JOHN F. KENNEDY
SPACE CENTER

KSC-TR-1073
September 15, 1970

TURBIDIMETRIC DETERMINATION OF SULFITE ION IN INHIBITED ETHYLENE GLYCOL-WATER SOLUTIONS

September 18, 1970

Prepared by

Support Laboratory Section
MALFUNCTION ANALYSIS BRANCH
John F. Kennedy Space Center, NASA
Kennedy Space Center, Florida 32899

KSC FORM 16-12 (4/66)

1. Report No. KSC-TR-1073	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Turbidimetric Determination of Sulfite
Ion in Inhibited Ethylene Glycol-Water
Solutions

5. Report Date
September 15, 1970

6. Performing Organization Code
SO-LAB-22

7. Author(s) Helein D. Bullard, Lee D. Underhill,
and George L. Baughman

8. Performing Organization Report No.

9. Performing Organization Name and Address
Support Laboratory Section
John F. Kennedy Space Center, NASA
Kennedy Space Center, Florida 32899

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
John F. Kennedy Space Center, NASA
Kennedy Space Center, Florida 32899

13. Type of Report and Period Covered

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Abstract

A procedure for determining sulfite in inhibited ethylene glycol-water solutions is presented. Hydrochloric acid and potassium iodide are added to the glycol-water solution which is then titrated with potassium iodate solution to a turbidimetric end point provided by the oxidation of the 2-mercaptobenzothiazole inhibitor. The instrumental method using a colorimeter to detect the turbidimetric end point has a standard deviation of about 0.2 in the 0-20 μg Na_2SO_3 per ml concentration range.

17. KeyWords
Chemical Analysis, Glycols,
Sulfites, Thiols

18. Distribution Statement
STAR
(No limitations)

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 20	22. Price

KSC FORM OT-320 (7/69) (ONETIME FORM - REPRINT NOT AUTHORIZED)

INTRODUCTION

Sodium sulfite, 1% (w/w), is added to some sodium 2-mercaptobenzothiazole (NaMBT) solutions, (tradename NaCAP), to prevent oxidation of the NaMBT. When the resulting solution is used to prepare inhibited ethylene glycol-water solutions for Apollo spacecraft environmental control systems (1), the concentration of sodium sulfite is 18 parts per million or less. Several colorimetric methods for determining low concentrations of sulfite or sulfurous acid were investigated or considered. Fuchsin-formaldehyde (2-6) or pararosaniline-formaldehyde (7-8) have been used by a number of investigators. Steigmann (4), in his investigation of the use of fuchsin as a colorimetric reagent, stated that fuchsin-formaldehyde gives a color with sulfurous acid, thiosulfates, mercaptans, or thio-acids. He proposed using mercuric chloride to precipitate the last three, making the test specific for sulfurous acid. After a preliminary experiment confirmed that mercaptobenzothiazole (MBT) reacts with fuchsin-formaldehyde to produce an interfering color, saturated mercuric chloride solution was added to inhibited glycol-water solution to remove the interfering thiol. This procedure resulted in erratic loss of the sulfite. Attempts to use malachite green (9) to determine sulfite concentration were also unsuccessful, apparently due to interference by the MBT. Determination of sulfite by polarography was also investigated, but the acidic condition required to detect sulfite and the treatment necessary to remove oxygen led to unreproducible results. Attempts to determine the sulfite concentration of the glycol-water solution by conventional oxidation titration methods, using iodine or potassium iodate-iodide (10-11), were unsuccessful because a voluminous white precipitate preceded and obscured the normal end point. Identification of the precipitate as 2,2'-dithiobis[benzothiazole] (MBTS), an oxidation product of the MBT inhibitor, by infrared and mass spectrometry suggested using the appearance of the precipitate to indicate the titration end point. This paper describes an instrumental titration procedure for determining sulfite in inhibited glycol-water solutions. The method is based on the reaction of iodine, liberated by potassium iodate solution, with the sulfite in the glycol-water sample. An end point is reached when all the sulfite has been consumed and the iodine begins to oxidize the MBT, producing a turbid solution.

