 52.0 g/l uranium standard analyzed.

Table 3

Comparison of Experimental and Calculated Nitrate Concentration

| <u>Wavelengths (nm)</u> | <u>Experimental Total Nitrate</u> | <u>Calculated Total Nitrate</u> |
|-----------------------------|---------------------------------------|-------------------------------------|
| 416 & 426 | 2 | 1.96 (1)* |
| | 3 | 2.78 \pm 0.08 (2) |
| | 4 | 3.95 \pm 0.16 (3) |
| | 5 | 4.53 \pm 0.11 (3) |
| | 6 | 5.01 \pm 0.54 (2) |
| 416 & 403 | 2 | 1.72 (1) |
| | 3 | 2.99 \pm 0.08 (2) |
| | 4 | 3.18 \pm 0.24 (3) |
| | 5 | 4.19 \pm 0.57 (3) |
| | 6 | 7.09 \pm 2.00 (2) |
| 416 & 359 | 2 | 3.56 (1) |
| | 3 | 2.71 \pm 0.01 (2) |
| | 4 | 3.37 \pm 1.15 (3) |
| | 5 | 4.05 \pm 1.14 (3) |
| | 6 | 6.84 \pm 2.13 (2) |
| 426 & 403 | 2 | 1.88 (1) |
| | 3 | 2.85 \pm 0.02 (2) |
| | 4 | 3.66 \pm 0.17 (3) |
| | 5 | 4.38 \pm 0.21 (3) |
| | 6 | 5.71 \pm 0.30 (2) |
| 426 & 359 | 2 | 2.68 (1) |
| | 3 | 2.74 \pm 0.04 (2) |
| | 4 | 3.53 \pm 0.66 (3) |
| | 5 | 4.27 \pm 0.55 (3) |
| | 6 | 5.87 \pm 0.72 (2) |

*The numbers in parenthesis represent the number of solutions analyzed.

concentration. Again, the accuracy of the nitrate analysis is best if based on 416 and 426 nm data. Calculations with 359 nm data are most in error since there is only the slightest observable elevation in uranyl absorbance due to nitrate at this wavelength.

3.4 Effect of Temperature on the Uranium Spectra

Typical operating temperatures in reprocessing plants range from approximately 50-100°C. The accuracy of previous uranium monitors has also been influenced by the temperature of the environment in which the uranium analysis was made. A temperature study was made to determine whether compensations could be made in the simultaneous uranium procedure for fluctuations in temperature. An 104.1 g/l U sample in 4 M HNO₃ was linearly heated from 50-80°C in the sealed sample compartment of the T_M analyzer. The sample absorbance at each of the wavelength maxima was recorded vs. the resistance of a thermistor contained in the sample cell. The absorbance change is plotted vs. sample temperature in Figure 11. The absorbance increases linearly at a rate of 0.00145 absorbance units per degree centigrade for both the 416 and 426 nm maxima. Scott and Dierks (4) found a comparable temperature effect throughout the 0-140 g/l U range.

An absorbance change of 0.00145 ODU at both wavelengths would represent an error equivalent to 0.20 g/l U. Using a single observation at 416 nm, the corresponding error would be 0.3 g/l U per degree centigrade. The error from temperature can be minimized if a dual wavelength monitor is calibrated at the temperature at which it will be operating. Because the temperature effect is linear and consistent

