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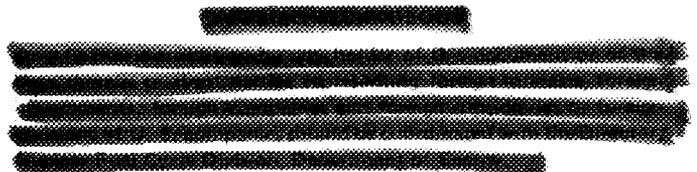
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**Experimental Parameters
in the Photometric
Analysis of Uranium in
TBP-Dodecane Solutions**

D. T. Bostick
J. E. Strain



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CONSOLIDATED FUEL REPROCESSING PROGRAM
(In-Line Analytical Sensor Development)

**EXPERIMENTAL PARAMETERS IN THE PHOTOMETRIC ANALYSIS
OF URANIUM IN TBP-DODECANE SOLUTIONS**

61
D. T. Bostick and J. E. Strain
Analytical Chemistry Division

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HIGHLIGHTS

A systematic study of the direct colorimetric determination of uranium in tributyl phosphate–dodecane solutions has been made. A number of parameters, including HNO_3 , TBP, mono- and dibutyl phosphate concentrations, temperature, and extent of solvent degradation, have been investigated to determine what effect they have on the accuracy of uranium analysis. The procedure, based on the absorbance of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ at 416 nm, was found to be independent of HNO_3 concentration and is not significantly affected by fluctuations in the concentration of TBP, MBP, and DBP under normal operating conditions. Phase separation occurs in hydrated organic samples at elevated temperatures; however, the accuracy of the photometric method is essentially independent of temperature fluctuations if the absorbance at 550 nm is used to correct 416-nm absorbance for sample opacity. Significant positive bias in assay results is observed in organic streams when spent TBP is recycled through the reprocessing facility. The absorbance from solvent coloration, produced by the presence of TBP nitrication products, must be subtracted from the total 416-nm absorbance to obtain an accurate analysis of uranium under these process conditions. The operating range of the procedure, using a 0.5-cm photometric cell, is 1 to 100 g/l U, with an estimated accuracy of ± 0.5 g/l U.

1. INTRODUCTION

The determination of uranium concentration in aqueous and organic process streams must be made on a continuous real-time basis to permit continual process optimization and material balance control in a nuclear fuel reprocessing facility. To this end, a dual-wavelength photometric procedure has been developed to monitor 1 to 200 g/l U directly in aqueous process streams at an accuracy better than 5%.^{1,2} The procedure, based on uranyl absorbance at 416 and 426 nm, does not require the addition of reagents to the process stream, is independent of the isotopic abundance of the uranium present, and is not significantly affected by stream contaminants and turbidity if the absorbance at an appropriate blank wavelength is also monitored. The in-line photometric instrumentation required for this analysis is relatively durable and mechanically simple, and can operate in a high radiation field.

An attempt has been made to extend this photometric method to the analysis of 1 to 100 g/l U in organic tributyl phosphate (TBP)-dodecane streams. Identical in-line instrumentation could then be used to monitor uranium concentration in any type of process stream with a minimum of stream alterations or disruptions. Instrument redundancy would also simplify fabrication, maintenance, and calibration requirements for uranium detection in the reprocessing facility.

Direct colorimetric analysis of uranium in organic process streams has been employed previously using rather unsophisticated photometric equipment. The first in-line detection system for organic uranium concentration compared the photometric output of a "blue" uranium transmission cell with that of a "red" turbidity cell.³ A second set of cells was used to monitor and correct the uranyl transmission for color formation in recycled TBP solvent. This simplified approach was used to determine 60 to 100 g/l U in 30% TBP at an accuracy of 2 to 9%. Frequently, however, large discrepancies were observed between in-line analyses and laboratory results, which could not be attributed to any known source. If uranium analysis was made in aged or degraded solvent, the results were consistently overestimated by at least 5%.

A more in-depth study of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ absorbance in TBP- HNO_3 found that all uranyl absorption peaks obey the Beer-Lambert law and could be used for the direct colorimetric determination of uranium in TBP with a standard spectrophotometer.^{4,5} The shape and intensity of the uranyl absorption peaks were independent of HNO_3 concentrations above 1 molar acid.^{4,5}

This report further investigates organic stream parameters that might affect uranyl absorption in TBP-dodecane solutions. In addition to solvent degradation and HNO_3 concentration, the influence of temperature, TBP, and mono- and dibutyl phosphate (MBP and DBP) concentrations on uranium analysis are discussed. Organic process stream conditions are also summarized. Under such conditions, it is recommended that a dual-wavelength photometric procedure be used to compensate for large fluctuations in any of the above parameters. Finally, uranium analysis based on uranyl absorbance at a single wavelength is described; this procedure simulates analysis under normal Purex-process operating conditions. It is hoped that this investigation will define the unknown discrepancies previously observed with uranium analysis in organic streams, thereby improving the accuracy and utility of the direct photometric determination of uranium in any Purex process stream.

2. EXPERIMENTAL

2.1 Reagents and Procedures

Uranium standards were prepared by adding weighed amounts of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Products Corporation) to TBP-dodecane solutions that had previously been acidified with HNO_3 . The organic uranium samples were mixed and the phases allowed to separate. The small water layer was collected and diluted to 1 ml with water. The uranium concentration was then determined with the dual-wavelength photometric procedure previously described.² The uranium concentration remaining in the organic phase was then calculated by subtracting the amount of uranium extracted into the aqueous phase from the total amount of uranium originally added to the acidified TBP-dodecane solutions. Generally, this correction amounted to less than 2% of the total uranium concentration.

The HNO_3 concentration in the uranium-TBP samples was determined directly in the organic sample with a potentiometric procedure developed by Wain.⁶ In this procedure the organic base [tributylamine (Aldrich Chemical Company)] is used as the titrant. Nitric acid standards, which have been analyzed previously by adding excess standard NaOH and then back titrating to a phenolphthalein end point with standard HCl, were used to standardize approximately 0.1 M tributylamine (TBA) in dodecane. Fifty microliters of 2 to 11 molar standardized HNO_3 was added to 50 ml of 100% TBP. Aliquots ranging in volume from 0.1 to 2 ml of 0.1 M TBA were added to the HNO_3 -TBP sample; the potential was observed 30 s after each addition. The amount of TBA added was sufficient to produce at least a 7-to-10-mV change from the previous potential reading. Figure 1 illustrates the potential curves obtained in the analysis of 0.06 to 0.4-meq HNO_3 . The point on the titration curves at which the second derivatives equal zero defines the end points of the titrations. The relative standard deviation in the determination of TBA concentration is less than 0.4%.

