Spectrophotometric Determination of Nitrite as 4-Nitroso-2,6-Xylenol

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▶ Nitrite reacts with 2,6-xylenol in acid solutions to produce 3,3′,5,5′-tetramethyldiphenoquinone; 3,3′,5,5′-tetramethylindophenol; and 4-nitroso-2,6-xylenol. Although the major product, the nitrosoxylenol, cannot be produced in 100% yield, suitable reaction conditions may be found in which the absorbance of this compound at 307–8 mμ may be made a linear and reproducible function of nitrite in the range 0 to 10 p.p.m. Diphenoquinone, under conditions of low acidity, leads to low results by competitive reduction of nitrite. The indophenol is produced by condensation of the nitrosoxylenol with excess reagent in solutions of high acidity (4:5:1 sulfuric acid–water–acetic acid by volume). In solutions of optimum acidity (5:4:1 sulfuric acid–water–acetic acid) this reaction is slow and avoidable by prompt spectrophotometric measurement. Halides reduce nitrite, but are effectively removed by addition of silver sulfate. No other common anions have been found to interfere. On the basis of the relative rates of nitration and nitrosation in this solvent system, nitrate, nitrite–nitrate in the presence of nitrate, and nitrate and nitrite are determined simultaneously.

THE FAMILIAR GRIESS-ILSOVAY colorimetric nitrite method (*4*) is so sensitive and well described in terms of sample variations that it is the method of choice for samples in which nitrite alone is important. However, for determinations of both nitrite and nitrate in the same sample the diazotization method becomes somewhat less suitable. The reaction does not apply to nitrate and either nitrate or total nitrite–nitrate must be determined by recourse to a second determination in which nitrate is measured. The majority of analytical procedures for nitrate are either seriously interfered with or are equally effective measures of nitrite. Thus for many applications, especially those in the area of air pollution, a rapid, accurate method for both nitrate and nitrite, individually and in sum, which would use one reagent would be desirable.

The present work reports the effects of reaction variables on the nitrosation reaction and describes methods for nitrite, and total nitrite–nitrate, and the simultaneous measurement of each.

EXPERIMENTAL

Apparatus. All apparatus used was identical with that described previously (*7*).

Reagents. Sulfuric acid, acetic acid, and the 2,6-xylenol reagent were those used in the nitration studies. Analytical reagent grade sodium nitrite was used to prepare determinate aqueous stock solutions of nitrite. This sample was of theoretical purity and no change in titer as measured by the iodometric procedure of Abeledo and Kolthoff (*1*) could be detected upon repeated recrystallization from water.

The method of Sabato (*9*) was used for the preparation of 4-nitroso-2,6-xylenol and the subsequent preparation of *p*-nitrosophenol. Yellow flakes with a metallic luster were obtained which decomposed at 170° to 171° C. in agreement with the data reported by von Auwers and Markowitz (*2*).

The 3,3′,5,5′-tetramethyldiphenoquinone was prepared from the reaction between sodium nitrite and xylenol in which no attempt was made to control either the rate of addition of acid or the temperature. The precipitate which formed was removed by filtration, washed with water, and recrystallized several times from benzene as red-orange needles. The melting point and spectrum of this compound were identical with an authentic sample (*5*). An additional yield was obtained by extraction of the filtrate and re-extraction of the xylenol and 4-nitrosoxylenol with aqueous alkali.

The 3,3′-5,5′-tetramethylindophenol was prepared by condensation of 2,6-xylenol with 4-nitroso-2,6-xylenol at room temperature for several days in 80% sulfuric acid in acetic acid. The dense blue-black solution was nearly intractable and only a small quantity of gun-metal green precipitate could be induced to separate from a strongly alkaline solution saturated with sodium chloride.

2,6-Xylenol (.01M). Dissolve 1.2216 grams of 2,6-xylenol (Eastman Organic Chemicals, No. 1772) and dilute to 1 liter with glacial HOAc.

Stock Nitrite Solution (100 p.p.m. of nitrite nitrogen). Dissolve 0.4929 gram of reagent grade sodium nitrite and dilute to volume in a 1-liter volumetric flask with distilled water.

