SPECTROPHOTOMETRIC DETERMINATION OF
NITRATE WITH 4,4'-DIAMINODIPHENYLSULFONE

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ABSTRACT

Nitrate reacts with 4,4'-diaminodiphenylsulfone (DDS) in concentrated sulfuric acid to form a yellow dye whose absorbance at 410 nanometers has been used for the spectrophotometric determination of nitrate in synthetic nuclear waste. The optimum sample volume and sulfuric acid and DDS concentrations for color development were determined. Twenty-three potential interfering ions were studied and their tolerance limits measured. Sodium hydroxide, acetic acid, and urea did not seriously interfere even at high levels. The effect of nitrite on the determination of nitrate was established and methods to destroy nitrites in acidic and basic media using urea are described. Even though a method for the total removal of nitrite was not found, a technique for measuring nitrate in the presence of five times more nitrite is discussed. Halide interference is removed by the addition of silver sulfate. The method has a molar absorptivity of approximately 2400 liter mole⁻¹ cm⁻¹. The method has been used to analyze synthetic nuclear waste and has a standard deviation of $\pm 7.3\%$ at the 100 μg nitrate level and $\pm 2.4\%$ at nitrate levels greater than 200 μg .

SPECTROPHOTOMETRIC DETERMINATION OF NITRATE WITH 4,4'-DIAMINODIPHENYLSULFONE

INTRODUCTION

Wastes from nuclear reprocessing plants contain large quantities of nitrates which have been neutralized and stored in tanks. Nitrate analyses of these wastes are required for characterization purposes and for the evaluation of in-tank solidification (ITS) programs to reduce the volume of nuclear waste, such as the 242-S pilot plant, for vacuum crystallization.

A spectrophotometric determination of nitrate^[1] based on the difference between nitrite analysis with and without the reduction of nitrate to nitrite has been used in the past. However, this method is extremely sensitive, requires large dilutions, and is subject to easy contamination. In addition the reduction of nitrate to nitrite is difficult to control and therefore the technique is not easily adaptable to routine analyses. The major advantages of the procedure are its sensitivity and selectivity. Nitrate specific ion electrodes^[2,3,4] have been successfully used to analyze these types of samples. They are particularly applicable to samples high in nitrate which can be analyzed using standard techniques.^[5,6,7,8] Metcalf^[4] has indicated that the reliability of the nitrate electrode is questionable for nitrate concentrations less than $10^{-3}M$ in high-salt matrices. Therefore a method that would have medium sensitivity but still be rapid and accurate was needed to supplement the specific ion procedure. A spectrophotometric procedure using 4,4'-diaminodiphenylsulfone described by Szekely^[9]

had been investigated earlier and looked promising providing interferences from nitrite and chloride could be removed. Therefore it was decided to investigate this procedure in greater detail with potential applications to the analysis of nitrates in nuclear waste.

SUMMARY AND CONCLUSIONS

A spectrophotometric method for the determination of nitrates was investigated and its applicability to the analyses of synthetic nuclear waste tested. The procedure is based on the analysis of a yellow dye, 3,3'-dinitro-4,4'-diaminodiphenylsulfone, which is formed when nitrate reacts with 4,4'-diaminodiphenylsulfone (DDS) in sulfuric acid. The molar absorptivity of the method is about 2400 liters mole⁻¹ cm⁻¹. [9]

The optimum conditions for color development were investigated. Full-color development was found to occur when the ratio of the volume of DDS to the total sample volume was greater than 3.0 and the sulfuric acid concentration was greater than 13.0M. In order to prevent a precipitate from forming at high nitrate levels (500 µg) it was necessary to increase the DDS concentration to 4.0 g/liter in concentrated H₂SO₄. Complete color formation was developed by placing the sample in a boiling H₂O bath for 15 minutes. When these conditions were followed, a color that was stable for over two hours was formed whose absorbance at 410 nanometers (nm) provided a linear relationship with nitrate concentration.

Numerous interferences that may occur in nuclear waste were studied. Sodium hydroxide did not interfere until 6 milliequivalents were added to a nitrate standard. The effect of nitrite on the color formation and its removal were investigated in detail. Nitrite was found to give

either positive or negative interference effects depending on whether the samples were acidic or basic. Urea was capable of reducing high nitrite concentrations by as much as a factor of five in basic solutions. However this reduction factor decreased as the nitrite concentration was reduced and the hydroxide concentration increased. Total removal of the nitrite ion from basic solutions was not possible; but a technique for determining the interference of nitrite from the spectra was established. Destruction of nitrite with urea from sulfuric and acetic acid systems was found to be unsatisfactory due to the decomposition products of nitrous acid which gave high results with no spectral indication of an interference. Even though a thorough method for destroying nitrites was not found, reasonable nitrate results may be obtained with nitrite concentrations five times greater than nitrate.

The effect of 23 different ions on the procedure were studied and their tolerance levels determined. When this work is included with that of Szekely,^[9] over 50 ions and compounds have been investigated for interfering effects. The following ions were found to interfere the greatest: Cl^- , I^- , Br^- , F^- , Fe^{+2} , MnO_4^- , BrO_3^- , and IO_3^- . Silver sulfate was found to be effective in improving the tolerance limits of chloride which should also be applicable to other halides. The other ions are not normally found at levels high enough to interfere in the highly caustic waste solutions.

The method was applied to synthetic nuclear waste samples from the 242-S vacuum crystallizer pilot plant. The accuracy and precision for spike recoveries on analyses of these samples was $94.7 \pm 8.6\%$. A single sample was analyzed repeatedly with and without spikes. The spike recoveries for this sample were $99.4 \pm 13.5\%$. The actual analyses

precision for this sample without spikes was 19.73 ± 0.67 g/liter or about 3.5% of the average value. Day-to-day analyses of nitrate standards gave accuracy and precision values of $105.3 \pm 7.3\%$ at the 100 μg nitrate level and $99.8 \pm 2.4\%$ for nitrate levels greater than 200 μg . Further work to improve the nitrite removal procedure and to improve the precision at the lower nitrate levels would be valuable. However this method should be adequate for providing the necessary support for the specific ion electrode method to determine nitrates in nuclear waste. In addition the procedure may find application in other fields of chemistry where a rapid and accurate analysis is required for intermediate nitrate concentrations.

EXPERIMENTAL

REAGENTS

4,4'-diaminodiphenylsulfone (DDS) - 4.0 g/liter

Dissolve 4.0 grams of DDS in 1000 ml of reagent-grade concentrated sulfuric acid. The solution is very light-brown in color and stable for several months. The DDS received from K and K Laboratories of California was used without further purification.

Urea - 100 g/liter

Dissolve 10.0 grams of reagent-grade urea into 100 ml of deionized H_2O .

Nitrate Standard - 1000 $\mu\text{g}/\text{ml}$ NO_3^-

Dissolve 1.630 grams of oven-dried KNO_3 (reagent-grade) into deionized H_2O and dilute to volume in a 1000-ml volumetric flask.