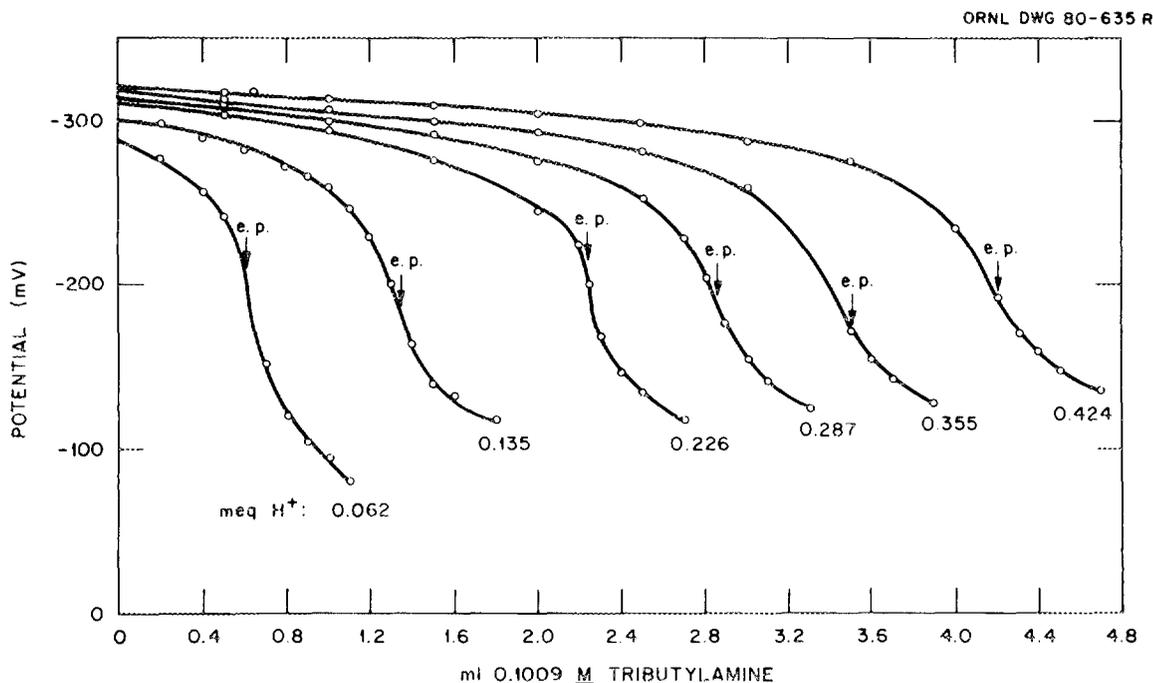


Fig. 1. Potentiometric titration of 0.06 to 0.4-meq HNO_3 .

The concentration of HNO_3 in organic uranium samples is determined by adding up to 10 ml of the sample to 40 ml of 100% TBP. It is important that the TBP diluent be free from traces of water to prevent an overestimation of hydrogen ion concentration resulting from uranium hydrolysis. Again, 0.1 to 2 ml of standard TBA was added to the uranium sample. The end point was located using the second derivative of the data (described above). The end-point potential, occurring at about -170 mV, cannot be used for the detection of the titration end point because its value is influenced by the sample uranium and HNO_3 concentrations, the condition of the combination electrode, and the dryness of the TBP diluent. An estimation of the hydrogen ion concentration determined by the calculation of the second derivative of the titration data is reproducible to within 1%. Because 0.005 to 1 M HNO_3 concentrations can be determined directly in organic samples simply and with excellent accuracy, this potentiometric procedure may also be applicable to acid analysis in plutonium as well as uranium-TBP-dodecane solutions.

Dibutyl phosphate standards were prepared from practical grade DBP (55% DBP, 45% MBP) purchased from Alfa Products. The DBP was purified by washing the mixed organophosphates with one-half volume 0.1 M HNO_3 , followed by two washes with one-half volumes of water. The purified organic phase was then titrated potentiometrically with NaOH to determine the exact concentration of DBP.

Monobutyl phosphate standards were obtained by diluting practical grade DBP by a factor of 5 with 30% TBP-dodecane. The solution was then washed with an equivalent volume of water. The aqueous phase was collected and washed with an equivalent volume of CCl_4 to remove any remaining DBP. Finally, the purified MBP concentration was determined potentiometrically by titration with NaOH.⁷

Recycled TBP-dodecane solutions were obtained from two sources. Organic solvent was collected from a miniature Purex test facility after it had been used to separate uranium and plutonium in a series of mixer-settler tanks. This organic solution was used to estimate the extent of TBP coloration after a single pass through a reprocessing facility. Tributyl phosphate, which had been recycled three times through a Purex plant, was obtained from the Savannah River Laboratory in Aiken, South Carolina.

2.2 Instrumentation

The potentiometric determination of HNO_3 in organic uranium samples was performed using a Radiometer PHM64 pH meter. The digital meter is sensitive to 0.1-mV changes in the potential of a sample. The potential changes were monitored with a Corning 476056 Ag-AgCl combination electrode. Using this equipment, the potential reading of the sample varies between ± 3 to 7 mV of the average potential, depending on the acidity and water content of the organic sample being analyzed. The combination electrode requires little preconditioning and is normally soaked in 100% TBP when not in use. Occasionally the electrode must be refilled with 4 M KCl saturated with AgCl, since KCl is soluble in TBP.

Photometric measurements were made using a Cary model 14 recording spectrophotometer and quartz cells of 0.2-to-1-cm path length. Samples were analyzed vs an air blank. A Beckman TM analyzer and a DB-G spectrophotometer were used to record the absorbance changes of organic uranium samples as the sample temperature was linearly increased from 20 to 60°C at 1°C/min. A 1-cm optical cell containing the sample was placed in the heating block of the TM analyzer. A thermistor, which had been calibrated prior to the temperature study, was immersed in the cell to accurately follow temperature changes in the sample. The absorbance changes at 416, 426, and 550 nm were followed with the spectrophotometer.

3. RESULTS AND DISCUSSION

Organic Purex streams are made up of a number of constituents whose concentrations fluctuate in an amount that depends on the given process being performed during fuel reprocessing, the amount and type of radiation present in the stream, the extent to which the organic solvent is recycled, and the degree to which such environmental factors as temperature and flow rate are controlled in the reprocessing cycle. The average uranium concentration can vary from 1 to 100 g/l in organic Purex streams. In any given TBP stream, the uranium concentration may fluctuate by 20% of the average stream concentration. The typical TBP concentration selected for the separation and purification of uranium and plutonium is a 30% dilution in an *n*-hydrocarbon solvent. The TBP concentration is usually controlled to within a range of 28 to 32% TBP in *n*-dodecane. Recent studies, however, suggest that the separation of fission products from uranium and plutonium is improved, and the radiation damage to the organic solvent is reduced if the TBP concentration is no greater than 3 to 7%. Uranium analysis in the future may, therefore, be required in organic solutions containing much less TBP. The average HNO₃ concentration in organic streams ranges from 0.01 to 0.3 molar. These values may be expected to fluctuate by $\pm 15\%$. Several organic contaminants may also be present in trace to millimolar concentrations. Tributyl phosphate in a radiation field will decompose to form mono- and dibutyl phosphate. Projected concentrations of these by-products are 10⁻⁴ and 10⁻³ molar respectively; these projected values⁸ are thought to be overestimated by a factor of 5 or 10. Nitric acid can also degrade TBP by forming colored nitrification products. The exact identity and concentrations of these components are unknown, although their presence has interfered in the past with the analysis of uranium in organic streams.