EXPERIMENTAL

Reagents

Potassium iodate solution (1 ml = 1 mg Na_2SO_3) was prepared by dissolving 0.566 gram KIO_3, Fisher Certified Reagent, previously dried at 120°C for 1 hour, and 0.5 gram sodium bicarbonate in distilled water and diluting to one liter. Potassium iodate is a primary standard.

Potassium iodate solution (1 ml = 0.1 mg Na_2SO_3) was prepared by diluting the above solution tenfold.

Potassium iodide solution, 5% (w/v) aqueous solution.

Sodium sulfite solution, aqueous, 1000 μg/ml, was prepared by dissolving 1.0152g Na_2SO_3 (Baker Analyzed Reagent, 98.5% assay) in distilled water and diluting to one liter. This reagent is not very stable and frequent standardization against KIO_3 is necessary.

Sodium sulfite solution, glycol-stabilized, 1000 μg/ml, was prepared by sealing liquid sulfur dioxide (Matheson Anhydrous Grade, 99.98% min.) in small glass bulbs, breaking the bulbs in a heavy-walled stoppered flask containing 10 ml 20% NaOH and 90 ml of 35% ethylene glycol (Baker Analyzed Reagent) solution in distilled water, and diluting to one liter with the 35% ethylene glycol solution. The glycol-sulfite solution is quite stable.

Starch indicator solution. A trace of mercuric iodide was added as a preservative.

Hydrochloric acid, 6N.

Apparatus

The titrations were performed using Metrohm titration equipment, available from Brinkmann Instruments, Inc., Westbury, New York. The equipment consisted of a Potentiograph E 436, Multi-Titration Stand E 436 E, with a 5 ml buret, and a Spectro-Colorimeter E 1009 with titrating equipment.

The titration vessel was a 19 X 105mm cylindrical cuvette which was open to the atmosphere. Mechanical stirring with a glass spiral was employed at the maximum rate which did not cause air bubbles to be drawn into the sample solution. The positions of both the stirrer and the buret delivery tip were adjusted to the maximum depth which did not obstruct the light path.

The Spectro-Colorimeter is connected to the Potentiograph by a cable and the chart drive of the Potentiograph is directly coupled to the buret piston providing automatic recording of transmitted light versus titrant volume.

Procedure

Add 1.0 ml of 6N HCl and 5 drops of KI solution to 10.00 ml of inhibited ethylene glycol-water sample. Titrate automatically with KIO_3 solution (1 ml = 0.1 mg Na_2SO_3) at a wavelength of 550 nm and a titration speed of about 0.35 ml per minute. Continue the titration past the portion of the titration curve where the change in transmittance is linear with respect to the change in volume. Determine the end point graphically by extrapolating this linear portion of the titration curve back to the point where it intersects the extended baseline (Figure 1).

Prepare a blank by placing 50.00 ml of the inhibited ethylene glycol-water sample and 5.0 ml 6N HCl in a fritted glass vessel (coarse porosity) and passing nitrogen through the mixture for one hour at a rate of 0.2 - 0.3 ft^3/hr. Add 5 drops of KI solution to 11.00 ml of the acidified and deaerated solution and titrate to determine the blank value.

RESULTS AND DISCUSSION

Turbidimetric titrations usually involve determining the completion of a precipitation reaction. This procedure to determine sulfite is somewhat unusual in that the initiation of a precipitation reaction provides the end point of a volumetric titration. Thus, the comparison standards required for conventional turbidimetry are unnecessary. In addition, the requirements for stable small particle size as discussed by Hochgesang (12) and Meehan and Chiu (13) are less restrictive in determining when precipitation begins. Agglomeration of the MBTS precipitate does occur when the solutions are allowed to stand after titration, but constant stirring during titrant addition and the probable co-solvent action of ethylene glycol promote apparent uniform particle size during initial MBT oxidation and permit a relatively precise location of the "start point" of the precipitation (the end point of the sulfite titration).

