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Chemistry

THE GASOMETRIC DETERMINATION

OF

NITRITE AND SULFAMATE

by

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THE GASOMETRIC DETERMINATIONOFNITRITE AND SULFAMATEIntroduction

This investigation was made to develop a rapid and precise method for the determination of small quantities of nitrite in the presence of large amounts of foreign ions and diluents. It was found during the investigation that a simple modification of the procedure would enable a similar determination of sulfamate to be made. The determination is based on the rapid quantitative reaction of nitrite with sulfamate in acid solution:

and the subsequent measurement of the volume of nitrogen evolved. This reaction is the basis for a titration method for sulfamic acid which was first suggested by Baumgarten and Margraff (1).

The few interferences with the method ordinarily occur in alkaline solution. These are those substances that nitrite will oxidize or will reduce when the sample is acidified and those substances that react with sulfamic acid in acid solution to give gases which are nonabsorbable in alkali. Halogens and chlorates react with sulfamic acid to give nitrogen; permanganate, ferric iron, and chromic acid do not react (2). Concentrated (81%) nitric acid reacts with sulfamic acid to give nitrous oxide; dilute acid (less than 75%) does not react.

A survey of the apparatus useful for measuring a small volume of nitrogen showed that a modified micro Dumas apparatus was most feasible. In this apparatus, the nitrogen is evolved in a reaction flask and is swept into an azotometer with a stream of pure carbon dioxide which is removed by absorption in caustic.

Summary

A gasometric determination has been developed that can determine 1.2×10^{-5} g. of nitrite with a precision (99% limits) of $\pm 8\%$. The method is highly specific and few interferences are encountered. The entire procedure requires twenty minutes.

For the determination of sulfamate, the modified procedure gives a precision of $\pm 5\%$ for samples containing 2 mg. of sulfamate. Interferences with the method are limited to the compounds that contain the amino ($-\text{NH}_2$) group.

No standard solutions are required and the manipulation of the somewhat complex apparatus is simple. The apparatus is rugged and can be adapted easily for remote control operation.

NITRITE DETERMINATION

Apparatus

The apparatus is diagramed in figures 1 to 3. The carbon dioxide generator is essentially that described by Niederl and Niederl (3), but the safety vent is modified in that a sintered glass disk is used in place of the filter paper assembly. In use, the carbon dioxide in the Dewar flask is kept to a sufficiently high pressure so that gas is continually vented through this disk. The heater is often necessary to augment the "heat leak" of the flask in order to provide gas in the quantities needed. After 24 hours of flushing, the blank is 0.002 to 0.003 ml. per 100 ml. gas used. One filling of dry ice is sufficient for several weeks' determinations; however, the flask was re-charged every week during this investigation. The gas holder is similar to the one described by Niederl and Niederl (3). The manipulation of the mercury is by use of a pressure lift. Pressure of the incoming gas is regulated by the pressure regulator to a value just sufficient to raise the mercury to level "L" (Figure 1). Thus mercury cannot be accidentally forced into the train. The pressure regulator is the one described by Carson (4).

The reactor design (Figure 2) permits complete outgassing of the reaction flask and reagent. Stopcock A permits back flushing of the reaction flask head, which prevents premature reaction of the sample with any sulfamic acid splashed there during the previous determination. It also serves to shorten the train during outgassing, as the air in the reaction flask can be vented through it rather than through the entire train on the outgassing sweep. Funnel F provides a means of flushing out the reactor between samples; again to prevent premature reaction of the sample. The reagent supply vessel's capacity is sufficient for a hundred or more determinations and is outgassed (once per filling) by suitable adjustment of stopcocks B and C. Reagent is added to the outgassed sample by turning stopcock C so that carbon dioxide can enter the reagent supply vessel, but not the reaction flask, and stopcock B so that liquid can rise in the tube and pass into the capillary. The volume of the capillary is about 0.5 ml.; this amount of 0.1 N reagent is sufficient to decompose any sample that can be measured in the azotometer. When the capillary is full, stopcock B is turned so that carbon dioxide from the generator forces the reagent into the reactor flask.

Figure 3 gives the diagram of the micro azotometer used. The measuring portion consists of a 1 mm capillary with scale (mm) attached. In use, the nitrogen collects in a large bubble at the base of the capillary. At the end of a run, this bubble is forced into the capillary by lifting the leveling bulb and opening the stopcock. The gas bubble is measured by measuring the length of the capillary occupied. The capacity is 187.3 microliters for a 200 mm length. The capillary was assumed to be of uniform bore.

Figure 4 gives the diagram of the semimicro azotometer used. This is a standard piece of equipment available from supply houses. The capacity of the calibrated portion is 1.5 ml. Volumes of gas can be read to 0.002 ml.