All of the above stream constituents may affect the accuracy of the direct photometric determination of uranium in organic streams. Therefore, the influence of each component on UO₂(NO₃)₂ · 2TBP absorbance is described in terms of its estimated concentration range in the stream; modifications in the photometric procedure are suggested where corrections are required.

3.1 Variations in Uranyl Absorbance with HNO Concentrations

The visible absorption spectrum of 54.9 g/l U in 30% TBP and 0.23 M HNO₃ is shown in Fig. 2. The absorption spectra of uranium in organic streams are essentially the same as those observed in aqueous samples, although the absorption peaks are more nearly resolved. The major absorption lines occur at 416, 426, and 403 nm. In the presence of constant TBP and HNO₃ concentrations, the absorbance at each wavelength maximum is linearly proportional to the uranium concentration (Fig. 3). Neither HNO₃ or fresh TBP solvent absorb in this region of the spectra.

Uranyl absorbance in aqueous samples was found to be dependent on HNO₃ concentration. Therefore, an effort was made to extend the work of previous studies in which uranyl absorbance was observed in TBP-dodecane samples containing 1 molar or greater HNO₃. Uranium is known to hydrolyze at low HNO₃ concentrations in the presence of even trace amounts of water, thus amplifying the uranyl absorbance. The analysis of uranium in the organic phase included solutions containing 0.005 to 0.5 M HNO₃.

The absorbance of UO₂(NO₃)₂ · 2TBP was observed for the uranyl absorption maxima in 30% TBP. Data presented in Table 1 indicates that the absorbance at all uranyl wavelengths is unaffected by the HNO₃ concentration above 0.01 molar acid. At acid concentrations below this level, the absorbtivities are elevated because of uranyl hydrolysis. Because the product

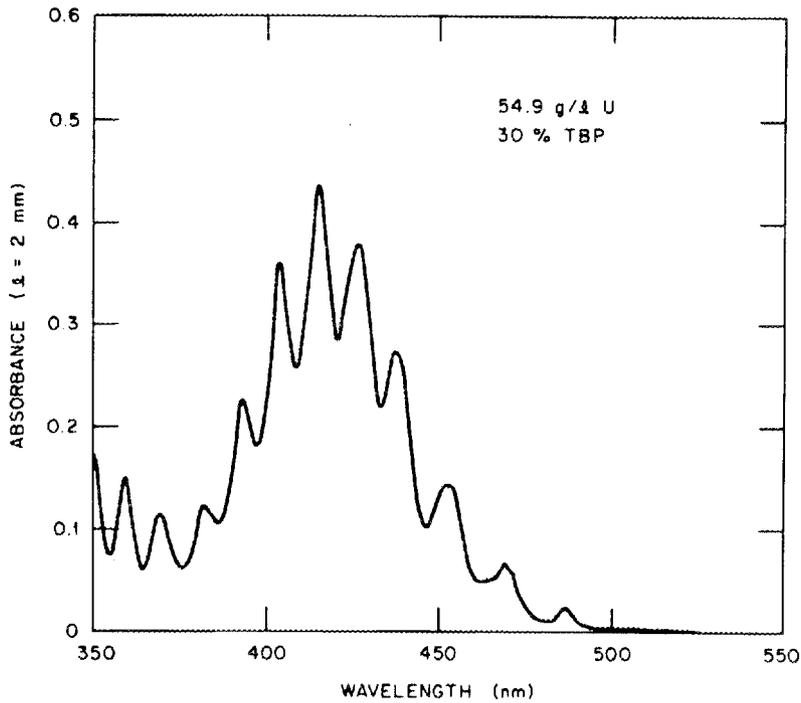


Fig. 2. Visible spectra of uranium in 30% TBP-dodecane solution.

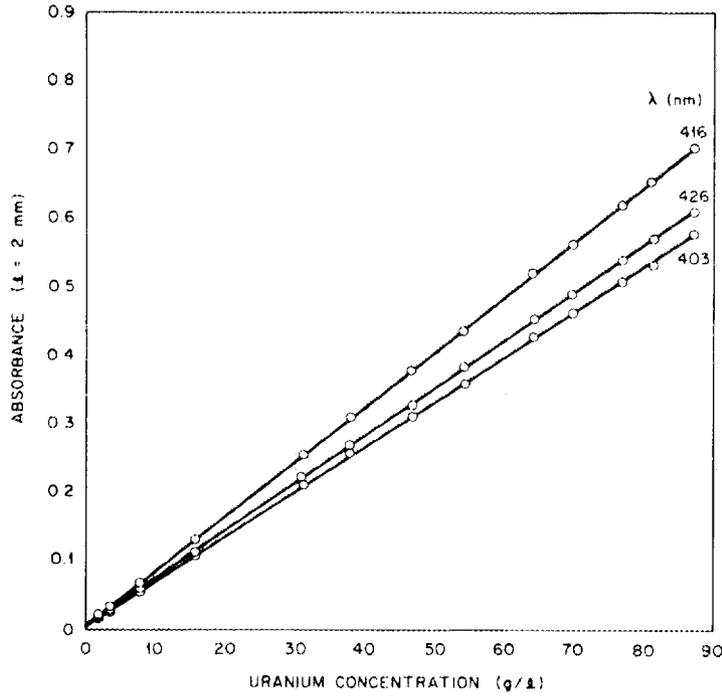


Fig. 3. Uranium calibration curves at 416, 426, and 403 nm.

Table 1. Variation of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ absorbtivity with HNO_3 concentration

HNO_3 (M)	$\epsilon^{416} \times 10^2$ ($\text{cm} \cdot \text{g}/\ell$) ⁻¹	$\epsilon^{426} \times 10^2$ ($\text{cm} \cdot \text{g}/\ell$) ⁻¹	$\epsilon^{403} \times 10^2$ ($\text{cm} \cdot \text{g}/\ell$) ⁻¹
0.00835	4.00	3.45	3.31
0.0133	3.97	3.44	3.28
0.0217	3.97	3.45	3.28
0.0312	3.97	3.46	3.28
0.114	3.96	3.45	3.25
0.207	3.98	4.46	3.25
0.274	4.00	3.50	3.27
0.422	3.98	3.51	3.26
Average	$3.98 \pm 0.4\%$	$3.47 \pm 0.7\%$	$1.27 \pm 0.6\%$

uranium streams contain at least 0.01 M HNO_3 (in 30% TBP), any single wavelength maximum can be used to monitor the uranium concentration and remain unbiased by fluctuations in acid concentration. The 416-nm maximum would be the wavelength of choice for most applications, since it has the greatest and most reproducible absorbtivity coefficient of the wavelengths studied.