Acid Mixtures. Mix 5 volumes of concentrated H_2SO_4 and 3 volumes of distilled water. Also mix equal volumes of concentrated H_2SO_4 and H_3PO_4 (both reagent grade). Cool to room temperature.

All reagent solutions, reaction mixtures, and solvents were prepared as previously described.

Procedures. CONSTRUCTION OF STANDARD CURVE. Nitrite Alone. From stock nitrite solution prepare standards to be 2.0, 4.0, 6.0, and 8.0 p.p.m. in nitrite nitrogen. Pipet 8.0 ml. of 5:3 sulfuric acid–water mixture (v./v.) into 50-ml. Erlenmeyer flasks. Pipet 1.00 ml. of nitrite standard and 1.00 ml. of .01M 2,6-xylenol into flasks, swirl gently, and allow 5 minutes' reaction time (Caution: Add reagent immediately after addition of nitrite since nitrite slowly decomposes in this acid medium). Measure the absorbance of solution at 306–7 mμ, correct for blank, and construct a standard curve.

Nitrite Plus Nitrate. Prepare a stock solution of 100 p.p.m. nitrate nitrogen by dissolving 0.7221 gram of reagent grade potassium nitrate in distilled water and diluting to 1 liter. From stock solutions of nitrate and nitrite prepare standard solutions to contain 5.0 p.p.m. of nitrate nitrogen each, and 2.0, 4.0, 6.0 p.p.m. of nitrite nitrogen. Pipet 8.0 ml. of 1:1 sulfuric acid–phosphoric acid (v./v.) into 50-ml. Erlenmeyer flasks. Pipet 1.00 ml. of nitrite standard and 1.00 ml. of .01M 2,6-xylenol into flasks, swirl gently, and allow 5 minutes' reaction. Measure the absorbance of solution at 307 mμ, correct for blank, and construct a standard curve.

DETERMINATION OF NITRITE IN SAMPLE. Nitrite Alone. Prepare an aqueous sample such that it contains 0 to 8 p.p.m. nitrite nitrogen. Treat the sample as outlined in the first paragraph for construction of a standard curve. From the absorbance reading at 306–7 mμ read the nitrite concentration from the standard curve.

Nitrite Plus Nitrate. Divide an aqueous sample containing both nitrite and nitrate into two portions. Treat one portion as outlined above for construction of a standard curve, and measure the absorbance of the solution at 307 mμ. To the other portion add sufficient solid sulfamic acid to destroy nitrite and proceed as outlined in the second paragraph for construction of a standard curve. Measure the absorb-

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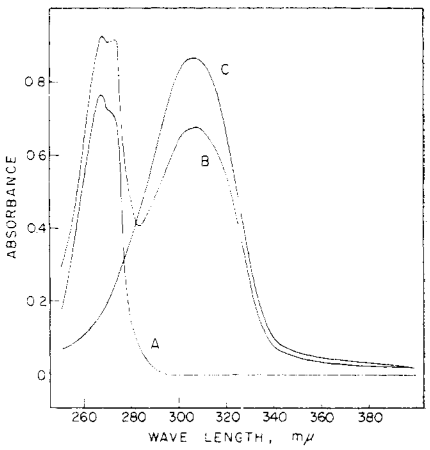


Figure 1. Spectra of (A) 1.00 × $10^{-3}M$ 2,6-xylenol; (B) nitrosation mixture (6.0 μg. nitrite N); and (C) 4.29 × $10^{-5}M$ 4-nitroso-2,6-xylenol in 5:4:1 H_2SO_4–H_2O–HOAc

ance of solution at 307 mμ and 324 mμ. From the absorbance reading of the first portion subtract the reading of the second at 307 mμ and obtain nitrite concentration from the standard curve.