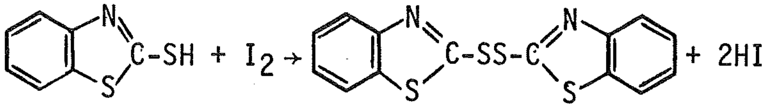
The wavelength of 550 nm was chosen to avoid a wide absorption band centered at approximately 430 nm. The choice of wavelength was not affected by the color of the precipitate since MBTS is white.

Titration speeds of 0.35 ml/min or slower gave constant results. Faster titrant additions were not adequately mixed because the solution could not be stirred faster without turbulence.

The basic reactions involved in this determination are given by equations (1) and (2). The reaction in equation (3) occurs after the reaction of the total sulfite content and indicates the end point.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (1)$$

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+ \qquad (2)$$



(3)

To show that the inhibitors in glycol-water solutions (Table 1 gives the composition of these solutions) do not interfere with the stoichiometric reactions of iodine and sulfite, increments of an aqueous Na_2SO_3 solution were added to a Type I Glycol-Water solution and the sulfite was titrated instrumentally. The sulfite additions caused no change in the shape of the titration curve (Figure 1) and the titration results (Figure 2) show the expected linear relationship between sulfite added and iodate required, demonstrating that the inhibitors do not interfere. To investigate the accuracy of the method, aliquot portions of a glycol-stabilized sulfite standard solution, prepared using a known weight of anhydrous sulfur dioxide, were added to inhibited glycol-water solutions. When 116 μg Na_2SO_3 were added, triplicate determinations yielded values of 112, 111, and 111 μg. The deviation among the results was 0.3% and the error from the true value was 4.3%. To demonstrate the precision of the method, the sulfite content of two inhibited ethylene glycol-water solutions was determined repeatedly. The results, given in Table 2, indicate that the standard deviation is constant in the desired sulfite range.

The difficulties encountered in the conventional determination of sulfite and the instability of sulfite solutions have been discussed by several investigators (14-18). Siggia, Whitlock and Tao (14) observed in analyzing pure sodium sulfite iodometrically that "many results would agree fairly well, but a significant number of analyses would yield low, erratic results." Siggia and his co-workers turned to an alternate procedure for determining sulfite. Haller (15) investigated the cause of erratic results in determining sulfite. He theorized that copper and iron salts leached from the walls of the reaction vessel catalyze the oxidation of sulfite by the oxygen dissolved in the solution. His addition of 5% glycerol, a polyhydric alcohol, to the strongly basic (10% NaOH) solution prevented loss of sulfite even when oxygen was blown through the solution or when the solution was heated. He attributed this effect to the combination of the "negative catalyst" (glycerol) with the "positive catalysts" (copper and iron salts). Urone and Boggs (16) also found 5% glycerol effective in stabilizing sulfite solutions. Ruff and Jeroch (17) used mannitol, another polyhydric alcohol, as a "negative catalyst" in determining sulfite. Baker and Day (18) observed that sulfurous acid is readily oxidized by dissolved oxygen in the presence of dilute acids and that the oxidation is greatly facilitated by reaction between acids and alkalis in the solution. Haller concluded that a certain loss of sulfur dioxide is therefore bound to occur when the alkaline sulfite solution is acidified before titration, but he showed that the glycerol addition was also capable of preventing the catalytic oxidation caused by acidifying the solution. He did not discuss loss of sulfite by diffusion into the air.

Ethylene glycol, another polyhydric alcohol, apparently is also effective in protecting sulfite. One Type I Glycol-Water solution (pH 8.5) containing 3 micrograms of sodium sulfite per milliliter was stored in a brown glass bottle. It showed no loss of sulfite during three months although the bottle was opened numerous times to remove solution during that period.