3.2 Variation of Uranyl Absorbance with TBP Concentration

The solvent composition primarily influences the total amount of uranium soluble in the organic phase and, therefore, defines the operating range for uranium concentration in a given organic process stream. Uranyl absorbance was found to be linearly proportional to the uranium concentration at any uranyl wavelength, regardless of the TBP concentration selected for the process (Fig. 4). However, the sensitivity of the photometric analysis was found to increase slightly with TBP concentration. This affect is best observed by plotting the absorbance change (at a given uranium concentration) vs the TBP content of the sample, as presented in Fig. 5. The absorbance of a uranium sample increases with TBP concentration, and this increase in sensitivity becomes more dramatic as the uranium concentration increases. The extent to which TBP elevates uranyl absorbance can be described mathematically, using the following equation for a given uranium standard (in Fig. 5).

$$A_{416} = A_{416}^{\circ} + dA_{416}/dTBP \cdot (\text{TBP}) \quad (1)$$

The extrapolated intercept, A_{416}° , is the absorbance of a uranium standard in the absence of TBP; $dA_{416}/dTBP$ is the slope of a given uranium concentration. Although Fig. 5 shows absorbance values obtained for only 416 nm, similar plots can be made for each of the remaining uranyl wavelength maxima.

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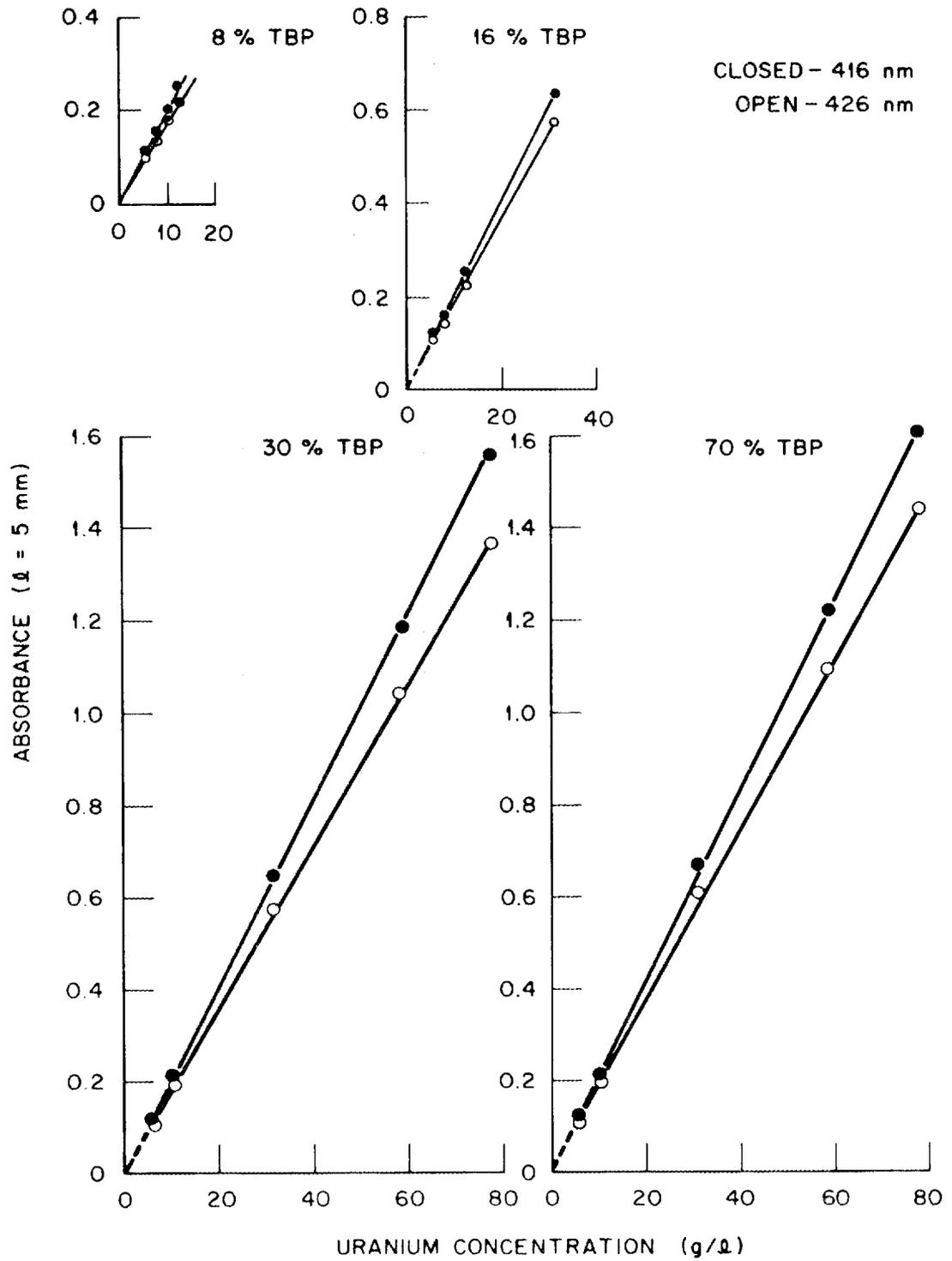


Fig. 4. Uranium calibration curves at 8, 16, 30, and 70% TBP.

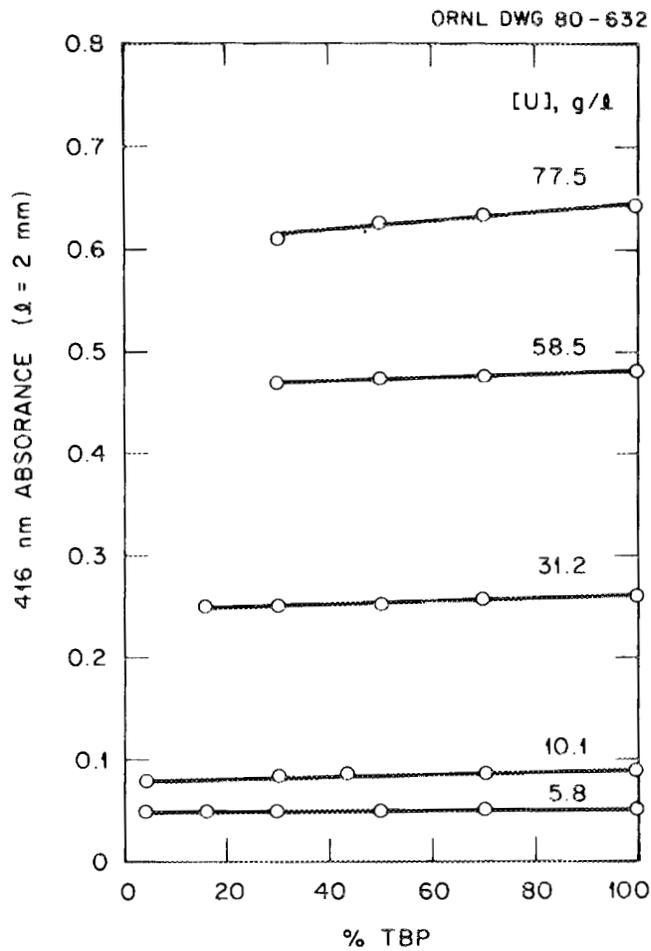


Fig. 5. Variation in uranyl absorbance with TBP concentration.