RESULTS AND DISCUSSION

The general spectral character of the reaction mixture of nitrite and 2,6-xylenol in a solvent similar to that used for the nitration procedure (5:4:1 v./v. H_2SO_4–H_2O–HOAc) proved to be predominantly that of 4-nitroso-2,6-xylenol as illustrated in Figure 1. Closer examination of the 260–80 mμ region indicated the existence of other products. Calculation of yield from molar absorptivities shown in Table I clearly demonstrated extensive loss. The yield under the conditions of Figure 1 was only 60% of that expected from the quantity of nitrite added. A series of reactions in which the H_2SO_4–H_2O–HOAc ratio was varied while the nitrite and xylenol concentrations were held constant at 6.0 p.p.m. of nitrite nitrogen and $10^{-3}M$ xylenol, respectively, produced the behavior depicted in Figure 2. Several points of variation in comparison to similar nitration reactions were apparent: the final absorbances were extremely variable with replication and did not become constant at the lower acidities, and the absorbances at 307–8 mμ in the solutions of higher sulfuric acid content approached a steady but low final value quickly. Examination of the spectra produced at the extreme ends of the acidity range investigated, 10% aqueous acetic acid and 6:3:1 H_2SO_4–H_2O–HOAc, shows that 4-nitroso-2,6-xylenol is produced throughout (Figure 3). The appearance of an absorbance maximum at 421 mμ in the aqueous acetic acid solvent and a peak at 515 mμ in higher acidity solvents, coupled with examination of detail in the 260 mμ region, indicated that the side reactions were not simple and in fact changed with acidity. The spectra of the diphenoquinone and indophenol shown in Figure 4 compare very closely with the extraneous absorbances in the reaction mixtures. The net result as measured by the absorbance at 307–8 mμ for this series of reactions is shown in Figure 5. The reactions occurring when nitrite is added to 2,6-xylenol may be formulated as follows. In the range 0 to 37.5% H_2SO_4 the reactions are predominantly:

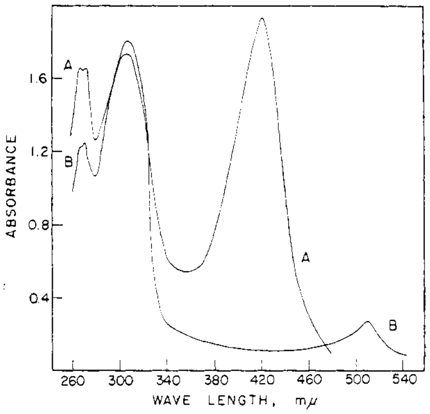


Figure 3. Spectrum of nitrite–2,6-xylenol reaction mixture in 9:1 H_2O–HOAc (A) and 6:3:1 H_2SO_4–H_2O–HOAc (B)

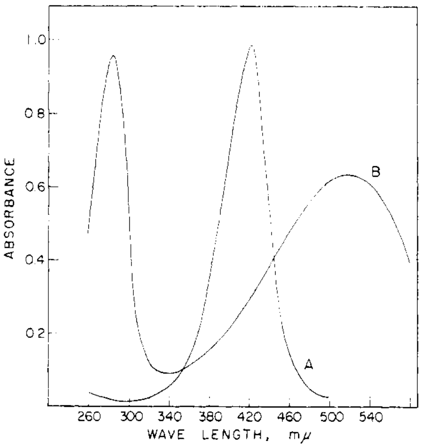


Figure 4. Spectra of 1.5 × $10^{-5}M$ 3,3′,5,5′-tetramethyldiphenoquinone in 9:1 H_2O–HOAc (A) and 3,3′,5,5′-tetramethylindophenol in 21:19 H_2SO_4–H_2O (B)