Silver Solution - 1000 $\mu\text{g/ml}$ Ag

Dissolve 1.445 grams of reagent-grade silver sulfate in 100 ml of deionized H_2O . If necessary, add 1M H_2SO_4 to help the dissolution.

APPARATUS

Boiling water bath.
Volumetric flasks, 25-ml.
Recording spectrophotometer.
Absorption cells, 1-cm.

SAFETY CONSIDERATIONS

Special care should be taken in handling concentrated H_2SO_4 . Avoid contacting skin or clothing with the acid. When diluting with H_2O , pour the H_2SO_4 in slowly with continuous stirring to avoid excessive splattering. When heating solutions in boiling water, the water bath should not be so full that the flask would overturn and cause dangerous splashing. Flasks may be kept upright by placing weighted discs over them. Spills on skin or clothing should be washed with large amounts of water.

Since the physiological effects of DDS are not known, it should be handled with care and hands thoroughly washed after direct contact.

GENERAL PROCEDURE

A sample with a volume of less than 1 ml is pipeted into a dry, 25-ml volumetric flask. If nitrite is potentially present in the samples, add 100 μl of 100 g/liter urea and swirl the flask to mix. Since the time required for nitrate destruction is dependent on pH, no specific

amount of time has been designated for this step. However it has been found that removal of nitrite is more complete if the solution is allowed to stand for longer times after adding urea. If halides are present, pipet 100 μg of Ag^+ into the flask and swirl for mixing. If the sample is highly caustic, a brown NaOH precipitate will form. If the sample is acid, only the white AgCl precipitate is visible. Following the removal of these interfering ions, 5 ml of DDS is placed in the flask and swirled to mix. The contents will heat up from the dilution of H_2SO_4 and the yellow color should begin to form. Place the flask in a boiling water bath for 15 minutes to allow the color to completely develop. After heating the flask, allow the contents to cool 5 minutes and then bring the flask to volume with deionized H_2O . Permit the flask to cool to room temperature and again bring to volume. After the flask is cool and at the proper volume, add a stir bar and mix well. If halides are present it is necessary to centrifuge a portion of the sample before measuring its absorbance at 410 nm versus a reagent blank. The method is calibrated by carrying aliquots of nitrate from 50 μg to 500 μg through the procedure.

RESULTS AND DISCUSSION

DETERMINATION OF THE OPTIMUM PARAMETERS

For the initial work on this procedure, the method described by Szekely^[9] was used: 4 ml of 2.0 g/liter DDS and no urea or silver. When the procedure was calibrated using this technique it was found that the sensitivity was less than that described by Szekely and the high calibration point, 500 μg nitrate, formed a precipitate and gave low percent recoveries. For a 100 μg nitrate aliquot an absorbance (A) of 0.179 was observed compared with Szekely's 0.310.

Interestingly, our molar absorptivity was about 2800 liters mole⁻¹ cm⁻¹ compared with Szekely's 2400 liters mole⁻¹ cm⁻¹. Since the sensitivity was lower than expected, attempts were made to scale the procedure down to a 10-ml flask. In this calibration 1.5 ml of 2.0 g/liter DDS were used and aliquots of 100 µg/ml NO₃⁻ from 100 to 500 µl were pipeted into the flask using one deionized H₂O rinse for the pipet. This time the color of the 300, 400, and 500 µl aliquots of nitrate failed to develop completely. When the experiment was repeated using total sample volumes less than 200 µl, a proper calibration was obtained indicating that the color development was a function of the concentration of either DDS or H₂SO₄. A test was designed to determine the limitations on sample volume. A 100 µg (100 µl) sample of the 1000 µg/ml NO₃⁻ standard and 10-ml flasks were used in all tests; however the number of 100 µl deionized H₂O rinses were increased so that the ratio of the volume of DDS to total sample volume decreased steadily. The heating time was increased to 30 minutes and the volume of DDS held constant at 1.5 ml. The results of these tests are shown in Table I. These data indicate that the ratio of the volume of DDS to total sample volume should be kept greater than 3:1 or that the molarity of H₂SO₄ should be greater than 13.0M in the color-developing mixture if reasonable percent recoveries are to be obtained. Therefore any other reagents such as Ag⁺ or urea added to the procedure should be high enough in concentration so that only small volumes would be needed. Also, the volumetric flask should be dry before beginning the method in order to insure control of the sample volume. Since the volume limitation was critical to the procedure, automatic pipets with plastic tips were used in many of the tests for adding nitrate and additional reagents without rinsing.

TABLE I
EFFECT OF SAMPLE VOLUME ON COLOR DEVELOPMENT
OF 100 $\mu\text{g NO}_3^-$ WITH DDS

<u>Total Sample Volume</u> <u>μl</u>	<u>Ratio</u> <u>Volume of DDS (1.5 ml)</u> <u>Total Sample Volume</u>	<u>H₂SO₄</u> <u>M</u>	<u>Absorbance</u>	<u>%</u> <u>Recovery</u>
200	7.5	15.9	0.478	105.2
300	5.0	15.0	0.483	106.3
350	4.3	14.5	0.470	103.4
400	3.7	14.2	0.460	101.2
450	3.3	13.8	0.462	101.6
500	3.0	13.5	0.454	99.8
600	2.5	12.9	0.438	96.4
700	2.1	12.3	0.258	56.8
800	1.9	11.7	0.257	56.5

The effect of the concentration of DDS on the method was studied by analyzing a 400 $\mu\text{g NO}_3^-$ aliquot with different volumes of 2.0 g/liter DDS. Twenty-five milliliter flasks were used in the experiment and the solution was again heated for 30 minutes. The results of this test are shown in Table II.

TABLE II
EFFECT OF DDS CONCENTRATION ON COLOR
DEVELOPMENT OF 400 $\mu\text{g NO}_3^-$

<u>Volume</u> <u>2.0 g/liter DDS</u>	<u>Absorbance</u>	<u>%</u> <u>Recovery</u>	<u>Comments</u>
2 ml	-	-	Precipitated during dilution.
3 ml	-	-	Precipitated during dilution.
4 ml	0.445	62	Precipitated in cell after 15 minutes.
5 ml	0.715	100	Stable.
6 ml	0.711	99	Stable.

These data indicated that there was either insufficient

DDS or H_2SO_4 to prevent precipitation when less than 5 ml of 2.0 g/liter DDS was used. This precipitate was similar to that seen on the 500 μg nitrate standard of the original calibration. When a 500 μg nitrate standard was run using 5 ml of 2.0 g/liter DDS no precipitate formed immediately and 102.4% recovery was obtained. However, when the absorbance of this sample was measured versus time the absorbance began to decrease within five minutes after placing the sample in the cell due to precipitate formation. The color of the 400 μg nitrate standard analyzed with 5 ml of 2.0 g/liter DDS was stable for over two hours. In order to overcome the formation of the precipitate a 4.0 g/liter DDS solution was prepared. When a 500 μg nitrate standard was analyzed using 4 ml of 4.0 g/liter DDS, the precipitate formed as before. Re-analyzing the 500 μg standard with 5.0 ml of 4.0 g/liter DDS resulted in a clear solution that was stable for over two hours and gave 100% recovery. Since 5 ml of 2.0 g/liter DDS gave a precipitate with 500 μg nitrate and 5 ml of 4.0 g/liter DDS did not, it would appear that the precipitate formation may be a function of both DDS and H_2SO_4 concentrations.