The intercepts A_{416}° and the slopes $dA_{416}/dTBP$ are directly proportional to the uranium concentration of the standards. These relationships are illustrated for 416- and 426-nm data in Figs. 6 and 7. Figure 6 indicates that A_{416}° can be rewritten in terms of uranium concentration as

$$A_{416}^{\circ} = 0.0046 + 3.93 \times 10^{-2}(U) \quad (2)$$

According to Fig. 7, $dA_{416}/dTBP$ can be rewritten as

$$dA_{416}/dTBP = 1.10 \times 10^{-4} + 2.83 \times 10^{-5}(U) \quad (3)$$

By combining Eqs. 1 and 3 the TBP effect on 416-nm absorbance can be derived numerically as

$$A_{416} = 3.93 \times 10^{-2}(U) + 2.83 \times 10^{-5}(U)(TBP) + 1.10 \times 10^{-4}(TBP) + 0.005 \quad (4)$$

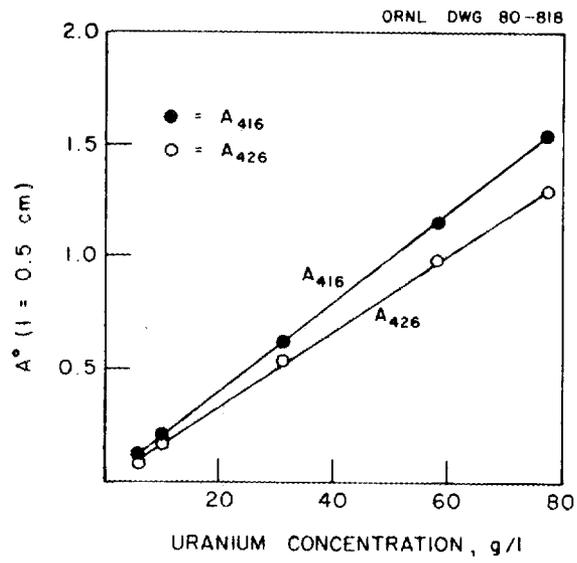


Fig. 6. Uranium concentration vs A° .

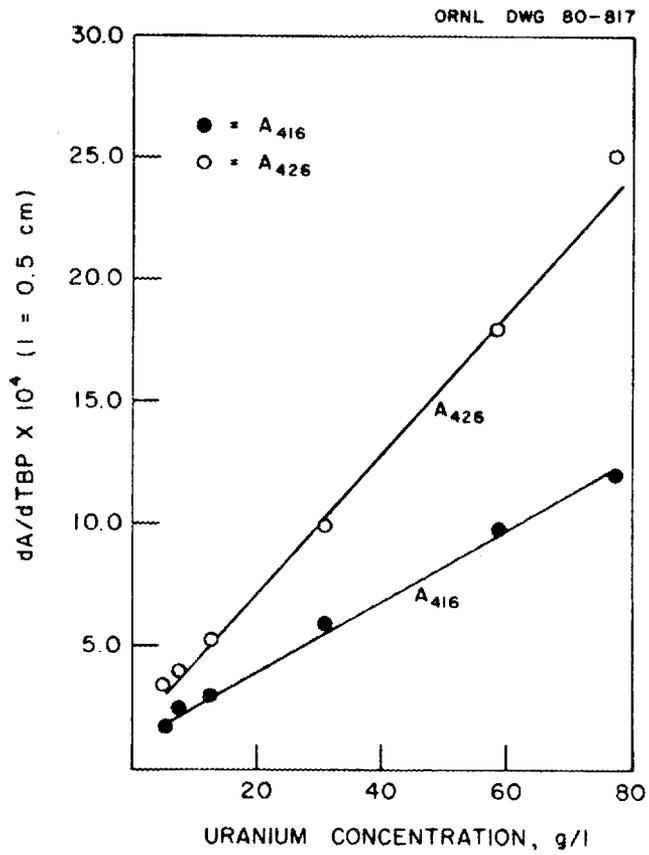


Fig. 7. Uranium concentration vs $dA/dTBP$.

The influence of TBP concentration on 426 - nm uranyl absorbance can be defined similarly as

$$A_{426} = 3.30 \times 10^{-2}(U) + 6.18 \times 10^{-5}(U) (\text{TBP}) + 1.31 \times 10^{-4}(\text{TBP}) + 0.007 \quad . \quad (5)$$

The above equations are derived for absorbance data obtained using a 1-cm path-length cell and uranium and TBP concentrations in units of grams per liter and percent dilution respectively. A comparison of Eqs. 4 and 5 suggests that 416-nm data is more sensitive to uranium concentration and is less sensitive (by a factor of 2) to fluctuations in TBP concentration. This single wavelength can therefore be used to determine the uranium concentration in an organic process stream if the absorbance is calibrated for a given TBP concentration. In the case of a 30% TBP dilution, the uranium calibration equation is numerically equivalent to

$$A_{416}^{1 \text{ cm}} = 4.01 \times 10^{-2}(U) + 0.0083 \quad . \quad (6)$$

The 416-nm absorbance will not vary by more than ± 0.003 optical density unit (ODU), or an equivalent uranium concentration of ± 0.08 g/l U if the solvent composition varies by $\pm 2\%$ TBP.

For those samples in which the TBP concentration is unknown or varies by more than $\pm 10\%$, a dual wavelength procedure can be used to calculate organic uranium concentration. By combining Eqs. 4 and 5, the following simplified simultaneous equation can be derived for uranium determination.

$$(U) = 20.2A_{416} - 9.28A_{426} - 1.71 + 9.28\sqrt{(A_{426} - 2.18A_{416} + 0.184)^2 + A_{416}} \quad . \quad (7)$$

The sample concentration can be determined with an accuracy of 2% if the calculation is based on 416- and 426- nm absorbance. A simultaneous dual wavelength equation can also be written to determine TBP concentration. The accuracy of the calculation is very poor, however, often differing by a factor of 2 from the true TBP concentration, and therefore is not useful from an analytical standpoint.