The addition of ethylene glycol to standard sulfite solutions results in a much more stable solution. Whereas aqueous sulfite solutions lose strength rather rapidly, a 35% ethylene glycol solution containing 1000 μg Na_2SO_3 per ml showed no loss of sulfite in three weeks. In addition, no loss of sulfite was detected when oxygen was passed through the solution for two hours at a rate of 0.1 ft^3/hr or when nitrogen was passed through the solution for 17 hours at the same rate.

The sulfite content of these high concentration solutions was determined by iodate titration using starch indicator. In one determination using the standard ASTM procedure, the odor of sulfur dioxide was detected when the solution was acidified just prior to titration. The standard procedure was modified by adding all but 1 ml of the iodate reagent before acidification and then completing the titration. The modified titration gave somewhat higher and more reproducible values than the standard titration.

The complexity of the glycol-water solutions and the probability that different samples might contain one or more components from different manufacturing lots required a method of obtaining a blank more representative of the sample than a mixture of laboratory reagents might be. Accelerating the loss of sulfite from an acidic sample solution appeared to be a convenient method to obtain this blank. Nitrogen was passed through acidified Type I Glycol-Water solutions with and without additional Na_2SO_3 for various lengths of time as shown in Table 3. From this data, a deaeration time of one hour appeared to be sufficient to totally remove sulfite in the 0-20 μg/ml concentration range.

Detection of sulfite in inhibited glycol-water solution by a completely independent method was achieved using polarography. In acidic media, sulfur dioxide is polarographically reduced to H_2SO_2 at -0.37 volts vs. S.C.E. (19). None of the other components of the inhibited glycol-water solution are polarographically active in the 0 to -1 volt range and the only other reduction wave observed is due to the presence of dissolved oxygen. Removal of the interfering oxygen was accomplished by strongly basifying the solution and deaerating with nitrogen. Polarographic studies showed that some sulfite is removed from the solution by deaerating at the nominal pH of 8.5 and demonstrated that all sulfite is removed by deaerating the strongly acidified solution for one hour, confirming the results given in Table 3.