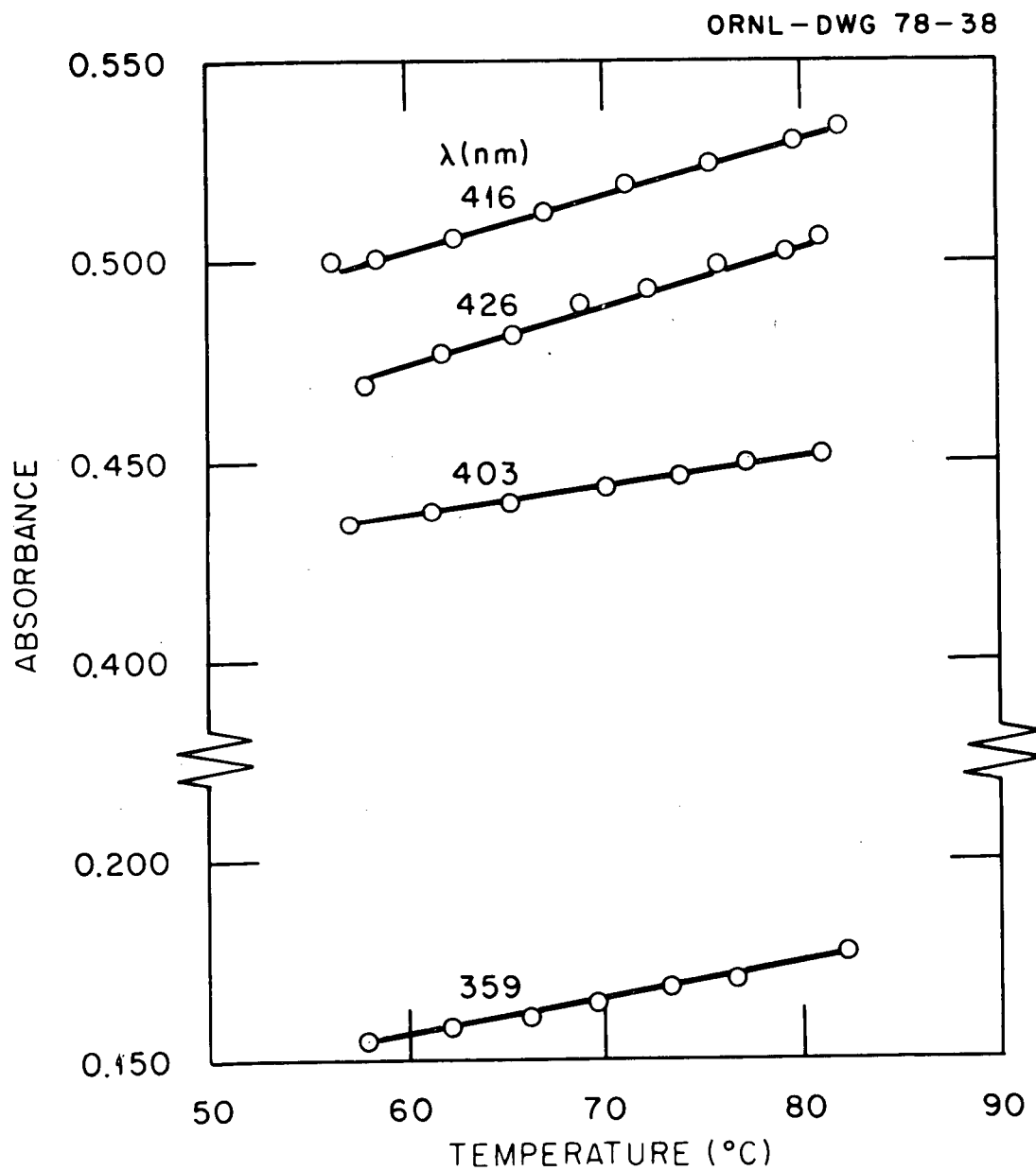


Figure 11. Effect of Temperature on Uranium Absorbance

throughout the uranium concentration range, an automatic electronic correction can be instituted in the procedure, if temperature fluctuations are great enough to significantly affect the accuracy of the uranium analysis.