3.3 Variation of Uranyl Absorbance with MBP and DBP Concentration

In the presence of fission products, TBP will degrade to DBP and to a lesser extent MBP and phosphate. Dibutyl phosphate forms a stable complex with uranium that cannot be totally stripped from organic streams. To reduce product loss, the concentrations of these organic by-products are minimized by solvent clean-up procedures such that they remain below millimolar levels in the TBP streams. Uranyl absorbance was observed in the presence of 0.5 to 10 mM MBP and DBP. Both organic phosphates elevated the uranyl absorbance, the 426-nm line being more enhanced than the 416 nm maximum. The following

equations summarize the behavior of 12.5 g/l U absorbance (illustrated in Figs. 8 and 9) in the presence of MBP and DBP:

$$A_{416} = 4.83 \text{ MBP} + 0.521 \quad (8)$$

$$A_{426} = 8.41 \text{ MBP} + 0.458 \quad (9)$$

$$A_{416} = 4.02 \text{ DBP} + 0.518 \quad (10)$$

$$A_{426} = 5.66 \text{ DBP} + 0.458 \quad (11)$$

The intercepts are equivalent to the absorbance of 12.5 g/l U in 30% TBP; the slopes indicate the relative sensitivity of each wavelength to molar MBP and DBP concentrations.

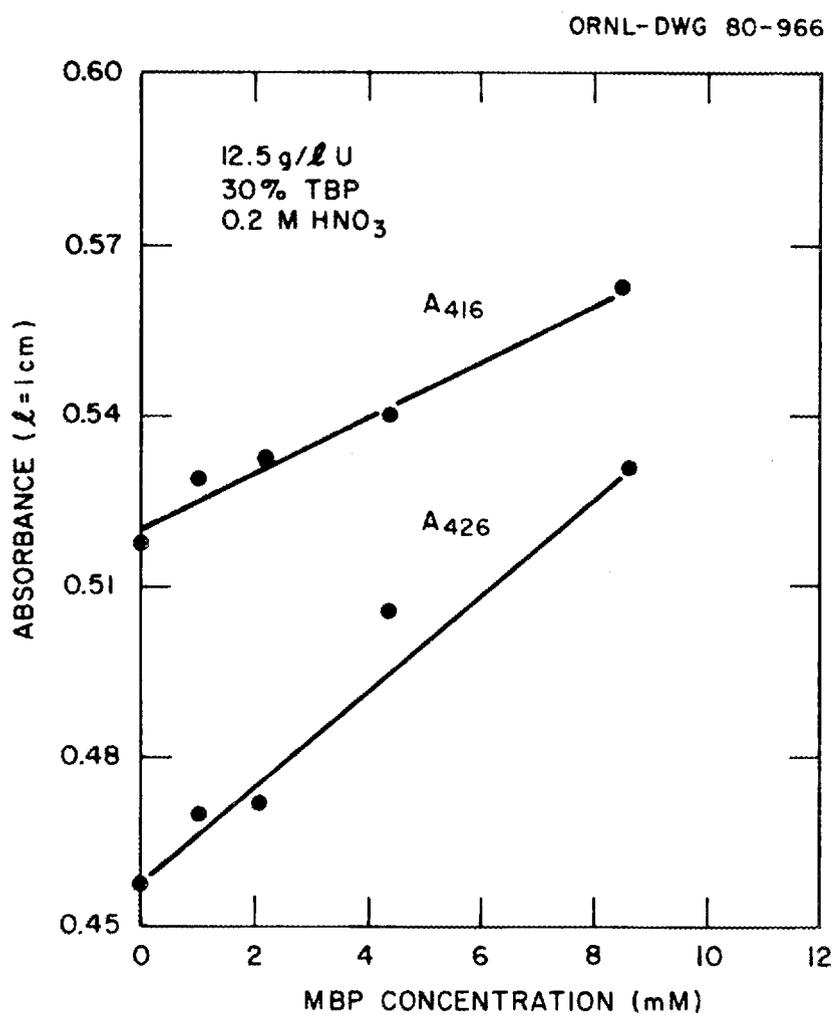


Fig. 8. Variation of uranyl absorbance with MBP concentration.

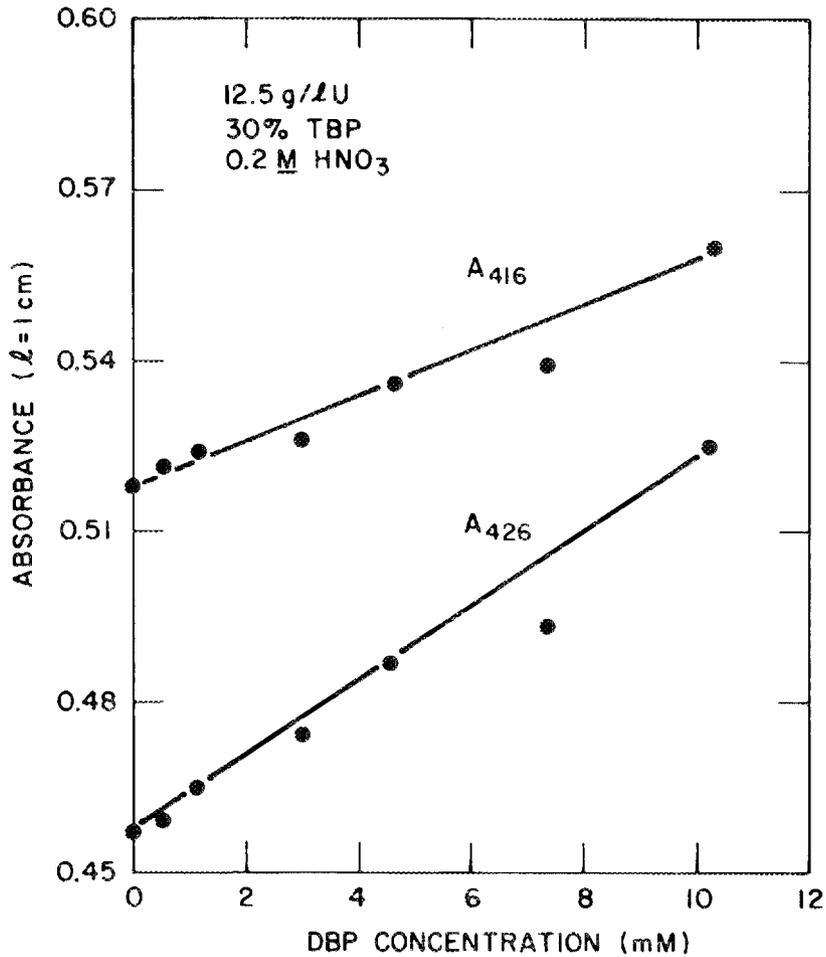


Fig. 9. Variation of uranyl absorbance with DBP concentration.

The projected MBP concentration in irradiated TBP streams will not exceed 0.1 mM and, therefore, will not increase the optical density of the sample by more than 0.001 ODU for either uranyl maximum. The DBP concentration will not exceed 1 mM, which corresponds to an increase in uranyl absorbance of less than 0.005 ODU, or an overestimation of uranium concentration equivalent to 0.1 g/l U. Because of the minimal effect of either of these low-level TBP by-products on uranyl absorbance, the single 416-nm wavelength can be used photometrically to accurately monitor organic uranium concentration in irradiated TBP streams.