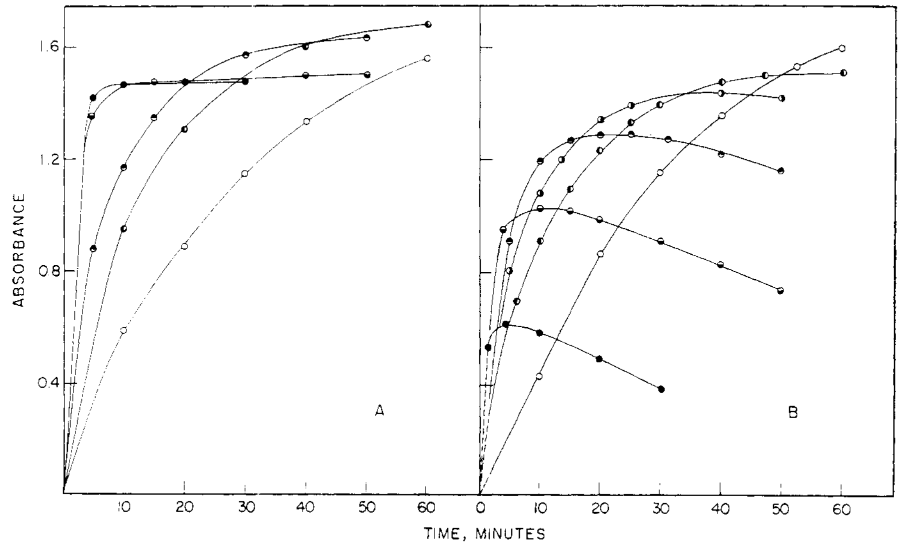


Figure 2. Absorbances vs. time for nitrite-2,6-xylenol reaction in H_2SO_4–H_2O–HOAc mixtures: ○-0:9:1, ◐-1:17:2, ◑-1:8:1, ⊖-3:15:2, ⊖-2:7:1, ●-5:13:2 by volume at 307–8 mμ (A) and 421–4 mμ (B)

$$[NO_2^-] + \text{xylenol} \rightarrow \text{4-nitroso-2,6-xylenol} \quad (1)$$

and

$$[NO_2^-] + \text{xylenol} \rightarrow \text{diphenoquinone} \quad (2)$$

In the above equations, $[NO_2^-]$ is used as a general description; no identifica-

Table I. Wavelengths of Maximum Absorption and Molar Absorptivities for 4-Nitroso-2,6-Xylenol in Various Solvents

Solvent composition, volume	λ_{max}, mμ	a_{max}
HOAc	305	20,100
9:1 H_2O–HOAc	308	19,900
1:8:1 H_2SO_4–H_2O–HOAc	307–8	20,400
2:7:1 H_2SO_4–H_2O–HOAc	307–8	19,600
4:5:1 H_2SO_4–H_2O–HOAc	307	20,600
5:4:1 H_2SO_4–H_2O–HOAc	306	20,400
4:4:1:1 H_2SO_4–H_3PO_4–H_2O–HOAc	307	21,300

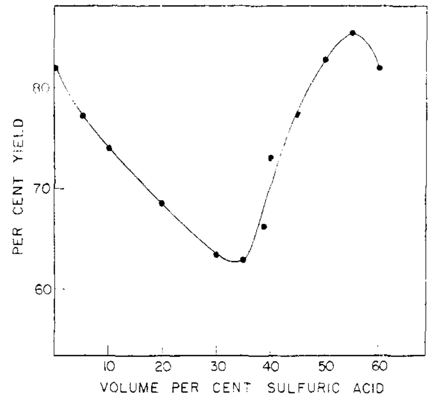


Figure 5. Yield of 4-nitroso-2,6-xylenol *vs.* volume per cent H_2SO_4 for *nitrite-2,6-xylenol reaction in* H_2SO_4–H_2O–HOAc

(constant 10% H_2O by volume)

tion of species present is assumed. No clear explanation of the decrease is available; it is believed that the decrease in nitroso-xylenol production is due to differences in rates of Equations 1 and 2, and in molecularities of the two reactions. Comparison of Figure 2*A* in which the nitrosoxylenol absorbance is followed, with that of Figure 2*B* shows the initial rate of diphenoquinone reaction to be much faster and dependent to a greater extent upon acidity. The data of Figure 2 are qualitative only; further work on the kinetics of these reactions is being carried out in these laboratories. Bayliss and Watts have shown the nitrous acid system to be complex with at least four if not five species variously present depending on acidity (*3*). The equations may be written:

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \quad (3)$$

$$2HNO_2 + H^+ \rightleftharpoons N_2O_3 + H_3O^+ \quad (4)$$

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+ \quad (5)$$

$$HNO_2 + H_2SO_4 \rightleftharpoons NO^+ + HSO_4^- \quad (6)$$

$$N_2O_3 \rightleftharpoons NO^+ + NO_3^- \quad (7)$$

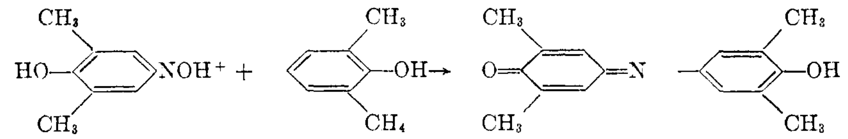
In solutions of low acidity the equilibria of importance are those of Equations 3 and 4; Equation 5 may also occur to some extent although the evidence for the existence of this species lies in the necessity for some intermediate species between Equation 3, 4, and 6 to account for the analytical nitrite concentration. Present evidence suggests an alternate reaction:

$$N_2O_3 + H^+ \rightleftharpoons NO + HNO_2 \quad (8)$$

A material balance for nitrogen for reaction conditions (10% aqueous HOAc) in which only nitrosoxylenol and diphenoquinone were produced and both were stable showed that in order to form these products by Equations 1 and 2 it was necessary to produce 2.5 moles of the diphenoquinone per mole of nitrite not reacting as in Equation 1. Since nitrite is not stable in these solvents (vide infra) loss by volatilization and the like could only increase this ratio. A ratio as large as this which corresponds to no reasonable oxidation-reduction stoichiometry suggests the presence of a free radical reaction. The diphenoquinone is produced alternatively by alkaline air-oxidation which is regarded as a free radical reaction (*5*).

Acid concentrations in the range 37.5 to 50% (v./v.) sulfuric acid produce an increased yield of the nitrosoxylenol. The explanation for this lies in the increasing predominance of Equation 6 and thus an increased rate of nitrosoxylenol production. In these and all other reactions concerned with this work the ratio of nitrite to xylenol was always less than 1:10; since nitrogen is the deficient reactant, these effects observed are largely the result of competitive reactions.

Beyond 50% sulfuric acid the yield once again decreases. In this range spectral examination in the 500-mμ region showed that the apparent yield of nitrosoxylenol was being decreased by a consecutive reaction to produce the indophenol (*6*):



Although the absorptivity of the diphenoquinone (ca. 30,000 in these solvents) and the visible color (λ_{max} = 515 mμ) of the indophenol are attractive as spectrophotometric data for possible nitrite methods neither has proved suitable at present. The indophenol forms only slowly as can be seen from the curves for 2:7:1 and 5:13:2 H_2SO_4–H_2O–HOAc of Figure 2*A*. In these two mixtures the predominant reactions are nitrosation followed by condensation to produce the indophenol which does not absorb appreciably at 307–8 mμ (cf. Figure 4).

The diphenoquinone is not stable in these acidic solvents, being reduced to the corresponding hydroquinone. An observation of the spectrum of the region 250–80 mμ involving an obvious modification of the reference solution to reveal detail under the 2,6-xylenol peak at 272 mμ showed that as the diphenoquinone peak at 421 mμ disappeared a second peak at 260 mμ appeared. This reaction was hastened by addition of acid as shown in Figure 6. The absorbance-time behavior at 421 and 260 mμ were in 1:1 correspondence after the addition of acid (160 minutes). This peak at 260 mμ was identified with the hydroquinone by examination of a zinc–acetic acid reduced solution of the diphenoquinone. Treatment of an acetic acid–diphenoquinone solution containing zinc dust, at the boil, with a trace of sulfuric acid resulted in the decolorization of the solution and, after quenching in water, the recovery by filtration of a white crystalline material. This has been tentatively identified as the hydroquinone by the disappearance of the C—O and quinoid vibrational-rotational spectrum of the diphenoquinone and appearance of aromatic (~700 cm.$^{-1}$) and C—OH (3200 cm.$^{-1}$) vibrational modes in the infrared.

Despite the multiplicity of reaction paths it is possible to make the absorbance at 307–8 mμ of 4-nitroso-2,6-xylenol a reproducible measure of nitrite.

The order of addition of nitrite and xylenol to the acid is important as shown in Table II. The data of column 2 are reproduced in part in Figure 5. Although column 3 indicates less variation with acidity, the reproducibility is not comparable to the reverse procedure. The lower yields of column 3 are due in large measure to the instability of acidic nitrite solutions. Bayliss and Watts (*3*) report that nitrite is stable even in acid solutions except over the interval 55–60% by weight sulfuric acid which is the region of interest in the present work. Nitrite in acid solutions exhibits a moderately intense and variable absorption at ca. 250 mμ (a_{max} = 3900) (*3*). In the present work it was determined that nitrite in 5:4:1 solvent absorbs at 250