Figure 1

Location of Instrumental Titration End Point

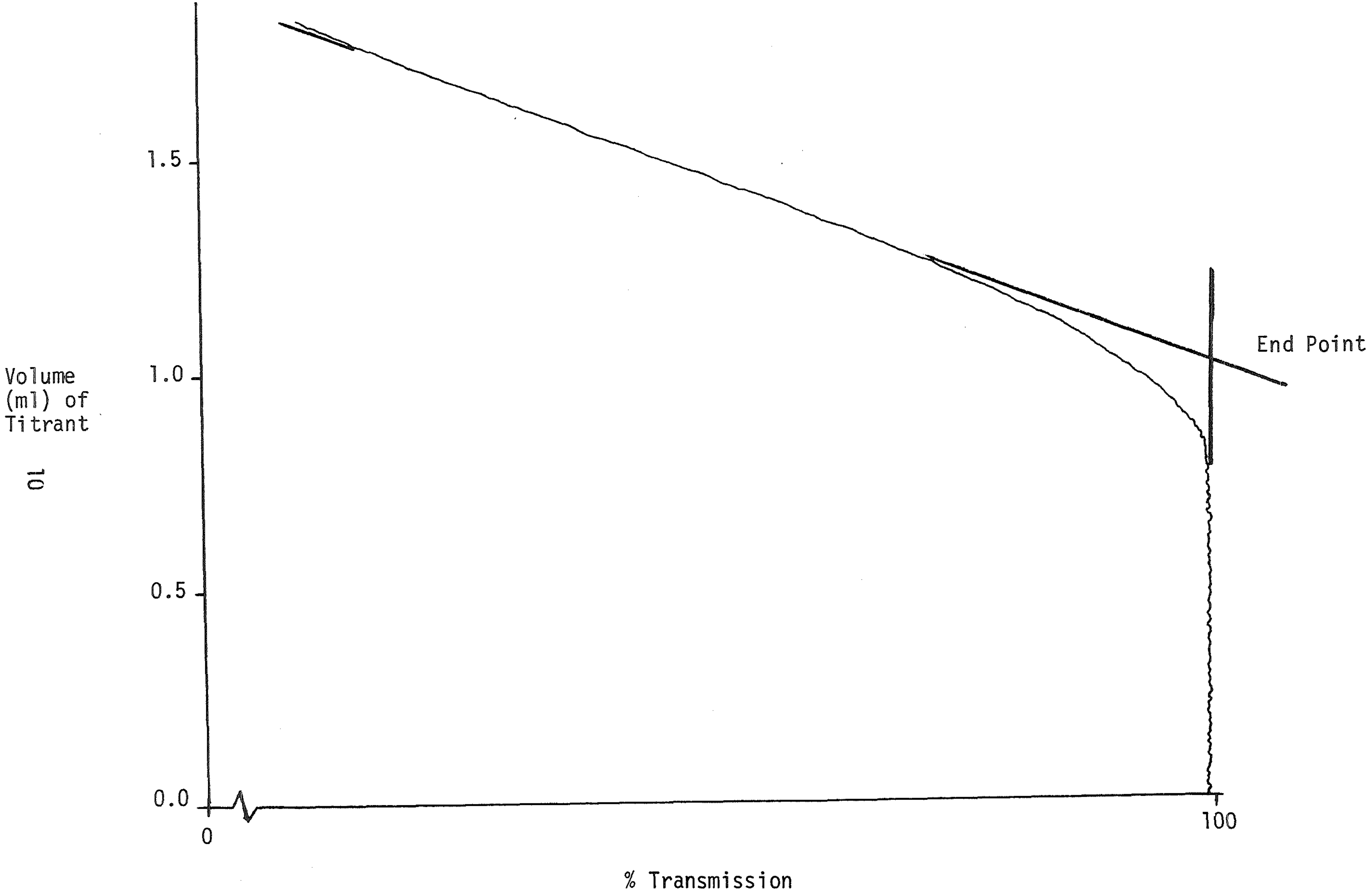


Figure 2

Demonstration of Stoichiometric Oxidation of Sulfite in Inhibited Ethylene Glycol-Water Solution Using Iodate Titrant (1 ml = 102.4 µg Na_2SO_3)