3.4 Variation of Uranyl Absorbance with Temperature

The operating temperature in Purex streams will generally fluctuate by 5°C about the average value of 40°C. The effect of these temperature variations was studied as a function of both uranium and TBP concentrations. As the temperature of an organic sample increases from ambient to 60°C, fine water droplets form and decrease sample transparency. The

water is reabsorbed by the TBP, and the sample clarifies as the solution cools. The rate and extent at which second-phase formation occurs is dependent on the rate at which the organic sample is heated. Figure 10 suggests that uranyl absorbance can be corrected for temperature effects by monitoring and subtracting 550-nm absorbance from the observed 416-nm absorbance. The corrected 416-nm absorbance is then only marginally influenced by variations in sample temperature.

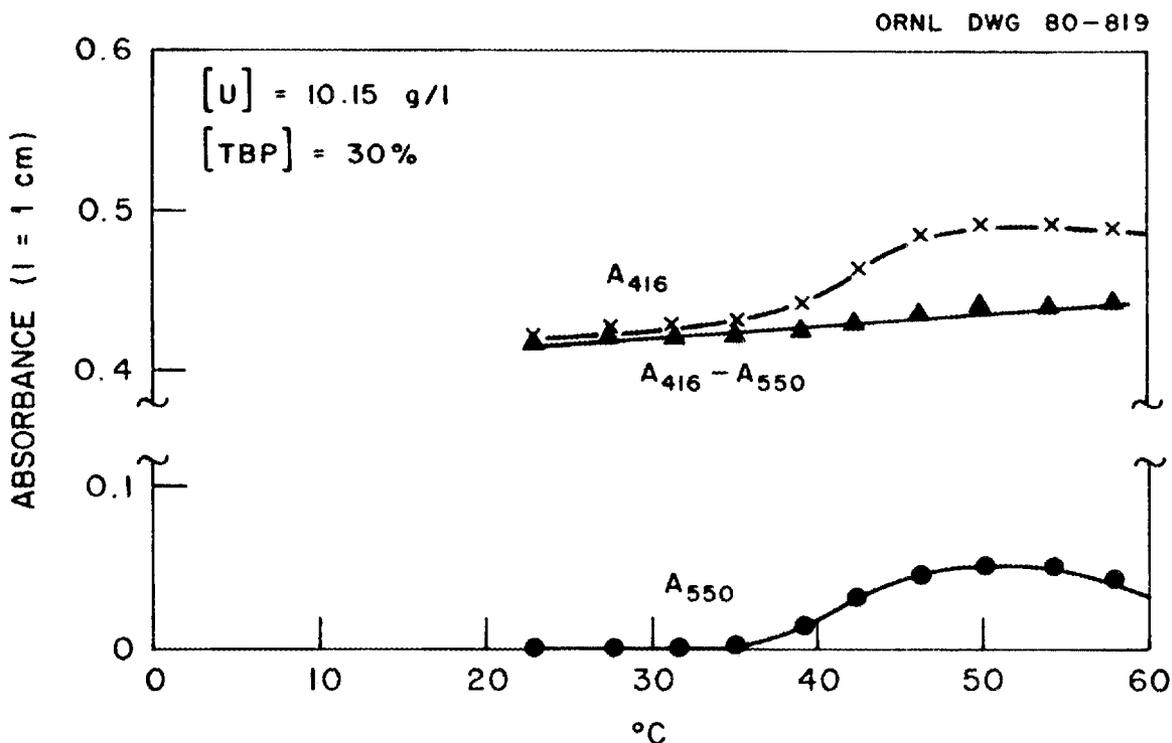


Fig. 10. Variation in uranyl absorbance with temperature.

The slight dependence of the corrected 416-nm absorbance on temperature was found to be a function of both TBP and uranium concentration. The trace water is much more effectively complexed, and second-phase formation is retarded at higher TBP concentrations (Fig. 11). The concentration of sample uranium also decreased sample turbidity by complexing any trace water present. Figure 12 suggests that the effect of temperature on the corrected 416-nm absorbance is negligible for solutions containing greater than 10 g/l U in 30% TBP. Because sample temperature will deviate by less than 5°C, and not by the 40°C presented in the above studies, monitoring the 550-nm absorbance for sample opacity should be sufficient to correct for the predicted variations in stream temperature at even lower uranium and TBP concentrations.

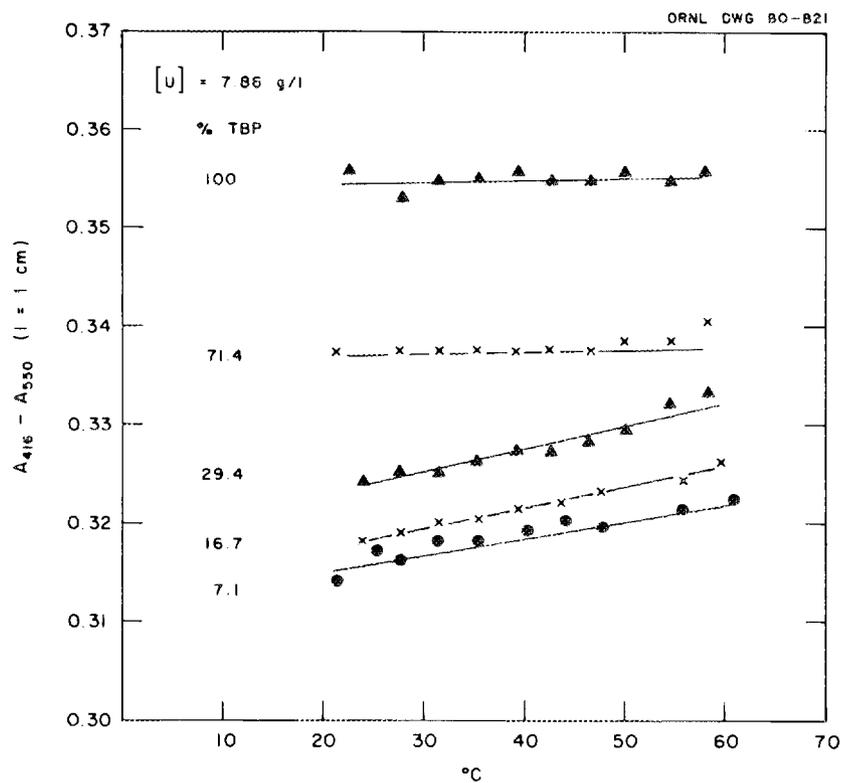


Fig. 11. Relative effect of temperature on the corrected uranyl absorbance as a function of TBP concentration.