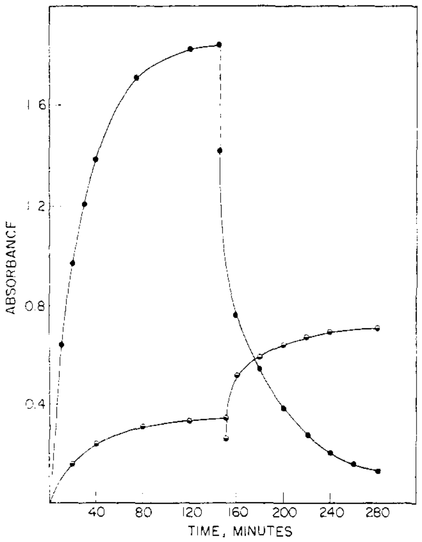


Figure 6. Absorbance at 421 mμ (●) and 260 mμ (◒) *vs.* time of a nitrosation mixture in 10 ml. 9:1 H_2O–HOAc

Dotted portion indicates addition of 3 ml. H_2SO_4.

Table II. Effect of Order of Addition of Nitrite and 2,6-Xylenol Reagent on Yields of 4-Nitroso-2,6-Xylenol

Sulfuric acid–water–acetic acid, by volume	Per cent yield[a] 2,6-Xylenol, added last	Sodium nitrite, added last
3:6:1	63.5	67.6
7:11:2	62.9	63.5
4:5:1	73.1	67.6
9:9:2	77.2	66.9
5:4:1	82.7	64.9
11:7:2	85.4	62.2
6:3:1	81.9	62.9

[a] 100% yield based on nitrite taken and molar absorptivity of 4-nitroso-2,6-xylenol in solvent mixture.

Table III. Effect of Nitrite on Maximum Absorbance of 4-Nitroso-2,6-Xylenol in 5:4:1 Sulfuric Acid–Water–Acetic Acid by Volume

Nitrite present, μg.	Absorbance at 306 mμ Observed	Corrected
6.0	0.835	0.790
12.0	0.879	0.789
24.0	0.979	0.797
48.0	1.147	0.787

Table IV. Effect of Cooling on Yields of 4-Nitroso-2,6-Xylenol

Sulfuric acid–water–acetic acid, by volume	Per cent yield[a] Uncooled	Cooled
15:21:4	66.3	87.4
5:4:1	82.7	95.3
43:29:8	84.0	94.3
11:7:2	85.4	90.8
6:3:1	81.9	91.5

[a] Yields calculated as in Table II.

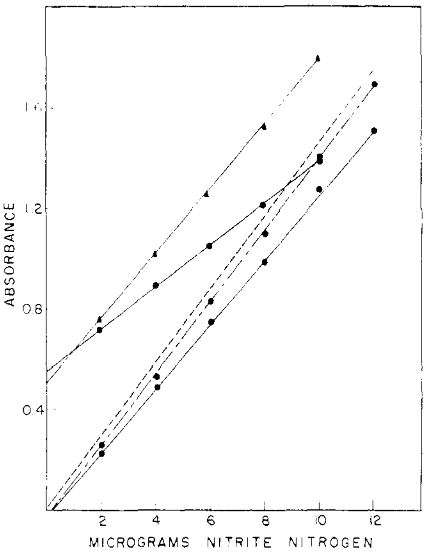


Figure 7. Absorbance vs. micrograms nitrite nitrogen for simultaneous nitration and nitrosation in 4:4:1:1 H_2SO_4–H_3PO_4–H_2O–HOAc at 307 mμ (▲) and 324 mμ (●) and nitrosation in 5:4:1 H_2SO_4–H_2O–HOAc at 307 mμ

— Uncooled, –·– Cooled, --- Expected for 100% yield.

mμ with a_{max} = 3510 and absorbs appreciably at 306 mμ (a = 1050) as shown in Table III. Spectral examination of such solutions with time showed that nitrite decomposed at the rate of approximately 0.4% per minute at room temperature. Thus the lower yields of column 3 are due to decomposition of the nitrite before reaction.

If the reactants are cooled before mixing, the yields and precision are improved as shown in Table IV. This is caused by an increased stability of nitrite at low temperatures, and a favorable free energy of reaction difference between Equations 1 and 2 which favors Equation 1.