The effect of sample volume was found to be unchanged when 4.0 g/liter DDS was used in lieu of the 2.0 g/liter reagent. The effect of adding additional H_2SO_4 to determine if the limitations on sample volume may be increased or the formation of the precipitate removed was not studied at this time but may be of future interest.

During these studies the heating time in the procedure varied from 15 to 30 minutes. Since the rate of color development appeared to be slower for larger sample volumes, the time was increased to 30 minutes for these studies. The effect of time and temperature are discussed in greater detail by Szekely^[9] who found that by placing the samples

in a cold water bath, heating to boiling, and holding there for two minutes, complete color development occurred. We chose to place the samples directly into a boiling H₂O bath. For sample sizes less than 500 μ l and with uncomplicated matrices, the color formation was complete in about five minutes. However for larger sample sizes and more complicated matrices, this time was not adequate; therefore a 15-minute heating time was adopted for all samples. Differences in this work and that of Szekely,^[9] such as the precipitation formation, absorbances and molar absorptivities, and the sample volume effect, are not easily explained; however the DDS reagent purity was one aspect of the method that was not established and may explain some of these differences.

EFFECT OF SODIUM HYDROXIDE ON THE METHOD

Since the concentration of NaOH in the nuclear waste being analyzed was as high as 18M, it was necessary to establish the limitations of the method for caustic samples. Tests in which 200 μ g of nitrate were spiked with varying quantities of NaOH were conducted and the results shown in Table III.

Blanks were run to estimate the amount of NO₃⁻ in the two NaOH solutions used in the study. Percent recoveries were calculated by subtracting the appropriate blank reading from the direct absorbance reading. Most of the results for the corrected percent recoveries are biased high; however this may be due to inaccurate blank subtractions. The low recovery for the 6.0 milliequivalent NaOH test is probably due to the sample volume effect described. Since percent recoveries at high NaOH concentrations are reasonable and since dilutions of nuclear waste are normally required before analyses, no NaOH tests at higher concentrations were performed.

TABLE III
EFFECT OF NaOH CONCENTRATION ON THE
DETERMINATION OF NITRATE WITH DDS

	<u>NaOH</u> <u>meq</u>	<u>NO₃⁻</u> <u>μg</u>	<u>Absorbance</u> <u>A</u>	<u>%</u> <u>Recovery</u>	<u>Corrected</u> <u>% Recovery</u>
<i>1M</i> NaOH, μl					
250	0.25	None	0.005	-	-
100	0.10	200	0.343	103.3	102.8
250	0.25	200	0.349	104.8	103.5
500	0.50	200	0.331	100.2	97.6
1000	1.00	200	0.366	109.2	104.0
<i>4M</i> NaOH, μl					
500	2.00	None	0.020	-	-
500	2.00	200	0.376	111.8	106.6
1000	4.00	200	0.403	118.7	108.4
1500	6.00	200	0.351	105.3	89.9

NITRITE INTERFERENCE AND REMOVAL RESULTS

Szekely^[9] found that nitrite (NO₂⁻) interfered by giving high results when present at 20 ppm or greater; however he does not describe the extent of interference at that level. He also mentions that NO₂⁻ interference may be removed by urea but does not describe the procedure used. Considerable effort was made to characterize the effect of nitrite and to find a convenient method for its removal since it can be a major component, whose concentration may exceed nitrate, in caustic radioactive nuclear waste.

Before attempting to destroy nitrite with urea, the effect of NO₂⁻ on the procedure was determined. A 200 μg nitrate aliquot was spiked with varying quantities of 1.03 g/liter nitrite and the color developed using 5 ml of 4.0 g/liter DDS. This amount of DDS and a 15-minute heating time were used in all succeeding tests. The results of these tests are shown in Table IV.

TABLE IV
EFFECT OF NITRITE ON THE DETERMINATION
OF NITRATE WITH DDS

<u>NO₃⁻</u> <u>μg</u>	<u>NO₂⁻</u> <u>μg</u>	<u>Absorbance</u> <u>A</u>	<u>%</u> <u>Recovery</u>	<u>Comments</u>
200	100	0.323	98.1	Peak: 400 nm Pk/350-1.62
200	250	0.313	95.6	Peak: 400 nm Pk/350-1.04
200	500	0.265	83.2	No peak Pk/350-0.56
200	1000	No peak	-	No peak

* Calculation is based on absorbance at 400 nm.

The addition of NO₂⁻ caused the peak of the spectrum to shift from 410 to 400 nm and at high concentrations the peak flattened and finally became nonexistent. This effect is best seen in Figure 1. Another means of estimating the effect of nitrite may be obtained by measuring the ratio of the absorbance of the peak to the valley at 350 nm. This criterion was used in later experiments to estimate the effectiveness of urea in destroying nitrite by using the graph in Figure 2. A blank scan in which 250 μl of NO₂⁻ was carried through the procedure with no nitrate present gave a flat baseline response until it reached about 420 nm where it gradually began to increase exponentially as the ultraviolet region was approached. The blank had a reading of 0.1 A at 350 nm. The changing shape of the curves in Figure 1 is probably the result of a decreasing amount of nitrated DDS and the increasing spectrum from the nitrite. Szekely reported a high percent yield for NO₃⁻ when NO₂⁻ was present. This high yield was probably due to the decomposition of nitrous acid to nitrate when the DDS in H₂SO₄ was added. Interestingly, this positive effect was noticed in

FIGURE 1

EFFECT OF NITRITE ON THE ABSORPTION SPECTRA OF 200 µg NITRATE WITH DDS

FIGURE 2
EFFECT OF NITRITE ON THE RATIO OF THE ABSORBANCE OF
THE NITRATE-DDS PEAK TO THE VALLEY AT 350 nm

tests where the sample was acidified (Tables VI and X) in the presence of urea before adding the DDS but was not noticed in this experiment in which the acid (H_2SO_4) is added with DDS and no urea is present.

The destruction of nitrite with urea is based on the following reaction:

Since the samples to be analyzed were highly caustic, the effectiveness of this technique which depends on the nitrous acid concentration was questionable. Also, the caustic and radioactive natures of the samples could lead to rapid hydrolysis or decomposition of the urea. Therefore the amount of urea added should be as large as possible to allow for these possible losses and to help compensate for the undesirable equilibrium conditions. The effect of urea concentration on the determination of 200 μg of NO_3^- is shown in Table V.