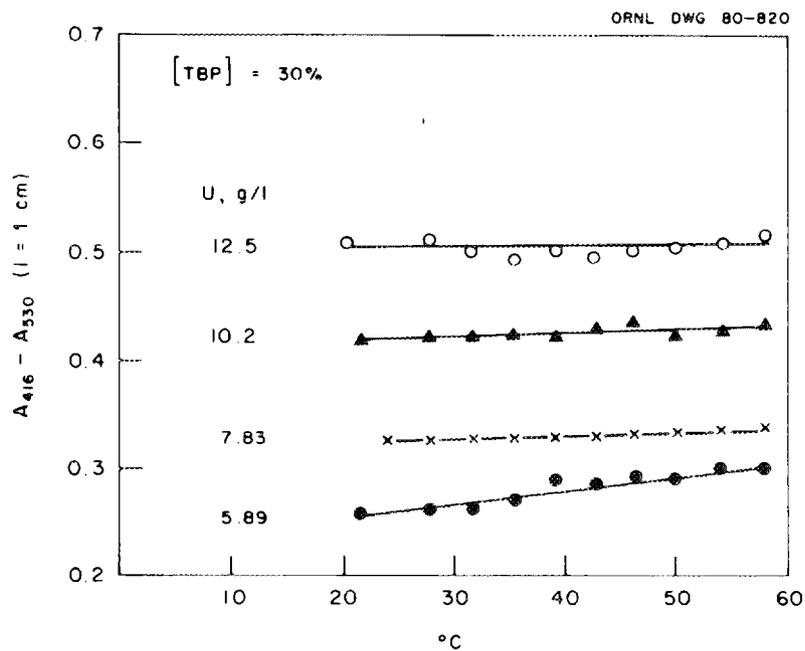


Fig. 12. Relative effect of temperature on the corrected uranyl absorbance as a function of uranium concentration.

3.5 Spectral Interference of Recycled TBP

During fuel reprocessing, the TBP solvent contacts concentrated HNO_3 aqueous streams. The acid reacts with the organophosphate to form yellow nitrification products that interfere with the photometric determination of uranium. Organic solvent collected after a single run in a miniature Purex facility exhibited an absorbance at 416 nm of approximately 0.1 ODU, which is equivalent to 2 g/l U (Fig. 13). Normal solvent reclamation procedures include washing spent TBP solutions with Na_2CO_3 and water prior to reintroducing the solvent into the head-end of the process. However, these colored by-products are not extracted from the spent solvent and will accumulate with each pass through the reprocessing system. Thus TBP, which has been recycled through the reprocessing plant three times, accumulates sufficient nitrification by-products to increase the apparent uranium concentration by 8 g/l U. A second photometer will therefore be required to monitor spent TBP absorbance at 416 nm prior to recycling the organic solvent. If a process has not been devised to remove these nitrification products during solvent recovery, subtraction of solvent color photometrically should eliminate overestimation of uranium concentration downstream from the position of solvent entry.

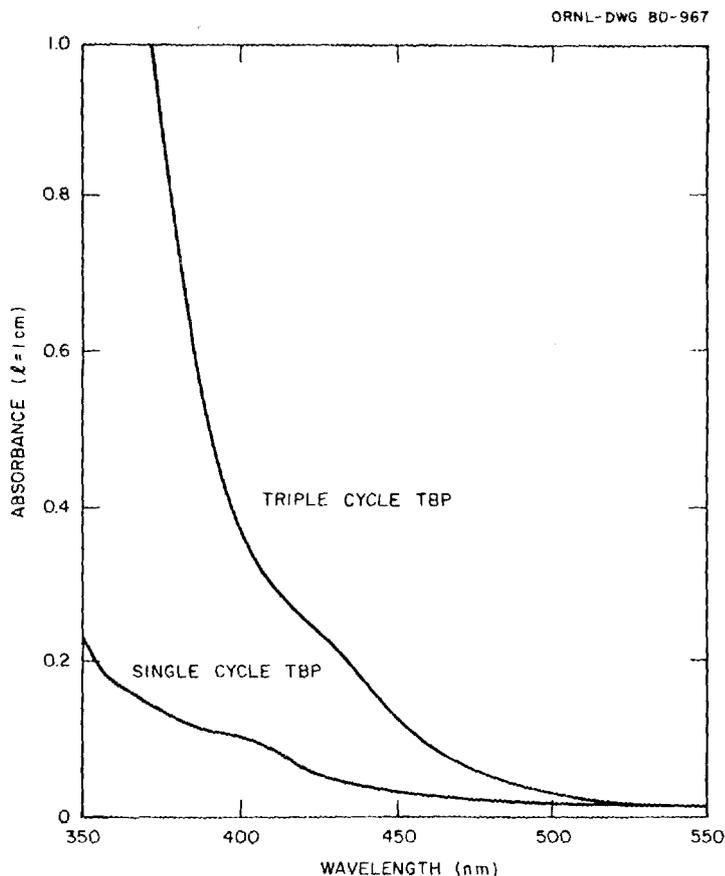


Fig. 13. Visible spectra of single-cycle and triple-cycle TBP.

4. CONCLUSION

A number of organic stream parameters have been studied to determine what effect they will have on the photometric determination of uranium in TBP-dodecane solutions. Nitric acid in organic streams will not affect uranyl absorbance at any wavelength maxima at concentrations above 0.01 molar acid. Below this value, uranium will hydrolyze in hydrated TBP-dodecane solvent and elevate the uranyl absorbtivity coefficients. The influence of TBP concentration on uranyl absorbance is a function of the uranium concentration in the sample. Even at elevated uranium levels, the solvent composition only marginally influences uranyl absorbance. Both MBP and DBP enhance the absorbance of a given uranium standard. Again, the extent by which the absorbtivity coefficients increase is only slight. Temperatures above 35°C cause second-phase formation, which is represented as fine, dispersed water droplets. If the TBP and/or uranium concentrations are high, the temperature effect can be eliminated by monitoring sample turbidity at 550 nm. Spent TBP contains yellow nitrification products that also absorb at uranyl wavelength maxima. If the organic streams contain recycled TBP, the color of the solvent must be subtracted photometrically prior to uranium analysis.

In summary, the majority of stream parameters, present at levels predicted under normal operating conditions of a fuel reprocessing plant, will affect organic uranyl absorbance only minimally. Therefore, few corrections need be incorporated in the photometric analysis of uranium in TBP-dodecane streams to ensure analytical accuracy. For most applications, uranium concentration can be determined based on the uranyl absorbance at 416 nm, which is corrected for sample turbidity by simultaneously monitoring 550-nm absorbance. An accuracy of 0.5 g/ℓ U should be obtainable in streams containing 1 to 100 g/ℓ U, greater than 0.01 M HNO₃, 30 ± 2% TBP, less than 0.001 M MBP or DBP, and temperatures varying by 5°C. If either the TBP concentration is unknown or it varies by greater than 10%, a dual wavelength procedure incorporating 426-nm uranyl absorbance in the calculation can be used to determine uranium concentration to within 2% accuracy. This same procedure may be applicable to solutions containing MBP or DBP concentrations above 1 mM. Finally, a second monitor will be required to correct 416-nm absorbance for solvent color if spent TBP is recycled through the reprocessing facility. This correction is only slight, however, if the spent TBP is recycled a single time through the plant.

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