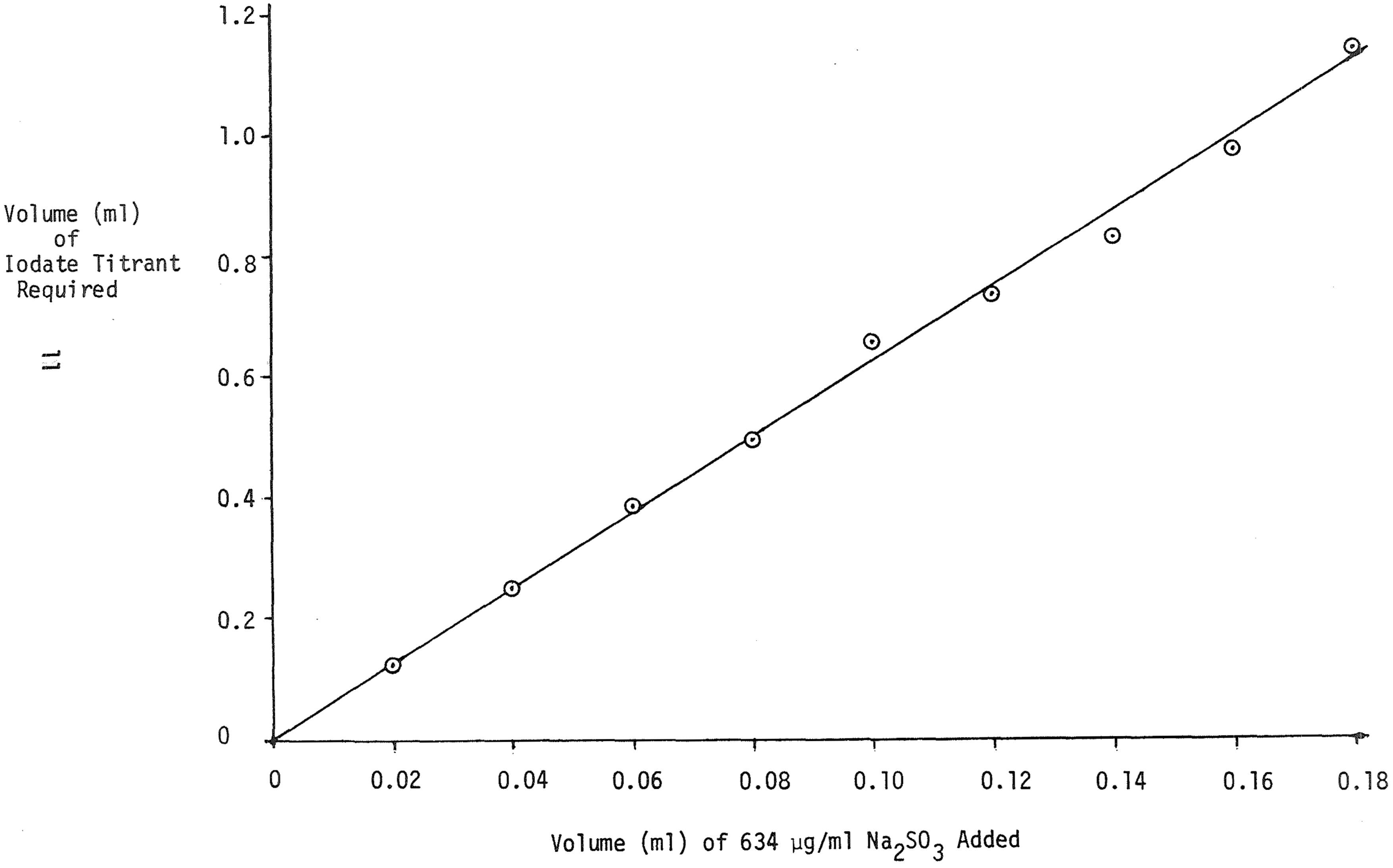


Table 1

Composition of Inhibited Ethylene Glycol-Water Solutions (1)

Requirement	Type I	Type II
Ethylene Glycol, % by weight	35.00	62.50
Triethanolamine Phosphate, % by weight	1.60	1.60
Sodium Mercaptobenzothiazole, % by weight	0.09	0.09
pH	8.5	7.5

Table 2

Precision of Turbidimetric Determination of Sodium Sulfite in Inhibited Ethylene Glycol-Water Solutions

Na_2SO_3, µg/ml

	Low Concentration	High Concentration
	3.4	19.8
	3.8	19.6
	4.2	19.4
	3.9	19.2
	4.1	19.3
	3.9	19.4
	4.0	19.2
	4.0	19.2
	3.9	19.1
	4.1	19.6
Average	3.9	19.4
Standard Deviation	0.22	0.23
Relative Standard Deviation	5.6%	1.2%

Table 3

Removal of Sulfite by Acidification and Deaeration of Inhibited Ethylene Glycol-Water Solution

	Deaeration Time, Minutes	Volume (ml) KIO_3 Required	Sodium Sulfite Concentration (μg/ml)
Type I Glycol-Water	0	0.630	3.0
	15	0.490	1.6
	30	0.400	0.6
	60	0.340	0.0
	90	0.340	0.0
Type I Glycol-Water	0	0.640	3.1
	60	0.330	0.0
Type I Glycol-Water plus added Na_2SO_3	0	1.405	10.9
	60	0.330	0.0

Bibliography

(1) National Aeronautics and Space Administration, Specification MSC-SN-W-0040, Ethylene Glycol-Water Solutions, Requirements for, March 15, 1969.