FIGURE 4
AZOTOMETER

Procedure

Using a micropipet (normally 200 μ l), the sample is added to the reaction flask, and the pipet rinsed several times with water. The sample size can be varied to evolve the amount of nitrogen that can be conveniently measured in the azotometer used -- approx. 0.5 - 1.0 ml. in the semimicro azotometer, and 80 μ l in the micro azotometer. For samples with very low nitrite content the reactor flask is increased to the size necessary to hold the sample. The reactor flask is attached to the reactor, and the apparatus swept with 200 ml. of carbon dioxide (two gas holders-full). If the train had been used previously on that day, this gas is vented through stopcock A and Funnel F, Figure 2. If the train had not been used that day, the gas is passed through the entire train. In this case additional gas as necessary is used to remove all the air from the apparatus. The removal is complete when microbubbles appear in the azotometer. The gas flow is now shut off at the gas holder, and the system tested for leaks in the train by lowering the leveling bulb of the azotometer. When the bulb is lowered, a leak will generally appear as a continual stream of bubbles. The bubbling of gas should cease after a few bubbles enter the azotometer.

The sulfamic reagent (0.1 N H_2SO_4 + 0.1 N $\text{H}_2\text{NSO}_3\text{H}$) is now introduced. Figure 5 gives the position of the stopcocks during this step in the determination. Part A shows the position while the capillary is being filled. Part B shows the position after. The gas holder is now filled and brought to pressure by manipulation of the air-lift pressure. The solution in the reaction flask is heated by water very near the boiling point (but not actually boiling) contained in a large test tube which is brought up around the reaction flask. Stopcock B is opened cautiously to the position in part C, Figure 5, to allow reagent to enter the reaction flask. Stopcock B is turned again to position "B", Figure 5. The contents of the reaction flask are again heated by the water bath, and the gas from the generator is allowed to pass into the train at such a rate so that the cooling of the reactor contents does not cause a partial vacuum. As soon as the violent reaction in the reaction flask ceases, and the vessel has cooled for a minute, the gas rate from the generator is increased so that about 1 bubble per second enters the azotometer. This rate must be very slow to prevent undesirable large bubbles of nitrogen in the azotometer. When most of the nitrogen has passed into the azotometer, as shown by the decreased size of the bubbles, the sweeping rate is increased to approx. 0.2 ml. per second, until the gas holder is three-fourths empty, whereupon the gas rate is increased to 0.5 ml. per second. The gas rates are estimates, and the whole time of reaction and sweeping is 20 minutes. Only one gas-holder full of gas (100 ml.) is used for the sample sweep. The azotometer bulb is raised, stopcock A (Figure 1) of the reactor is opened to vent, and the sample flask removed. Water is added to the funnels and the apparatus thoroughly rinsed. The next sample flask is placed on the reactor, and the air swept out as above. During the sweep, the azotometer leveling bulb is adjusted, and the reading of the volume of gas taken. Pressure and temperature are also noted. The azotometer is then emptied of nitrogen by opening the stopcock and raising the leveling bulb.

At the end of a day's runs, the azotometer is removed from the train and the leveling bulb and tubing removed. The bulb and tubing are allowed to drain

FIGURES
MANIPULATION OF REACTOR
STOPCOCKS

but are not rinsed. If the tubing is rinsed, the dilute alkali formed attacks the rubber and causes the appearance of a marked discoloration in the next day's alkali. The azotometer is thoroughly rinsed, and the stopcock removed. This stopcock is not replaced until just before use to prevent sticking. It must be heavily greased, preferably with white vaseline.

Calculations

To compute g/L of nitrite, the following formula is used:

$$g/L = (V - b) \times \frac{T_o \times (P - c)}{T \times P_o} \times m \times \frac{NO_2}{N_2} \times \frac{10^6}{S}$$

Where V = observed volume of N_2

P = observed pressure of N_2

T = observed temperature of N_2 in degrees Kelvin

b = correction to volume of N_2 contributed by:

1. calibration of azotometer
2. adhesion of alkali on wall
3. blank of N_2 in CO_2 used

c = correction to barometric pressure contributed by:

1. aqueous tension above the alkali
2. barometer corrections (brass scale, etc.)

m = mass of 1 ml. of N_2 at $0^\circ C$ and 760 mm = 1.2505 mg/ml.

$\frac{NO_2}{N_2}$ = factor for nitrite in nitrogen = 1.6428

S = sample size in microliters

T_o = $273^\circ K$

P_o = 760 mm Hg.

Substituting for the constants, the formula reduces to:

$$g/l = 738.2 \frac{(V-b)(P-c)}{(S)(273.1+t)}$$

Where t = observed temperature in degrees centigrade.

