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MASTER

RADIO-RELEASE METHODS FOR THE EVALUATION
OF ATMOSPHERIC POLLUTION. SULFUR DIOXIDE*

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1. Introduction

Atmospheric pollution has grown into a problem of national concern in recent years. Because of this, efforts have been directed toward the determination of sulfur-bearing air pollutants, primarily sulfur dioxide. However, the exact danger level of sulfur dioxide is still disputed as was noted in a recent article [2].

Jacobs [4] presents a survey of the methods presently being used for airborne sulfur dioxide. Altshuller [1] reviews recent work. Stephens and Lindstrom [6] offer a new spectrophotometric method based on the formation of the ferrous phenanthroline complex. Because of the high sensitivity possible with the radio-release technique, we selected this method as a new approach to the determination of sulfur dioxide.

The radio-release technique is potentially one of the most useful radio-isotope analytical methods, although it has not been widely used. In addition to sensitivity, the technique has the advantages of selectivity and speed. Also, the method often lends itself to self-contained automated systems.

The radio-release method is based upon the selective reaction of the sought constituent with a radioactive reagent of known specific activity. During the reaction, activity is released as a gas or as an easily separable chemical species. The amount of sought constituent can be calculated from the amount of activity released, the specific activity of the reagent, and the stoichiometry of the reaction. Alternatively, the calculations can be avoided by reference to standard sample determinations. Richter and Gillespie have applied the technique to the determination of dissolved oxygen in water [3,5] and were able to measure lower concentrations than are possible with other existing methods.

The present method for sulfur dioxide is based on the release of radio-iodine according to the reaction:

The reaction is carried out in solution by forcing air through a bubbler train containing a basic potassium iodate solution. After the sample has reacted, the solution is acidified, and the liberated iodine is extracted. The activity of this solution is determined, and the amount of sulfur dioxide is calculated.

2. Experimental

2.1 Reagents and Apparatus

Analytical reagent grade chemicals were used whenever possible. The Isotopes Division, ORNL, supplied the carrier free iodine-131 tracer as iodide, which was converted later to KIO_3 reagent. Anhydrous sulfur dioxide (99.98%) and other compressed gases were manufactured by Matheson. Distilled water was used in all experiments after first being purged with argon.

A gas bubbler and extraction system was constructed as shown in Fig. 1.. Point A is a small glass-wool filter used to remove any particulate material in the gas stream. Flasks B and B' are the primary and secondary reaction bubblers; C is a final scrubber for blowby protection; D is the solvent extraction flask. The E flasks are required for solvent and acid additions. The complete system was constructed of glass with a minimum number of joints and was designed so that negligible contamination of the reagents by the atmosphere would occur.

Gas samples were introduced into the system by means of a double vented flask connected to the input of the system. Samples can be pushed through the system with compressed air or pulled through with a vacuum. No difference was observed using either method.

Sulfur dioxide samples were prepared by diluting the appropriate amount of gas with hydroxide scrubbed air. For very dilute samples, two dilution steps were needed.

Activity measurements were made with a 3" x 3" sodium iodide well-type scintillation detector connected to a conventional high-speed scaler of ORNL design. Counting times were adjusted for most samples so that a total count of at least 5×10^4 was collected (0.88% counting error at 95% confidence level).

2.2 Procedures

Radioactive potassium iodate was prepared by the oxidation of iodide ion with permanganate. Three millicuries of I^{131} tracer solution was placed in a 25-ml. reflux flask and 1.0 mg. of potassium iodide was added. A sufficient amount of 0.05 N sulfuric acid was added (if necessary) to adjust the pH to 8-7. The flask was fitted with a small reflux condenser and three drops of a saturated potassium permanganate solution were added. Water was added to bring the total volume to about 5 ml., and the solution was gently

refluxed. Additional permanganate was added after 10 minutes to just restore the purple color. Refluxing was allowed to continue for another 20 minutes. After the solution had cooled, it was transferred to a tube and centrifuged for five minutes. The clear solution was decanted from the manganese dioxide precipitate into a 20-ml. beaker. The solution was heated just to the boiling point and sufficient potassium iodate was added to saturate the solution. After cooling, the crystals of potassium iodate were collected and dried. The yield was 1.22 gm. of material having an approximate specific activity of 2 mc./gm.

The radio-reagent stock solution was prepared by dissolving 1.0 gm. of the active potassium iodate in 20 ml. of water and then diluting to 100 ml. This solution was stored in a bottle to which 100 ml. of chloroform were added. During the useful life of the reagent, a small amount ($< 0.1\%$) of elemental iodine is generated in solution due to radiation decomposition. The purpose of the chloroform is to extract any iodine formed in the reagent so that the reagent blank can be kept to a minimum.

A 10-normal sulfuric acid solution and 5- and 1-normal sodium hydroxide solutions were prepared conventionally.