(2) S. Atkin, Anal. Chem. 22, 947 (1950).

(3) W. M. Grant, Anal. Chem. 19, 345 (1947).

(4) A. Steigmann, J. Soc. Chem. Ind. 61, 18 (1942).

(5) A. Steigmann, Anal. Chem. 22, 492 (1950).

(6) M. E. Taylor, et al, Lunar Module Cooling System Chemical Analysis Program, Report Number D2-118278-1, The Boeing Company, Contract No. NASw-1650, December 22, 1969.

(7) P. W. West and G. C. Gaeke, Anal. Chem. 28, 1816 (1956).

(8) F. P. Scaringelli, B. E. Saltzman, and S. A. Frey, Anal. Chem. 39, 1709 (1967).

(9) S. Honda and S. Kobayashi, Osaka Kogyo Gijutsu Shikenso Kikko 17 (1), 87-9 (1966); Chem. Abs. 66, 43470h (1967).

(10) M. J. Taras in "Standard Methods of Chemical Analysis", Sixth Ed., Vol. Two, p. 2488, F. J. Welcher, Ed., D. Van Nostrand, Princeton, N. J. 1963.

(11) ASTM D 1339-62T, Tentative Methods of Test for Sulfite Ion in Industrial Water, Non-Referee Method C in "Manual on Industrial Water and Industrial Waste Water", 2nd Ed., American Society for Testing and Materials, Philadelphia, Pa., 1964.

(12) F. P. Hochgesang in "Encyclopedia of Industrial Chemical Analysis", Vol. 2, p. 692, F. Snell and C. Hilton, Ed., Interscience Publishers, Inc., New York, N. Y., 1966.

(13) E. J. Meehan and G. Chiu, Anal. Chem. 36, 536 (1964).

(14) S. Siggia, L. R. Whitlock and J. C. Tao, Anal. Chem. 41, 1387 (1969).

(15) P. Haller, J. Soc. Chem. Ind. 38, 52-56T (1919).

(16) P. Urone and W. E. Boggs, Anal. Chem. 23, 1517 (1951).

(17) O. Ruff and W. Jeroch, Ber. 48, 409 (1905).

(18) J. Baker and F. Day, Analyst 37, 439 (1912).

(19) L. Meites, "Polarographic Techniques", 2nd Edition, P. 621, Interscience Publishers, Inc., New York, N. Y., 1965.

SPECIAL DISTRIBUTION

National Aeronautics and Space Administration
John F. Kennedy Space Center
Kennedy Space Center, Florida 32899

FP-C	R. Cerrato	
IS-DOC-12LD	Library-Documents	(3)
SO-LAB-2	R. Yorio	
SO-LAB-22	G. L. Baughman	(40)
SO-LAB-3	C. Hoppesch	
LTV-P13	R. P. Shatsky	(3)

National Aeronautics and Space Administration
Manned Spacecraft Center
Houston, Texas 77058

ES	J. N. Kotanchik
ES	W. R. Downs

NASA Scientific & Technical Information Facility
P.O. Box 33
College Park, Maryland 20740

Attn: UST (3)

Boeing Company
Seattle, Washington 98100

Materials and Processes Lab Attn: M. E. Taylor

Grumman Aerospace Corporation
Bethpage, New York 11714

Materials Engineering, Plant 25 Attn: Charles Smith
QC Lab, Plant 10 Attn: Walter Kogel

North American Rockwell Corporation
Downey, California 90240

Dept 191-202, Mail Stop AB89 Attn: H. M. Clancy

Total: 58