Values for some of the corrections can be found in Niederl and Niederl, p. 95, (aqueous tension, and adsorption of alkali on the wall). Barometer corrections are obtainable from standard handbooks. The other corrections are experimentally determined. The blank should be determined by performing an actual run without a sample. It is necessary not to "zero" the azotometer for this determination since the volume of the blank is so small, but to use the expedient of lowering the level in the azotometer to a convenient mark, read the azotometer, run the blank and determine the blank value by difference. It is important that gas from the generator be vented at all times through the safety valve, as otherwise the quantity in the gas holder will vary and thus the blank also.

Results

Two solutions of sodium nitrite standardized by titration with permanganate were analyzed by the method. The sample size taken was 202.03 microliters. The results obtained are given in Table I.

TABLE I

<u>DETERMINATION OF NITRITE</u>		
g/l added	4.399	0.593
Approx. volume of N ₂ collected	0.50 ml.	0.070 ml.
g/l Found	4.407	
	4.389	0.600
	4.389	0.621
	4.382	0.610
	4.371	0.610
	4.389	0.621
	4.362	0.597
	4.388	0.574
	4.405	0.574
	4.397	0.617
	4.396	
	4.407	
	4.403	
Average	4.391 g/l	0.603 g/l
Precision*	± 0.033 g/l	± 0.046 g/l
	± 0.8%	± 7.6%

*Given as 99% limits.

SULFAMATE DETERMINATION

Preliminary Investigation

The reaction of sulfamate and nitrite to give nitrogen can be used to determine sulfamate as well as nitrite. A difficulty arises due to the fact that the final reaction mixture is an acid solution of nitrite, which on prolonged sweeping with inert gas evolves variable quantities of nitric oxide, which is nonabsorbable in alkali; consequently an absorption section for nitric oxide removal must be added to the apparatus.

The common reagents in gas analysis for removal of nitric oxide are ferrous sulfate in dilute sulfuric acid, and acid permanganate. Tests with numerous types of scrubbers showed neither of the reagents to be effective under the

conditions of the determination. Other oxidizing agents were tried: hypochlorite and hypobromite, which are unsatisfactory since both give oxygen when treated with carbon dioxide; and ammonium hexanitratocerate, which was found unsatisfactory when the sweeping rate was above 50 ml/hr.

The scrubbing system adopted is based on the reaction of bromine with nitric oxide in the presence of water:

The scrubber system saturates the gas stream with bromine and water vapor. This combination gives very efficient scrubbing. Bromine vapor reacts with the mercury in the azotometer, so it must be removed from the gas stream. The best reagent for this purpose was found to be 2 M sodium sulfite. The use of acid sulfites would give more capacity, but they evolve sulfur dioxide which although readily absorbed by the 50% potassium hydroxide in the azotometer, forms the relatively insoluble potassium sulfite which clogs the azotometer.

Apparatus

Figure 6 gives the design and details of the scrubbers. Scrubber A contains liquid bromine below a water layer and saturates the gas stream with bromine and water vapor. Scrubber B is used to prolong the scrubbing and contains bromine water. Scrubber C holds the sodium sulfite solution to remove bromine vapor.

The remainder of the apparatus used is identical with that used in the determination of nitrite, except that the reagent vessel is now filled with 5% sodium nitrite. The scrubbers are inserted in the train between stopcock A (Figure 1) and the azotometer.

Procedure

The sample is added to the reactor flask, and acidified strongly with sulfuric acid. The procedure from this point on is identical with that for nitrite.

Calculations

The value of the sulfamate is given by a formula analogous to that used to compute nitrite except for the factor $\frac{\text{NH}_2\text{SO}_3}{\text{N}_2}$ (factor for sulfamate in nitro-

gen). The formula is $g/L = 1556.7 \times \frac{(V-b)(P-c)}{(S)(273+t)}$

Results

Table II gives the results of the few determinations of sulfamate performed. The solutions were made up by dissolving a weighed amount of primary stan-

FIGURE 6
SCRUBBERS

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standard sulfamic acid in water. These solutions were checked by standardization against base. The sample size used was 190.86 g/l.

TABLE II

DETERMINATION OF SULFAMATE

	<u>Solution I</u>	<u>Solution II</u>
Theory	7.14 g/l	10.66 g/l
Found	7.20 g/l	10.81 g/l
	7.21	10.84
	7.12	10.63
Average	7.17 g/l	10.27
		10.88
		10.75
		10.75
	Average	10.70 g/l
	Precision	± 0.53 g/l
		± 4.9%

Discussion

The method for the determination of nitrite and sulfamate outlined here is rapid, accurate, and highly specific. Interferences are few, and limited to a few classes of compounds. It possesses the advantages of not requiring standard solutions for the determination and the equipment, although somewhat complex, is rugged and simple to use. By use of large reactors, samples containing as little as 1.2×10^{-5} gram nitrite per sample have been analyzed, an amount not easily titrated.

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