TABLE V
EFFECT OF UREA CONCENTRATION ON THE
DETERMINATION OF NITRATE WITH DDS

	<u>mg Urea</u>	<u>Absorbance</u> <u>A</u>	<u>% Recovery</u>
Urea, 10 g/liter			
	1.0	0.344	103.5
	2.5	0.328	99.4
	5.0	0.339	102.9
	10.0	0.330	99.9
Urea, 50 g/liter			
	5.0	0.325	98.7
	12.5	0.330	99.9
	25.0	0.282	87.6

No significant effects from urea were noticed until 25 mg had been added. In order to keep the volume to a minimum it was decided to use 100 μ l of 100 g/liter urea in our nitrite destruction tests. A new calibration incorporating the use of urea resulted in an approximate 5% loss in sensitivity. The ratio of the absorbance at the peak (405 to 410 nm) to the valley at 350 nm for the calibration was always greater than 2.3.

Two nitrite standards, 1.0 and 10.0 g/liter, were prepared by dissolving reagent-grade KNO_2 in deionized water and including enough NaOH to make the final standard 0.004M in NaOH. The NaOH was added to prevent formation and decomposition of HNO_2 . In the first attempt to destroy nitrites a 200 μ g aliquot of NO_3^- was spiked with varying concentrations of NO_2^- followed by the addition of 100 μ l of 100 g/liter urea. The samples were swirled for mixing purposes after pipeting each reagent. One drop of concentrated H_2SO_4 was then added to insure that any NO_2^- was present as HNO_2 . The color was then developed as normal; the results are shown in Table VI.

TABLE VI
UREA DESTRUCTION OF NITRITE FOLLOWING SAMPLE
ACIDIFICATION WITH CONCENTRATED H_2SO_4

NO_2^- , μ g	Absorbance A	% Recovery	% $\text{NO}_2^- \rightarrow \text{NO}_3^-$
100	0.302	93.4	-
250	0.339	104.1	-
500	0.365	111.6	4.6
1000 (1 ml-1 g/liter	0.443	133.8	6.8
1000 (100 μ l-10 g/liter	0.398	121.0	4.2
2500	0.820	242.4	11.4

All the tests gave normal spectrums with peaks at 405 nm and peak-to-valley ratios (405/350) greater than 2.3. The

high percent recoveries are explained by the self-decomposition of HNO_2 ^[10] to form NO_3^- (Equation 2).

At NO_2^- concentrations of 2500 μg and greater, brown NO_2 fumes were visible which indicated the above reaction was probably taking place since NO gas reacts readily with O_2 in the air to form NO_2 gas.^[11] Wetters and Uglum^[10] point out that nitrous acid may also decompose by another mechanism (Equation 3). The gases involved in Equations 2 or 3 may be absorbed in the aqueous sample matrix to yield further NO_3^- .

The higher probability of a larger sample volume absorbing these gases may explain the differences in the two 1000 μg NO_2^- tests. When greater than 2500 μg of NO_2^- were added, a precipitate formed indicating that enough HNO_2 had decomposed to NO_3^- that insufficient DDS or H_2SO_4 were present to keep the species in solution. Obviously this method is inadequate for destroying nitrites. Since high results may be obtained with no changes in the spectrum, there is no way of distinguishing if nitrite is present. The effect of heating the sample to aid in removing NO and NO_2 gases before adding DDS was studied and showed no significant advantages.

The next attempt to remove NO_2^- with urea was done without concentrated H_2SO_4 . The pH was a function of the buffering effect of 100 μl of 100 g/liter urea and the 0.004M NaOH in the varying amounts of NO_2^- . No pH values were recorded because of the difficulty of measuring the pH of a very small volume in the bottom of a 25-ml volumetric flask. Two tests were run in which 200 μg of NO_3^- were spiked

with 2.5 mg of NO_2^- , urea added, and one solution allowed to stand 15 minutes while the other was heated in a boiling H_2O bath for 15 minutes. Finally, the DDS was pipeted and the color developed as described earlier. The spectra from these two samples were not characteristic of the NO_3^- -DDS spectrum but resembled earlier spectra from the nitrate studies in which no urea was added (Figure 1). The spectra for these tests looked like the 500 μg NO_2^- spectrum in Figure 1 with peak-to-valley ratios of 0.65 and 0.61 (heated sample). These ratios correspond to about 450 μg of NO_2^- remaining according to Figure 2. This means the nitrite concentration was reduced by a factor of 5 using this technique. The percent recovery for the 200 μg NO_3^- when the absorbance was measured at 410 nm was 86%. Even though this approach did not provide a complete removal of NO_2^- , it did allow its concentration to be reduced significantly and gave a spectrum that indicated nitrite was present at a possible interfering level. The next tests were conducted on lower concentrations of nitrite spikes with 200 μg of NO_3^- . Again the pH was regulated by the 0.004M NaOH in the NO_2^- and the urea. All but three samples were allowed to stand for one hour after adding urea and before pipeting DDS--two sat for two days and one overnight. The results of this test are shown in Table VII. All other conditions were the same as described earlier.

Peak shapes for these studies may be visualized from comparison of the peak/350 ratios with those in Table IV and correlating this with the spectra in Figure 1. The percent recoveries were based on actual peaks or the height of a plateau. Absorbances for peaks, when they occurred, were measured at 405 nm, plateaus were measured at 400 nm; and percent recoveries based on these values. These data indicate that nitrite concentrations five times greater than nitrate can be tolerated even though the spectral shape has

TABLE VII
UREA DESTRUCTION OF NITRITE
IN BASIC OR NEUTRAL MEDIA

NO_2^- , μg	<u>Absorbance</u> A	<u>Ratio</u> $\text{NO}_2^-/\text{NO}_3^-$	<u>%</u> Recovery	<u>Pk/350</u>	<u>Final NO_2^-</u> <u>Concentration</u> μg
2500 ^a	0.270	12.5	113.0	0.76	≈ 375
1000	0.325	5.0	100.1	1.08	≈ 250
1000 ^b	-	5.0	95.3	0.94	≈ 250
500	0.305	2.5	94.3	0.89	≈ 300
500 ^b	-	2.5	88.1	0.95	≈ 250
250	0.323	1.0	99.5	1.29	≈ 150
100	0.315	0.5	97.5	1.65	≈ 90

^aSat overnight.

^bSat two days.

changed. The fact that a change in the spectrum occurs when nitrite is present using this technique allows one to recognize a potential error in the analysis so that the sample may be checked further using nitrate spikes.