All of the experimental runs were performed by a general procedure as follows. The 3-way stopcock was closed to all positions and one milliliter of radioreagent and 15 ml. of 1 N sodium hydroxide were pipetted into each reaction bubbler, B and B'. One hundred milliliters of 5 N sodium hydroxide were added to the final scrubber C, and two milliliters of chloroform were placed in flask D. A vacuum line was attached to the exit side of the system, and the flow rate was roughly adjusted to 1 liter/minute by drawing argon through the system. The exact flow rate is unimportant since the system shows no deviation at flow rates from ≈ 100 ml./minute to ≈ 4 l./minute.

The sample to be analyzed was attached to the entrance side of the system and was allowed to flush out through the bubblers for a time suitable to the sample size (2-5 minutes). After flushing, the solutions in B and B' were drained and rinsed into flask D with water. Three milliliters of 10 N sulfuric acid were added to flask D and the liberated iodine was extracted into the chloroform. The phases were allowed to separate, and the lower layer was drained into a tube suitable for use in the well counter. A second and third extraction with two milliliter portions of chloroform served

to quantitatively remove the iodine from the aqueous phase. The sample was counted and the sulfur dioxide concentration determined.

2.2.1 Blank Determinations. Using the above procedure, the response of the system was determined using air, free of sulfur dioxide. The results of these experiments are shown in Table I. The sulfur dioxide equivalent found in the blank determination can be attributed to (1) traces of reducing substances in the reagents and (2) mechanical carry-over in the extraction. It is difficult to estimate the effect of the above variables separately. However, it is doubtful that further purification of the reagents will reduce the blank significantly.

2.2.2 Response of the System to Sulfur Dioxide. Duplicate standard samples of sulfur dioxide were analyzed, again using the standard procedure. The results of this series are shown in Fig. 2. A 0.07 μg blank was subtracted from each run. The results shown are essentially linear relationships from 0.1 to 25 μg . of sulfur dioxide. Higher concentrations of sulfur dioxide were not studied since it was assumed that samples could be reduced to this size without difficulty.

Eight samples containing 1.0 μg of sample were checked to test the reproducibility of the system. The results are reported to the nearest 0.01 μg . ($\sim 1\%$ counting error) in Table II. Note that one standard deviation amounts to about 5% of the sample size.

2.2.3 Interferences. Interference studies were made with materials that could be present in the atmosphere during a sulfur dioxide analysis. Since interference can occur in both the positive and negative directions, these tests were run in a 5.0 μg . sample of sulfur dioxide. The interference materials were obtained as compressed gases or as reagent grade liquids. The results of these studies are shown in Table III.

3. Discussion and Conclusions

A radio-reagent method is presented for the sensitive determination of sulfur dioxide in the atmosphere. The system exhibits a number of advantages when compared with existing methods. Foremost of these advantages is the extreme sensitivity and dynamic range of the method. Without changing any operational step or reagent, sulfur dioxide can be determined from 8×10^{-4} to 0.2 ppm. in a 100 liter gas sample. This range is not fixed, however, since the specific activity of the reagent can be varied over wide

limits both up and down. Flow rates can be suited to the particular application; no error was observed at any flow rate up to 4 l./minute. The method does not require the judgment of a skilled operator making possible a completely automatic remote monitoring station. Although the radio-reagent was synthesized with I^{131} , which requires a day-to-day decay correction, the reagent can also be made with longer half-life I^{125} to extend the useful life.

There are essentially no important variables in the method, and the only significant interference is hydrogen sulfide. However, this is not a real problem since hydrogen sulfide levels are typically lower than those of sulfur dioxide by more than two orders of magnitude [4].

The method should be generally adaptable to any gas system without modification of the basic system.

4. Bibliographical References

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TABLE I
BLANK DETERMINATIONS

<u>Sample</u>	<u>SO₂ Equivalent Found (x 10⁻² µg)</u>
1	6.8
2	6.7
3	7.1
4	7.0
5	7.3
6	7.1
7	7.0
8	6.8

Average = 7.0 +

Standard Deviation = 0.25

TABLE II
REPRODUCIBILITY OF SULFUR DIOXIDE DETERMINATIONS

<u>Sample</u> ^a	<u>SO₂ Found (μg)</u> ^b
1	1.02
2	0.96
3	1.04
4	0.92
5	0.89
6	0.94
7	0.98
8	1.00
Average	0.97
Standard Deviation	0.05

^a1.00 ± 0.02 μg. SO₂/sample.

^b0.07 μg. blank subtracted and resulting value rounded off to nearest 0.01 μg.

TABLE III
INTERFERENCES

<u>Sample^a</u>	<u>SO₂ Found (μg.)</u> <u>SO₂ Added (μg.)</u>
Benzene	1.00
Carbon Dioxide	1.00
Carbon Disulfide ^b	1.00 ^c
Carbon Monoxide	1.00
Formaldehyde	1.06 ^c
Hydrogen Chloride	1.00
Hydrogen Sulfide	1.44 ^c
Methanol	1.00
Nitrogen Dioxide	0.96 ^c

^a5.0 μg sample + 5.0 μg sulfur dioxide.

^bWashed with 0.5 N NaOH.

^cTwo or more runs.

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Fig. 1. Gas absorption train and reaction apparatus.

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Fig. 2. Response of radio-release system to sulfur dioxide.