3.5 Error Analysis in the Simultaneous Determination of Uranium and Nitrate

The uncertainty in estimating each parameter in equation 6 contributes to the total error in calculating uranium and nitrate concentration. An error analysis of the procedure was performed to determine which parameters most influence the accuracy of simultaneous uranium analysis. In this analysis the effect of small temperature fluctuations is not included since this error is negligible. The variance in uranium analysis ($S_{[U]}^2$) can be calculated from equation 9:

$$\begin{aligned}
 S_{[U]}^2 = & \left(\frac{\partial[U]}{\partial A_{416}}\right)^2 S_{A_{416}}^2 + \left(\frac{\partial[U]}{\partial A_{426}}\right)^2 S_{A_{426}}^2 + \left(\frac{\partial[U]}{\partial c_{416}}\right)^2 S_{c_{416}}^2 \\
 & + \left(\frac{\partial[U]}{\partial c_{426}}\right)^2 S_{c_{426}}^2 + \left(\frac{\partial[U]}{\partial N_{416}}\right)^2 S_{N_{416}}^2 + \left(\frac{\partial[U]}{\partial N_{426}}\right)^2 S_{N_{426}}^2 \\
 & + \left(\frac{\partial[U]}{\partial M_{416}}\right)^2 S_{M_{416}}^2 + \left(\frac{\partial[U]}{\partial M_{426}}\right)^2 S_{M_{426}}^2 .
 \end{aligned} \tag{9}$$

The error of each parameter is derived from the product of the partial derivative of equation 6 with respect to that parameter, multiplied by the variance of that parameter. The variance is simply the square of the standard deviation of each parameter and was determined experimentally. Table 4 lists the numerical values of each parameter with its standard deviation. Both the partials with respect to the slope (M) and the intercept (N) proportionality constants are dependent on the absorbance at the 416 and 426 nm maxima. Therefore, to calculate the error associated with these proportionality constants, a particular uranium concentration and its appropriate absorbance values must be assumed. A 166.5 g/l U standard in 4 M HNO_3 was selected since these values are typical for fuel reprocessing streams. The absorbance values are $A_{416} = 0.829$, and $A_{426} = 0.798$ for these concentrations; a ± 0.001 deviation in absorbance readings was assumed.

Table 5 lists the calculated error for each parameter. The greatest uncertainty in determining uranium concentration is associated with defining the intercept (N) and slope (M) proportionality constants and the correction factors (c) for both wavelengths. The error incurred from the absorbance reading becomes significant if the standard deviation is above ± 0.003 ODU. The summation of all the errors represents the variance in uranium analysis at 166.5 g/l and is equal to $80.8 \text{ g}^2/\text{l}^2$. The calculated uncertainty in uranium is thus ± 9.0 g/l or 5.4%.

The uncertainty in determining nitrate concentration was similarly calculated. The errors resulting from each of the parameters in equation 7 are also listed in Table 5. Using the same 166.5 g/l U

TABLE 4

Standard Deviation in 416 and 426 nm Constants

$$416 \text{ nm slope constant } (M_{416}) = 3.41 \times 10^{-4} \pm 9.47 \times 10^{-6}$$

$$426 \text{ nm slope constant } (M_{426}) = 4.61 \times 10^{-4} \pm 9.63 \times 10^{-6}$$

$$416 \text{ nm intercept constant } (N_{416}) = 3.70 \times 10^{-3} \pm 3.27 \times 10^{-5}$$

$$426 \text{ nm intercept constant } (N_{426}) = 3.10 \times 10^{-3} \pm 4.39 \times 10^{-5}$$

$$416 \text{ nm intercept correction factor } (C_{416}) = -1.47 \times 10^{-2} \pm 4.57 \times 10^{-3}$$

$$426 \text{ nm intercept correction factor } (C_{426}) = -2.20 \times 10^{-2} \pm 7.96 \times 10^{-3}$$