A series of tests was conducted using this technique to remove a constant amount of nitrite (250 μg) from samples with varying nitrate concentrations. In addition, a sample was analyzed in which the ratio of the NO_2^- -to- NO_3^- was equal but the amount of NO_3^- was at its maximum calibration level. The results of these tests are shown in Table VIII. These

TABLE VIII
EFFECT OF A CONSTANT AMOUNT OF NITRITE
ON THE ANALYSES OF VARYING NITRATE CONCENTRATIONS

<u>NO_2^-</u> <u>μg</u>	<u>NO_3^-</u> <u>μg</u>	<u>$\text{NO}_2^-/\text{NO}_3^-$</u> <u>Ratio</u>	<u>%</u> <u>Recovery</u>	<u>Peak/350</u> <u>Ratio</u>
250	50	5.	115.0	0.92
250	100	2.5	99.5	0.97
250	400	0.63	93.8	1.48
250	500	0.5	95.8	1.59
500	500	1.0	92.5	1.55

data indicate that when quantities of NO_3^- near the measurement limit are analyzed in the presence of larger quantities of nitrite, that a loss of precision and accuracy may occur. Due to the nature of the nitrite removal technique, the percent recovery for a standard is probably dependent not only on the ratio of NO_2^- -to- NO_3^- , but also on the absolute quantities of these materials added to the procedure.

It was mentioned earlier that as the pH or NaOH concentration increased that the effectiveness of the urea to decompose nitrite would be reduced. A 200- μg aliquot of NO_3^- was spiked with 500 μg NO_2^- and 100 μl of 4M NaOH and carried through the procedure. When the results of this sample were compared with the one analyzed under the same conditions but without NaOH, the percent recovery had decreased from 90% (no NaOH) to 64% and the peak-to-valley ratio decreased from 0.87 to 0.61. Therefore if caustic samples with significant amounts of nitrite were to be analyzed it would be necessary to reduce the hydroxide concentration by dilution or neutralization.

Since the method still did not provide for the complete reduction of nitrite and since accurate neutralization to a desired pH is difficult to implement, studies were undertaken to find a system for the removal of nitrite using either a different reducing agent or a different acidic medium for reduction with urea. Several techniques for removing nitrites are mentioned by Boltz.^[12] One of these^[13] describes the destruction of NO_2^- with urea from acetic acid; however details of acid concentration and other conditions are omitted. A series of tests was designed to determine if acetic acid could be substituted for H_2SO_4 (Table VI) to remove NO_2^- without forming NO_3^- . Tests to determine the amount of acetic acid that could be tolerated in the procedure were performed by spiking 200 μg NO_3^- with varying

quantities of acetic acid. The results of these tests are shown in Table IX.

TABLE IX
EFFECT OF ACETIC ACID ON THE DETERMINATION
OF NITRATE WITH DDS

<u>Volume</u> <u>μl</u>	<u>Acetic Acid</u> <u>M</u>	<u>Absorbance</u> <u>A</u>	<u>% Recovery</u>
100	1	0.321	98.4
250	1	0.316	97.0
500	1	0.326	99.6
750	1	0.328	103.3
100	10	0.310	95.3
250	10	0.300	92.4
500	10	0.310	95.3
750	10	0.310	95.3

The method is capable of tolerating large quantities of acetic acid. Tests to remove NO_2^- were carried out using various amounts of acetic acid. These tests and results are outlined in Table X.

TABLE X
NITRITE REMOVAL FROM ACETIC ACID WITH UREA

<u>NO_3^-</u> <u>μg</u>	<u>NO_2^-</u> <u>μg</u>	<u>Amount of</u> <u>Acetic Acid</u>	<u>%</u> <u>Recovery</u>	<u>Peak/350</u>	<u>%</u> <u>$\text{NO}_2^- \rightarrow \text{NO}_3^-$</u>
200	1000	200 μ l (0.1M)	168.1	1.08	13.6
200	1000	500 μ l (0.1M)	219.7	1.26	23.9
200	1000	100 μ l (1.0M)	276.0	1.57	35.2

The spectrum and peak/350 ratios from acidification with acetic acid indicated that not all of the nitrite had been destroyed. Sulfuric acid acidification (Table VI) gave peak-to-valley ratios greater than 2.3, indicating no remaining NO_2^- . Also the percent of nitrite converted to nitrate for H_2SO_4 acidification was less than that for the acetic acid. Therefore no real advantages were gained from the use of

acetic acid media in the reduction of nitrite.

Boltz^[12] refers to the use of other reducing agents such as sulfamic acid^[14] and thiourea^[15] for the reduction of nitrite to nitrogen. However, Szekely^[9] determined that sulfamic interfered at the 100 ppm level and therefore this reagent was not studied. Wetters and Uglum^[10] studied the effect of various reducing agents on the determination of nitrite and nitrate by measuring the ultraviolet absorption spectra of these ions at 355 and 302 nm, respectively. They found that hydrazine sulfate, hydroxylamine hydrochloride, sodium hydrogen sulfite, sodium metabisulfite, and L-ascorbic acid completely reduced NO_2^- when present at a concentration of 0.25M or greater. Since hydroxylamine sulfate reagent was convenient, it was tested for nitrite reduction for this procedure. Aliquots of 50 and 100 μl of 2M $\text{NH}_2\text{OH}\cdot\text{HSO}_4$ were added to samples containing 200 μg NO_3^- and 1000 μg NO_2^- in the sequence where urea was normally used. These samples failed to develop color. A test in which only nitrate was used with NH_2OH also did not develop color. Therefore $\text{NH}_2\text{OH}\cdot\text{HSO}_4$ could not be used to reduce nitrites. The major conclusion from all these tests was that nitrite could not be reduced easily without interfering with the color development or the generation of additional nitrate from nitrous acid decomposition. Ideally the desirable reducing agent would be one that could reduce NO_2^- to nitrogen gas in basic medium without reducing NO_3^- and without affecting the DDS-nitrate color development. Future work in this area should include the study of additional reducing agents and acid systems, closer attention to the pH effect on the rate of nitrite reduction, and a study on the order of addition of reagents. In all these studies urea was added before the acid. The effect of reversing this order may provide better nitrite reductions.

Alternate approaches to this problem could be found in the Wetters, Uglum^[10] method for NO_3^- and NO_2^- or from differential spectrophotometric methods^[1,12] in which all the NO_2^- is oxidized to nitrate or where all the NO_3^- is reduced to NO_2^- and the nitrate determined from the difference.

INTERFERING ION STUDY

Szekely^[9] studied 42 different ions and compounds for their effects on the method. However some ions were not included in this work or were not studied at high enough concentrations for our applications. In order to study interfering cations, solutions were prepared from oxides, sulfates, or acetates. Concentrations for the ions were based on direct weighings of the materials and their designated waters of hydration without further standardization. The interfering ions were spiked with 200 μg of NO_3^- . Urea was used and allowed to stand 30 minutes before pipeting the DDS and developing the color as described earlier. The results of this test are shown in Table XI.

