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Note

Gas chromatographic analysis of nitrate and nitrite ions in microgram quantities by conversion to nitrobenzene

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Although nitrite ion can be determined readily in microgram or submicrogram concentrations¹⁻³, the determination of nitrate ion is not so simple. The brucine method² requires day-to-day calibration, while the use of the specific ion electrode⁵ requires close control of ionic strength and is not particularly useful near 1 ppm. The use of tetraphenylphosphonium chloride⁶ is also limited near 1 ppm. The English method⁷ is very good above 14 ppm ($2.25 \cdot 10^{-3} M$), but the value of 222 for the molar absorptivity renders it useless below this concentration. Some of the other methods for nitrate ion determination are discussed by Bhatti and Townshend⁸. These authors present a spectrophotometric method for nitrate or nitrite ion based on conversion to nitrotoluenes, which have absorbance maxima near 284 nm in toluene.

As observed by Bhatti and Townshend, toluene itself absorbs strongly at 284 nm, and in trying to use this procedure, it was necessary to use a slit width of 3 mm. This is not at all desirable in a spectrophotometric procedure. It was decided to try to adapt their procedure to a gas chromatographic (GC) analysis. A preliminary examination of the toluene solution showed that both *o*- (62% w/w) and *p*-nitrotoluene were formed in the nitration. As this involved determining two products quantitatively, benzene was substituted for toluene in order that only one product, nitrobenzene, be produced.

EXPERIMENTAL

Gas chromatographic conditions

A Hewlett-Packard, Model 5750 research chromatograph was used with a 4 ft. \times $1/8$ in. glass column packed with 6.9% Apiezon M on Diataport S, 60-80 mesh; column temperature, 120°; argon-methane (95:5) flow-rate, 95 ml/min; ⁶³Ni detector temperature, 275°; injection port temperature, 140°; pulse, 150 msec; attenuator, \times 80. Areas under the peaks were measured with an Infotronics Digital Integrator, CRS-208 Model. Under these conditions, nitrobenzene has a retention time of about 151 sec, and *o*-nitrotoluene (internal standard) had a retention time of 228 sec.

Nitrate ion

One to five ml of sample solution was diluted to 5 ml with water. Five ml of benzene were added and vigorously mixed. Fifteen ml of sulfuric acid-water (3:1)

were added, the mixture vigorously shaken, the pressure relieved, and the flask placed in a water bath at $75 \pm 5^\circ$ for 5 min. The mixture was again shaken and cooled to room temperature. The benzene solution was diluted to give a nitrobenzene concentration of about $7 \cdot 10^{-9}$ g/ μ l and an aliquot of *o*-nitrotoluene (internal standard) was added to give a concentration of about $14 \cdot 10^{-9}$ g/ μ l. The concentrations give about equal areas under their respective peaks. A 1- μ l injection of this solution with a back-flush of 2 μ l of benzene gave an area count of about 2000 under each peak. After the peaks appeared, this injection was immediately followed by an injection of a standard solution containing each of the components in known concentrations.

Nitrite ion (or nitrite plus nitrate)

One to four ml of sample solution was pipetted into a 25-ml volumetric flask. One ml of 0.1 *N* potassium permanganate was added and the solution diluted to 5 ml. The rest of the procedure was like that for nitrate ion.

Calculation of the nitrobenzene concentration

The nitrobenzene concentration (nb) in g/ μ l in the unknown is as follows:

$$\frac{a \cdot (A_o)_s \cdot (A_{nb})_u \cdot c}{b \cdot (A_{nb})_s \cdot (A_o)_u} = nb$$

where *a* and *b* are the microliters of the internal standard, *o*-nitrotoluene, in the unknown, "u", and reference, "s", solutions; *A_o* and *A_{nb}* are the areas for *o*-nitrotoluene and nitrobenzene; and *c* is the g/ μ l of the nitrobenzene in the reference solution.

RESULTS AND DISCUSSION

The results for nitrate ion and nitrite ion separately and in mixtures are given in Tables I, II, and III. The yield of nitrobenzene is $90 \pm 8\%$ for nitrate ion from 0.12 ppm to 62 ppm, and $92 \pm 12\%$ for nitrite ion (after oxidation to nitrate ion) from 0.09 ppm to 37 ppm.

The experimental conditions used were those of Bhatti and Townshend⁸, except we found that using a water-bath at 75° gave more reproducible results. They studied various temperatures and acid concentrations and found that these conditions

TABLE I
DETERMINATION OF NITRATE ION

Concentration		No. of determinations	Found		
10^{-5} M	ppm		10^{-5} M	"	"
0.20	0.12	1	0.18	90	
1.00	0.62	6	0.88 ± 0.07	88 ± 7	
2.00	1.24	1	1.90	95	
4.00	2.48	2	3.50 ± 0.08	88 ± 2	
10.0	6.2	8	8.4 ± 0.8	84 ± 8	
100	62	2	96 ± 3	96 ± 3	
			Average	90 ± 8	

gave best reaction times. This is verified by our work, which shows recoveries of *ca.* 90%. This means that the nitration is about 95% complete, as repetitive GC injections give variations of 2–5%.

Because the GC procedure (this study) allows the direct observation of nitrobenzene, there are no inorganic interferences. However, blank determinations must be

TABLE II
DETERMINATION OF NITRITE ION

Concentration		No. of determinations	Found	
10^{-5} M	ppm		10^{-5} M	%
0.20	0.092	1	0.19	95
0.80	0.368	2	0.70 \pm 0.07	88 \pm 12
1.99	0.915	3	1.9 \pm 0.2	96 \pm 10
3.98	1.83	3	3.7 \pm 0.1	93 \pm 2
7.97	3.67	1	6.7	84
39.8	18.31	1	39	98
79.7	36.67	1	70	88
			Average	92 \pm 12

made of nitrate and/or nitrite ions in the reagents. In preparing our sulfuric acid-water (3:1), benzene was added before diluting in order to use the heat of dilution to convert nitrate ion to nitrobenzene. The mixture was then extracted six times with benzene (10 ml for each 200 ml of reagent). The combined blank for the nitrite ion determination was 0.12 ppm, while for the sulfuric acid only, it was 0.03 ppm. It is these blanks that set the lower limits for the determinations.

TABLE III
DETERMINATION OF NITRATE AND NITRITE IONS IN MIXTURES

Nitrate			Nitrite	Nitrite -- nitrate	
Present (10^{-5} M)	Found (10^{-5} M)	Recovery (%)	Present (10^{-5} M)	Found (10^{-5} M)	Recovery (%)
4.00	3.34	83.5	3.98	—	—
4.00	3.39	84.8	3.98	—	—
4.00	3.31	82.8	5.98	—	—
4.00	3.16	79.0	5.98	—	—
4.00	—	—	3.98	6.67	83.6
4.00	—	—	3.98	7.43	93.1
Average			Average		88 \pm 4

When permanganate is absent, and nitrite is present, nitrosobenzene is formed. This has an earlier retention time than nitrobenzene and therefore does not interfere with the nitrate determination in mixtures with nitrite. Unfortunately, the decomposition of nitrous acid is too rapid for this nitrosation to be quantitative, so this cannot be used as a basis for nitrite determination.

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