Table 5

Calculated Errors Associated with the Simultaneous
Determination of Uranium and Nitrate

| Errors in Uranium Analysis | | Errors in Nitrate Analysis | |
|--|--|---|--|
| $(\frac{\partial[U]}{\partial A_{416}})^2 S_{A_{416}}^2 = 0.499$ | | $(\frac{\partial[NO_3^-]}{\partial A_{416}})^2 S_{A_{416}}^2 = 1.41 \times 10^{-4}$ | |
| $(\frac{\partial[U]}{\partial A_{426}})^2 S_{A_{426}}^2 = 0.273$ | | $(\frac{\partial[NO_3^-]}{\partial A_{426}})^2 S_{A_{426}}^2 = 4.73 \times 10^{-4}$ | |
| $(\frac{\partial[U]}{\partial C_{416}})^2 S_{C_{416}}^2 = 10.4$ | | $(\frac{\partial[NO_3^-]}{\partial C_{416}})^2 S_{C_{416}}^2 = 4.16 \times 10^{-2}$ | |
| $(\frac{\partial[U]}{\partial C_{426}})^2 S_{C_{426}}^2 = 17.3$ | | $(\frac{\partial[NO_3^-]}{\partial C_{426}})^2 S_{C_{426}}^2 = 1.34 \times 10^{-2}$ | |
| $(\frac{\partial[U]}{\partial N_{416}})^2 S_{N_{416}}^2 = 12.7$ | | $(\frac{\partial[NO_3^-]}{\partial N_{416}})^2 S_{N_{416}}^2 = 5.99 \times 10^{-2}$ | |
| $(\frac{\partial[U]}{\partial N_{426}})^2 S_{N_{426}}^2 = 14.8$ | | $(\frac{\partial[NO_3^-]}{\partial N_{426}})^2 S_{N_{426}}^2 = 1.15 \times 10^{-2}$ | |
| $(\frac{\partial[U]}{\partial M_{416}})^2 S_{M_{416}}^2 = 19.1$ | | $(\frac{\partial[NO_3^-]}{\partial M_{416}})^2 S_{M_{416}}^2 = 7.60 \times 10^{-2}$ | |
| $(\frac{\partial[U]}{\partial M_{426}})^2 S_{M_{426}}^2 = 5.69$ | | $(\frac{\partial[NO_3^-]}{\partial M_{426}})^2 S_{M_{426}}^2 = 8.30 \times 10^{-2}$ | |
| $S_{[U]}^2 = 80.8$ | | $S_{[NO_3^-]}^2 = 0.388$ | |
| $S_{[U]} = \pm 8.99 \text{ g/l U}$ @ 166.5 g/l U | | $S_{[NO_3^-]} = \pm 0.62 \text{ M}$ @ 4M HNO ₃ | |
| $= \pm 5.4\%$ | | $= 15.5\%$ | |

standard, the total nitrate variance is 0.388 M^2 . Again, the error due to reading the absorbance becomes important if the uncertainty is greater than $\pm 0.003 \text{ ODU}$. The resulting standard deviation in nitrate calculation is $\pm 0.62 \text{ M}$ or 15.5% at 4 M HNO_3 .

4. CONCLUSION

The present modification of the photometric uranium analysis represents an improvement over previous procedures. Fluctuations in both the temperature and composition of fuel reprocessing streams affect the accuracy of the single-wavelength monitors. Nitrate concentration is found to be the major factor influencing the accuracy of the uranium analysis. The simultaneous analysis of uranium and nitrate eliminates this source of error by essentially basing the calculation on uranyl absorption extrapolated to zero nitrate. Such a technique permits the analysis of 20-200 g/l uranium in the presence of 2-6 M nitrate with an accuracy of 5%. The dual-wavelength method also provides another process control parameter by furnishing an estimation of nitrate concentration with an accuracy of 15%. The simultaneous procedure is affected slightly less by temperature fluctuations than the single wavelength method. If the temperature of the uranium sample is monitored with the dual wavelength method, temperature fluctuations can be compensated with a simple linear correction function. The simultaneous procedure might be incorporated into existing uranium monitors to allow accurate analysis under variable process stream conditions.

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