Chloride interfered by causing low results and without significantly changing the peak-to-valley ratio. The peak shape from Cl^- interference changed only a little and was distinguished by a flattening of the peak toward the ultra-violet region. Chloride presents a serious problem since small amounts of chloride can cause significant errors without indicating that it is present in the spectrum. Therefore a method to remove chloride using Ag_2SO_4 must be used and samples potentially containing chloride frequently checked with spikes. Fortunately most samples in the nuclear processing industry contain high ratios of nitrate-to-chloride. Bromide, iodide, and fluoride produce similar interferences. Iron(II) interference generates a spectrum that is similar

TABLE XI
EFFECT OF INTERFERING IONS ON THE DETERMINATION
OF NITRATE WITH DDS

<u>Material</u>	<u>Ion</u>	<u>µg Ion</u>	<u>% Recovery</u>	<u>Peak/350 Ratio</u>
NaCl	Cl ⁻	25 (nitrate 400 µg)	92.4	
		25	87.9	2.4
		50	83.9	2.2
FeSO ₄ (NH ₄) ₂ SO ₄	Fe ⁺²	500	20.0	None
		25	91.8	2.1
		100	72.4	1.7
Fe ₂ (SO ₄) ₃	Fe ⁺³	200	51.5	1.1
		100	97.0	2.2
		250	98.2	1.4
K ₂ Cr ₂ O ₇	Cr ⁺⁶	500	107.3	1.1
		50	95.3	1.7
		100	93.6	1.4
CuSO ₄	Cu ⁺²	500	115.3	0.7
		100	96.2	2.3
		500	100.7	2.7
NiSO ₄	Ni ⁺²	500	100.7	2.9
		100	96.7	2.3
		500	100.7	2.9
KI	I ⁻	25	75.6	2.7
		100	63.8	3.3
KBr	Br ⁻	25	86.2	2.3
		100	73.3	2.3
KMnO ₄	Mn ⁺⁷	25	87.8	2.0
		100	77.6	1.5
MnSO ₄	Mn ⁺²	100	91.0	2.7
		500	98.2	2.9
ZnSO ₄	Zn ⁺²	100	91.3	2.6
		500	101.3	3.0
Zr (SO ₄) ₂	Zr ⁺⁴	100	92.5	2.7
		500	101.0	2.9
NaF	F ⁻	25	89.6	2.5
		100	63.8	2.9
NaAlO ₂	Al ⁺³	1000	90.4	2.7
		5000	96.2	2.9
NaBrO ₃	Br ⁺⁵	50	83.3	1.8
		200	59.5	1.1
NaSiO ₃	Si ⁺⁵	100	95.3	2.6
		500	101.3	2.8
UO ₂ (C ₂ H ₃ O ₂) ₂	U ⁺⁶	100	97.3	2.4
		500	101.9	2.8
KIO ₃	I ⁺⁵	50	73.3	2.3
		200	81.9	1.8
Ba (OH) ₂	Ba ⁺²	100	71.6	3.2
		500	85.3	3.4
CdO	Cd ⁺²	100	91.9	2.7
		500	102.2	2.8
Sb ₂ O ₃	Sb ⁺³	100	93.6	2.8
		500	100.7	2.8
Na ₂ WO ₄	W ⁺⁶	100	88.2	2.4
		500	100.5	2.7
NaBiO ₃	Bi ⁺⁵	100	89.3	2.6
		500	98.5	2.7

to that of NO_2^- and is detectable by the peak-to-valley ratio. In highly caustic solutions the amount of Fe^{+2} should be insignificant due to its insolubility. Acid solutions of Fe^{+2} would not be stable unless a reducing agent were present. If Fe^{+2} were interfering it would be necessary to find an oxidizing agent that would oxidize Fe^{+2} to Fe^{+3} without changing the status of NO_2^- to NO_3^- and not interfere with the color development. Iron(III) interference studies gave good recoveries with lower than normal peak-to-valley ratios. This was probably due to the increasing absorbance in the ultraviolet caused by colored $\text{Fe}_2(\text{SO}_4)_3$. Chromium(VI) reacted with the DDS reagent, forming a brown-colored solution. This oxidation product did not interfere at the 100 μg Cr(VI) level; however its ultraviolet spectrum began overlapping the nitrate spectrum at the 500 μg level, causing high percent recoveries. Bromate at the 200 μg level caused the absorbance peak to shift to 360 nm and produced low results. Since the recoveries for these two ions were similar to those for permanganate, this effect may be due to the oxidizing nature of these ions. Barium, cadmium, and tungstate formed a precipitate on the addition of DDS. Precipitation of BaSO_4 seemed to have the greatest effect on the percent recovery. Cases in which the higher levels of interfering ions gave better recoveries than lower levels may be explained by nitrate contamination in the ion solutions or from the poor accuracy, as noted with standards, in the automatic pipets being used. These data coupled with the work of Szekely^[9] who studied many ions not discussed here provides a comprehensive study of interfering ions for this method. A list of ions studied by Szekely but not discussed here is shown in Table XII.

TABLE XII
ADDITIONAL INTERFERING IONS STUDIED BY SZEKELY

Ion	Concentration	Effect
	ppm	
K^+ , Na^+ , NH_4^+	1000	None
Ca^{+2} , Mg^{+2} , Hg^{+2} , Ag^+ , PO_4^{3-}	500	None
SO_3^{-} , $S_2O_8^{-2}$, $S_4O_6^{-2}$	500	None
Cr^{+3} , BO_3^{-3}	100	None
Co^{+2} , Pb^{+2} , MoO_4^{-2}	20	None
SCN^{-}	20	Negative
Cl_2 , Br_2	20	Positive
Sulfamic acid	100	Negative
Aliphatic alcohols	-	Negative
Pyridine	Large amounts	None
Aliphatic amines and amino acids	Large amounts	None
Aliphatic amino-alcohols	Large amounts	None
Ethyl acetate		Negative

SILVER SULFATE STUDIES TO REMOVE CHLORIDES

The addition of solid Ag_2SO_4 to remove Cl^{-} may be difficult to regulate on routine operations. Therefore a solution of Ag_2SO_4 that was 1 g/liter in Ag^+ was prepared and used in these studies; results are shown in Table XIII.

Tests A and B were run to determine the effect of removing Cl^{-} with Ag^+ from acid and basic samples. The samples in Test A were slightly acid due to a small amount of H_2SO_4 used to help dissolve the Ag_2SO_4 . When silver was added to the acid samples a white, coarse precipitate of $AgCl$ formed immediately. After the addition of the DDS the precipitate was not visible in the sample containing 25 μg Cl^{-} . However all samples were centrifuged before making any absorbance