The results shown in Tables II and IV and Figure 5 do not clearly demonstrate any possible interaction between cooling and order of mixing. In Tables V and VI are listed the results of experiments at two levels of acidity with cooling treatment at the higher level (Table V) and order of addition treatment at the lower level (Table VI). In addition, replication within groups was achieved by running replicate experiments. Some data under conditions of column 3, Table V, were previously available; for this column the data are based on nine replicates, for all others in Tables V and VI the replication was three. Analysis of variance of this Latin Square treatment indicates cooling to be the major effect with significant interaction at the 95% level. These experiments show that the effect of order of addition, while significant, is largely due to the temperature of reaction at the point of entry of the last adduct. In those reactions in which nitrite was added last the conditions were essentially those of adding water to a sulfuric–acetic acid solution. The heat of dilution of these mixtures of 9.0 ml. of 2:1 H_2SO_4–HOAc with 1.0 ml. of aqueous nitrite is sufficient to increase the temperature after mixing from 20° C. to 40°–41° C. The temperature at the point of entry into the acid is high enough to create considerable loss of HOAc and water vapor. On the other hand, the reverse procedure was one of adding acetic acid (the solvent of the xylenol stock solutions) to aqueous sulfuric–acetic acid; in this case the heat of dilution has been removed prior to reaction.

The foregoing observations serve to delineate suitable reaction conditions for the determination of nitrite as 4-nitroso-2,6-xylenol. First, the acidity is best maintained at, or slightly greater than, 5:4:1 (v./v.); higher acidities can be tolerated provided the measurements are made within 30 minutes. Longer time intervals decrease the apparent nitrite content by indophenol condensation. Second, the reactants should be cooled to the point where the final mixture is approximately at room temperature. This is most conveniently accomplished by cooling the H_2SO_4–HOAc solvent and the HOAc–2,6-xylenol reagent to dry ice–acetone temperatures, adding the aqueous sample to the acid, recooling, and adding the reagent.

A previous study of the nitrate-xylenol reaction showed that nitration proceeds best in either 6:3:1 H_2SO_4–H_2O–HOAc or 4:4:1:1 H_2SO_4–H_3PO_4–H_2O–HOAc (7). Nitrosation proceeds equally well in either solvent. In Table VII and Figure 7 are shown the results of simultaneous nitrate–nitrite de-

Table V. Reproducibility of Nitrosation in 5:4:1 Sulfuric Acid–Water–Acetic Acid by Volume

Nitrite N present, μg.	Relative standard deviation, % Uncooled	Cooled
2.0	4.83	3.71
4.0	1.66	0.36
6.0	1.20	0.49
8.0	1.68	0.56
10.0	0.88	0.56
12.0	0.82	0.60

Table VI. Reproducibility of Nitrosation of 4:5:1 Sulfuric Acid–Water–Acetic Acid by Volume

Nitrite N present, μg.	Relative standard deviation, % Reagent added last	Nitrite added last
2.0	6.55	1.37
4.0	0.71	2.03
6.0	3.93	3.47
8.0	1.63	4.71
10.0	3.96	2.29
12.0	0.83	1.19

Table VII. Reproducibility of Simultaneous Nitrate and Nitrite Determination in 4:4:1:1 Sulfuric Acid–Phosphoric Acid–Water–Acetic Acid at Constant 10.0 μg. Nitrate Nitrogen

Nitrite N present, μg.	Relative standard deviation, % Nitrate[a]	Nitrite[a]
0	0.28	0.46
2.0	0.53	0.97
4.0	0.16	0.10
6.0	1.49	1.23
8.0	0.86	0.54
10.0	0.21	1.13

[a] Nitrate measured at 324 mμ, nitrite at 306–7 mμ.