TABLE XIII
REMOVAL OF CHLORIDE INTERFERENCE WITH SILVER SULFATE

	Conditions	% Recovery
A1:	200 μg NO_3^- + 25 μg Cl^- + 100 μg Ag^+ 100 μl urea + DDS - neutral or acid	91.9
A2:	200 μg NO_3^- + 100 μg Cl^- + 100 μg Ag^+ 100 μl urea + DDS - neutral or acid	92.4
B1:	200 μg NO_3^- + 25 μg Cl^- + 100 μl 4M NaOH 100 μg Ag^+ + 100 μl urea + DDS - basic	91.2
B2:	200 μg NO_3^- + 100 μg Cl^- + 100 μl 4M NaOH 100 μg Ag^+ + 100 μl urea + DDS - basic	85.5
C1:	200 μg NO_3^- + 50 μg Cl^- + 100 μl urea + 100 μg Ag^+ + DDS - neutral or acid	102.0
C2:	200 μg NO_3^- + 100 μg Cl^- + 100 μl urea + 100 μg Ag^+ + DDS - neutral or acid	100.9
C3:	200 μg NO_3^- + 100 μg Cl^- + 100 μl 4M NaOH 100 μl urea + 100 μg Ag^+ + DDS - basic	92.5
D1:	200 μg NO_3^- + 100 μg Cl^- + 25 μl 4M NaOH + 100 μl urea + 100 μg Ag^+ + DDS - basic	88.2
D2:	200 μg NO_3^- + 100 μg Cl^- + 50 μl 4M NaOH + 100 μl urea + 100 μg Ag^+ + DDS - basic	91.0

measurements. The addition of Ag^+ to the basic samples gave a brown precipitate, probably Ag_2O , which disappeared and formed a fine white precipitate after the addition of DDS. When NaOH is present the removal of chlorides does not appear to be as efficient. The next series of tests ("C") was carried out to determine the result of adding urea before Ag^+ . This change gave better percent recoveries; however samples with NaOH still gave poorer results. The precipitation formations were the same as in Tests A and B. In Test D the effect of lower NaOH concentrations was investigated and found still to be low compared with neutral or acid solutions. The effectiveness of 100 μg Ag^+ on precipitating or complexing 100 μg Cl^- is questionable since not enough silver was present for a stoichiometric reaction. It

is therefore recommended that if greater than 25 μg of Cl^- are present in the sample, the amount of Ag^+ should be increased to 500 μg . The precipitation should be carried out in neutral or acid matrices, if possible, for optimum results. The addition of urea before silver appears to give better results. When applying this method to samples containing significant amounts of chloride, the results should be checked with spiked samples.

PRECISION AND ACCURACY

The results of day-to-day quality control checks on the calibration were run during the test and the results shown in Table XV.

TABLE XV
PRECISION AND ACCURACY OF NITRATE ANALYSES

<u>No. of Analyses</u>	<u>NO_3^- μg</u>	<u>Average % Recovery</u>	<u>Standard Deviation %</u>
5	100	105.3	± 7.3
12	200	96.4	± 3.3
11	300 to 500	99.8	± 2.4

All data $\bar{x} = 99.3 \pm 5.0\%$.

Some of the data from the 100 μg tests in which cloudiness was observed were not used to calculate the precision or accuracy. The reason for the cloudiness was not determined but may be due to the use of aged urea or DDS reagent. Samples analyzed with new urea gave improved results for the 100 μg points; however the precision of the slope and intercept for the calibration using new urea was worse, indicating that perhaps new DDS should have been used. When no nitrite is present the method should be calibrated without urea, which will result in higher sensitivity and possibly

better precision. Until a better explanation for the precipitation is found both the urea and DDS should be replaced and a new calibration run whenever deviations begin to occur at low nitrate levels.

A sample of synthetic waste was analyzed numerous times with and without nitrate spikes in order to determine the accuracy and precision on an actual sample. Spikes were made with 100 μg of the standard KNO_3 solution. The contents of this sample are outlined in Table XVI.

TABLE XVI
CONTENTS OF DISSOLVED SOLIDS SAMPLE OF SYNTHETIC WASTE
(8.4 g/100 ml H_2O)

<u>Ion</u>	<u>Concentration</u> <u>g/liter</u>
Na^+	25.0
Al^{+3}	4.2
NO_2^-	1.5
NO_3^-	19.7
CO_3^-	0.4
SO_4^-	1.7
OH^-	10.9

The results from this sample are given in Table XVII.

If spikes greater than 100 μg nitrate had been used, they would have probably provided a better indication of matrix interferences since the standard deviation at higher levels would have been less.

APPLICATIONS

This method was developed to analyze dissolved solids and supernatants from in-tank solidification studies on synthetic nuclear waste. A specific ion electrode is used

TABLE XVII
RESULTS OF ANALYSES OF DISSOLVED SOLIDS WASTE

<u>Dilution</u>	<u>g/liter NO₃⁻ Results</u>	<u>Spike Recovery</u>
1 ml-10 ml- 50 μ l	21.49	-
1 ml-10 ml-200 μ l	19.88	101.7
1 ml-10 ml-300 μ l	20.10	-
1 ml-10 ml-100 μ l	19.06	74.4
1 ml-10 ml-100 μ l	19.70	106.9
1 ml-10 ml-200 μ l	19.30	103.5
25 μ l	20.70	75.6
1 ml-10 ml-100 μ l	20.06	102.3
1 ml-10 ml-200 μ l	19.14	111.5
1 ml-10 ml-100 μ l	19.83	91.9
1 ml-10 ml-100 μ l	19.31	92.0
1 ml-10 ml-200 μ l	18.90	119.0
1 ml-10 ml-200 μ l	19.50	111.6
1 ml-10 ml-100 μ l	19.50	100.6
1 ml-10 ml-100 μ l	19.50	101.2

$\bar{X}$ = 19.73 $\pm$ 0.67 g/liter NO₃⁻.

Spike % recovery $\bar{X}$ = 99.4 $\pm$ 13.1%.

for high levels of NO₃⁻ ($>10^{-2}M$). However these samples contain large quantities of salts which cause the total ionic strength of the samples to vary. Analyses of low nitrate ($<10^{-3}M$) concentration by specific ion electrodes are more subject to errors caused by varying ionic strengths and possible interfering ions. The spectrophotometric method using DDS provides a means for analyzing these lower nitrate samples and provides an alternate method for the higher nitrate samples. Table XVIII gives the components and their ranges of concentrations for the synthetic nuclear waste that was analyzed using this method. On most samples, particularly the dissolved solids which were lower in nitrate, the ratio of nitrate-to-nitrite was greater than 5:1. Supernatants were normally analyzed by specific ion electrode with an occasional check with the colorimetric method. Eleven samples were analyzed with 200 μ g nitrate spikes.

TABLE XVIII
SYNTHETIC NUCLEAR WASTE COMPOSITION

Ion	Concentration Range of Solids*		Concentration Range of Supernatant	
	<u>g of Ion/g of Solids</u>		<u>M</u>	
Na	0.20	-0.36	7.4	-27.7
Al	0.001	-0.08	0.3	- 1.4
NO ₂ ⁻	3 x 10 ⁻⁶	-0.07	0.002-	2.7
NO ₃ ⁻	0.14	-0.67	1.5	- 5.7
CO ₃ ⁼	0.002	-0.09	0.01	- 1.0
OH ⁻	0.03	-1.3	7.6	-18.4

* NOTE: Between 4 to 10 g of solids were dissolved in 100 ml of deionized H₂O.

The spike recoveries on these samples averaged 94.7 ±8.6%. Some of these samples gave low results (80%); however when these were analyzed with a new calibration, recoveries were greater than 90%. Tests in which Ag⁺ was used to remove Cl⁻ in the samples did not show any improvement in the results. In addition to nuclear waste this method may find application in other chemical industries where a rapid, moderately sensitive, and selective nitrate analysis is required.

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APPENDIX

APPENDIX

DETAILED PROCEDURE FOR ANALYSIS OF NITRATE
WITH 4,4'-DIAMINODIPHENYLSULFONE (DDS)

Procedure	Comments
1. Pipet the sample into a clean, dry, 25-ml volumetric flask. Sample should contain 50 to 500 μg of nitrate. Pipet sample and rinses onto bottom of flask. At the same time begin a flask for a reagent blank.	<p>a. Rinse once with deionized H_2O (D-H_2O) for samples less than 500 μl. Do not rinse for larger sample sizes.</p> <p>b. Total sample volume should be less than 1 ml to insure total color development. Therefore flask should be dry.</p> <p>c. Flasks should be cleaned only with D-H_2O. Pipets should be cleaned with D-H_2O and acetone. Nitric acid should not be used for cleaning. Sulfuric acid may be substituted for HNO_3 if acid is needed.</p> <p>d. The sample should contain less than 1000 μg NO_2^-, 100 μg Fe^{+2}, 100 μg Cr^{+6}, 50 μg halide, 500 μg Fe^{+3}. See interfering ion studies.</p>
2. Add 100 μl of 100 g/liter urea to the bottom of the flask. Swirl the flask to mix and allow to stand 30 min if >250 μg of NO_2^- is present. Omit the urea if NO_2^- is absent; however calculate results using a calibration without urea.	<p>a. Urea is added to remove NO_2^-. The effectiveness of this reagent is a function of pH and nitrite concentration (see text).</p> <p>b. Less than 10 min are required for samples which contain less than 250 μg NO_2^-.</p>
3. Add 100 μl of 1 g/liter Ag^+ as silver sulfate	a. If over 50 μg of halide are present the amount of Ag^+

Procedure	Comments
swirl to mix. This step may be omitted if the halide ion concentration is 50 times lower than the nitrate.	should be increased so that it is 3 times greater than the halide. Solid Ag_2SO_4 may be needed to minimize increase in volume.
	b. The presence of halides (Cl^-) is noted by the formation of a white precipitate (AgCl) in acid solutions and a brown precipitate (Ag_2O) in basic solutions which dissolves in the H_2SO_4 from the DDS leaving only the AgCl .
4. Add exactly 5 ml of 4.0 g/liter DDS to the flask and swirl. Wash down the sides of the flask with the DDS.	a. A yellow color should begin to form. The flask and contents will be hot due to the dilution of H_2SO_4 . b. Any Cr^{+6} in the sample may be detected by a brown discoloration of the DDS.
5. Place the flask in a boiling H_2O bath for 15 min to insure complete color development.	The level of H_2O in the bath should be determined with the maximum number of flasks filled with 6 ml of H_2O before running samples since overfilling the bath may result in the flask overturning and dumping H_2SO_4 into hot H_2O causing dangerous splattering of acid. An alternate approach is to use a weighted collar on the flask to prevent it from overturning.
6. Remove the flasks from the bath and allow them to cool for 3 to 5 min.	Cooling is necessary before diluting with deionized H_2O to prevent excessive heating and splattering.
7. Carefully dilute the flasks with D- H_2O . Swirl the flasks when they are 3/4 full in order to obtain adequate	a. More heat is generated. b. If over 500 μg of NO_3^- are in the sample, a white precipitate may form due to

Procedure	Comments
mixing of the H_2SO_4 and H_2O . Continue to dilute and swirl until the flask is nearly filled to the mark.	insufficient DDS. Use a smaller sample size.
8. Place the flask in a cool H_2O bath and allow to stand for 15 to 20 min until they reach room temperature.	a. Flasks may be allowed to cool without a bath but may require 45 to 60 min to reach room temperature. b. It may be advantageous to change the H_2O in the bath after 5 to 10 min since it will become warm.
9. After the flasks have cooled bring them to mark with D- H_2O and stir thoroughly using a glass or Teflon stir bar.	a. Observe the flask carefully for precipitate which may form from too much nitrate or old reagents. b. Stir carefully since H_2O and H_2SO_4 do not mix readily in the neck of the flask. It may be necessary to mix when filling cells by filling and emptying the transfer pipet 4 or 5 times until no swirls appear in the flask or pipet.
10. If Ag^+ halides have precipitated it will be necessary to centrifuge a portion of the sample before placing it in the absorption cell.	
11. Fill a clean absorption cell with the sample and measure the peak absorbance at 410 ± 10 nm against a reagent blank by scanning the sample from 480 to 350 nm.	a. Samples containing Ag^+ halides should be carefully transferred following centrifugation to avoid introducing solids into the cell. Observe the cells and transfer pipets carefully for any precipitate that may be present. If precipitate is present determine

Procedure	Comments
	if it originated from Ag^+ halides, too much nitrate, or old reagents and correct accordingly.
	b. Cells should be cleaned by rinsing with deionized H_2O and ethanol. Cells should be thoroughly dried since ethanol may cause low results.

DISCUSSION

Nitrite interferences are detected by observing the spectrum and the absorbance ratio of the peak-to-350 nm as discussed in the document. [Good results (90 to 95% recovery) are possible for ratios greater than 1.5.] When the ratio falls to 1.0, the peak is flat and shifted to 400 nm. When measured at this point, 80 to 90% recoveries can be expected. Halide interferences are not detectable from the spectrum and require spikes for evaluation.

CALIBRATION

The method is calibrated by carrying aliquots of standard nitrate between 50 and 500 μg through the procedure and analyzing the data using a least squares evaluation. If urea is omitted from samples a separate calibration should be prepared omitting this step since a slight increase in sensitivity is observed. A typical calibration curve is shown in Figure 3.

FIGURE 3

TYPICAL CALIBRATION CURVE FOR THE DETERMINATION
OF NITRATE WITH 4,4'-DIAMINODIPHENYLSULFONE

EXAMPLE OF CALIBRATION DATA

<u>X</u>	<u>Y</u>
<u>NO₃⁻, µg</u>	<u>Absorbance (A)</u>
100	0.129
200	0.297
300	0.480
400	0.643
500	0.826

$$S = \text{slope} = 0.00174 \pm 0.00002 \text{ A}/\mu\text{g}$$

$$I = \text{intercept} -0.0047 \pm 0.006 \text{ A}$$

$$1/S = \frac{574.71 \mu\text{g}}{\text{A}}$$

$$\text{NO}_3^-, \mu\text{g} = (A - I) (1/S)$$

$$\text{NO}_3^-, \mu\text{g} = (A + 0.0047) (574.71)$$

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