Table VIII. Recovery of Nitrate and Nitrite

Nitrate N, μg.		Nitrite N, μg.	
Taken	Found	Taken	Found
10.0	9.88 ± 0.09	2.00	1.86 ± 0.02
10.0	9.90 ± 0.07	6.00	5.86 ± 0.03
10.0	9.92 ± 0.07	10.00	9.88 ± 0.16

terminations by nitration and nitrosation using the usual techniques of linear simultaneous equations to determine each component. The required absorptivity at 324 mμ for nitrosoxylenol and 307 mμ for nitroxylenol were determined by reaction of nitrite or nitrate alone. The 4:4:1:1 H_2SO_4–H_3PO_4–H_2O–HOAc mixture has been shown previously (*8*) to be equivalent to the 5:4:1 H_2SO_4–H_2O–HOAc mixture with respect to nitration yields and reproducibility. The sole difference between the two mixtures is a decrease in reagent stability in the latter. Determination by this method is less precise than may be desirable because of accumulated errors in absorbances at 324 and 307 mμ. The reproducibility of nitrosation in the presence of nitrate is clearly better than for nitrite alone (compare Table VII and Table V). This effect is evident even when the nitrate concentration is reduced to less than 1% of the nitrite at any level. The explanation for this effect is not yet clear but may be due to an increased stability of nitrite by formation of N_2O_4:

$$NO^+ + NO_3^- \rightleftharpoons N_2O_4 \qquad (9)$$

In any event this phenomenon allows a greater precision in nitrite determination by deliberate addition of nitrate at concentration levels which produce undetectable quantities of 4-nitro-2,6-xylenol.

A greater precision may be attained by a dual procedure in which both nitrate and nitrite are determined as above and nitrate subsequently determined alone from a second aliquot treated according to the nitrate procedure (*8*). The results attainable under these conditions are shown in Table VIII.

The data of Figure 2 and the corresponding data of Figure 2 of the previous paper (*7*) indicate the possibility of determining nitrite in the presence of nitrate by reaction in 4:5:1 solvent in which nitration proceeds but slowly. Inspection of Figure 2 shows this to be a make-shift procedure at best since the yield of nitrosoxylenol is low. In this regard it is re-emphasized that higher acidities can be tolerated because the interference of the consecutive reaction to produce indophenol is moderately slow while the oxidation to produce diphenoquinone is destructive and competitive.

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Dicesium Plutonium Hexachloride, a Proposed Primary Standard for Plutonium

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▶ Since the discovery of plutonium in 1940, no compound of the element has been reported which completely satisfies the requirements for a primary standard, although many have been investigated and, out of necessity, used as working standards. The salt, Cs_2PuCl_6, is suggested as a primary standard for plutonium. It can be easily prepared in a pure state and with a constant composition. It is stable, it has a high equivalent weight, and it is readily soluble in dilute acids.

IN RECENT years, many materials have been proposed and evaluated for use as primary analytical standards for plutonium. The material most widely used as a working standard has been metallic plutonium. The problem of obtaining metal of known purity has been overcome recently by a plutonium metal standard, available in limited quantities from the National Bureau of Standards, which is 99.97% pure. Other difficulties associated with the use of the metal as a standard have been discussed (*16*).

Anhydrous plutonium sulfate has been suggested, but has been considered too hygroscopic to prepare and store in a stoichiometric form (*2*, *6*). Recent work has indicated that it can be prepared, under special conditions, in a form that is not so hygroscopic (*17*, *19*). Plutonium sulfate tetrahydrate has been evaluated and is proposed as a primary analytical standard for plutonium (*16*).

A number of other compounds have been found deficient: plutonium tetraiodate because it contains coprecipitated iodic acid (*2*, *4*); hydrated plutonium fluoride because it hydrolyzes after several weeks (*10*); plutonium tetranitrate pentahydrate because it appears to be hygroscopic (*5*, *22*); plutonium dioxide because it is difficult to obtain in a stoichiometric form (*27*) and even more difficult to dissolve (*16*); and organic compounds because some have uncertain compositions and are susceptible to long-term changes in composition as a result of the plutonium alpha flux (*21*).

Anderson has described (*1*) the preparation of the anhydrous double salt, dicesium plutonium hexachloride. Kooi, Weisskopf, and Gruen have noted that this double salt is nonhygroscopic and have recommended it as a starting material for production of plutonium metal (*13*). Gruen pointed out these properties to the present authors in 1958 (*7*).

EXPERIMENTAL

Reagents and Apparatus. Plutonium metal, 99.8 + % purity. Average atomic weight, 239.12.

Cesium chloride, American Potash and Chemical Corp., technical grade,