

MIL-STD-1564A
NOTICE 1
23 January 1980

MILITARY STANDARD
PROCEDURE FOR CALIBRATION AND ANALYSIS
OF TRACE CONTAMINANTS
IN AVIATOR'S BREATHING OXYGEN
BY INFRARED SPECTROSCOPY

TO ALL HOLDERS OF MIL-STD-1564A:

1. THE FOLLOWING PAGES OF MIL-STD-1564A HAVE BEEN REVISED AND SUPERSEDE THE PAGES LISTED:

NEW PAGE	DATE	SUPERSEDED PAGE	DATE
iii	23 January 1980	iii	11 November 1977
iv	23 January 1980	iv	11 November 1977
v	23 January 1980	v	11 November 1977
vi	23 January 1980	vi	11 November 1977
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4	23 January 1980	4	11 November 1977
5	23 January 1980	5	11 November 1977
6	23 January 1980	5	11 November 1977
6a	23 January 1980	6	11 November 1977
6b	23 January 1980	6	11 November 1977
9	11 November 1977	(REPRINTED WITHOUT CHANGE)	
10	23 January 1980	10	11 November 1977

2. RETAIN THIS NOTICE AND INSERT BEFORE TABLE OF CONTENTS.

3. Holders of MIL-STD-1564A will verify that page changes and additions indicated above have been entered. This notice page will be retained as a check sheet. This issuance, together with appended pages, is a separate publication. Each notice is to be retained by stocking points until the Military Standard is completely revised or canceled.

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3.23 Wavenumber. The wavenumber is the number of waves per unit length. It may be represented by the symbol ω . The unit used in this standard is "reciprocal centimeters" or "cm⁻¹." It describes the number of waves per centimeter. Wavenumber is related to the wavelength.

$$\omega(\text{in cm}^{-1}) = \frac{10\,000}{\lambda(\text{in } \mu\text{m})}$$

4. GENERAL REQUIREMENTS

4.1 Instrument Parameters. Instrument parameters shall be set in accordance with procedures established by the instrument manufacturer. The analyst shall check parameters prior to calibration and reset if necessary. Parameters shall be checked at a minimum frequency of once every 30 days to ensure that they have not been changed since the previous calibration. A record of settings and checks shall be kept in a log book. Instrument parameters shall be the same for calibration and sample analysis. If conditions arise which necessitate changing these parameters, the instrument shall be recalibrated.

4.2 Pressure of Analysis. Calibration curves shall be prepared at 50 psig and the optimum scan pressure. Section 5 is written for 10 m cells whose optimum scan pressure is 135 psig. Instruments which have 20 m cells have an optimum scan pressure of 100 psig. When performing procedures described in section 5 optimum scan pressures other than 135 psig may be substituted directly for 135. However, values "76 mm Hg" in 5.6.3.2 and "150" in paragraph 5.8.3 will require adjustment with respect to the optimum scan pressure. The former should be 1/100th of the optimum scan pressure in absolute units. The latter should be the optimum scan pressure in absolute units.

4.2.1 Field Samples. Samples should be analyzed at the optimum scan pressure but may be analyzed between that value and 50 psig provided the absorbance values are normalized to the appropriate pressure of the calibration curve. Samples of insufficient quantity to pressurize the gas cell to 50 psig shall not be analyzed.

4.2.2 Contractor Samples. Samples must be analyzed at the optimum scan pressure to ensure detection of all contaminants in accordance with the specification. Government contract requires submittal of sufficient sample to analyze at that pressure. Samples of insufficient quantity to pressurize the gas cell to that pressure shall not be analyzed.

4.3 Pressure of System. Prior to each pressurization step of Section 5, check the valves to ensure that only those parts of the system will be pressurized which can withstand the intended pressure.

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4.4 Evacuation of System. Prior to each evacuation of a system previously used to analyze an oxygen sample, vent the system. Even though the vacuum pump is lubricated with tricresyl phosphate, it is still subject to reaction with pressurized oxygen under high shear conditions.

4.5 Carbon Dioxide Interference. In some IR gas cell systems such as that manufactured by Perkin Elmer Corp, a significant length of the light path passes through the atmosphere. In such systems, atmospheric carbon dioxide and water vapor will always be observed in the IR spectrum unless the light path is enclosed and purged with an inert gas. When it is impractical to purge the light path, the absorbance due to atmospheric carbon dioxide shall be determined daily with cell evacuated. Each sample should be then corrected for this blank value.

4.6 Maintenance. After a maintenance operation has been performed on the instrument, its calibration shall be checked. This may be accomplished by preparing a standard of known concentration and comparing its absorbance with the appropriate calibration curve. A significant difference from the expected absorbance shall be cause for recalibration.

4.7 Manifold and Tubing. Manifold and tubing shall be constructed of stainless steel or other oxygen compatible metal. Internal volume of this system shall be kept to minimum.

4.8 Alternate Methods. Section 5 contains approved methods for mixing standards and measuring absorbance. Other methods may be acceptable. Alternatives to the approved methods shall be submitted to San Antonio ALC/SFQT for review and for possible inclusion in this standard. Final acceptance of the method and technique employed at each laboratory designated to perform analysis of Aviator's Breathing Oxygen (ABO) shall depend on acceptable performance in the ABO Correlation Program.

4.9 Rounding-Off. For purposes of determining conformance to a procurement or use limit, an observed or calculated value shall be rounded-off so that the last place retained has the same position in relation to the decimal point as the last right-hand place of figures used in expressing the limiting value. The figure in the last place retained shall remain the same or shall have one added to it as described below. See Table I for examples.

4.9.1 When the next figure to the right of the last place to be retained is less than 5, do not change the figure in the last place retained.

4.9.2 When the next figure to the right of the last place to be retained is greater than 5, add 1 to the figure in the last place retained.

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TABLE I. Examples of Rounding-Off

Procurement/ Use Limit	Observed/ Calculated Value	Rounded- Off Value	Conforms to Limit	Reference Paragraph
2 max	2.15	2	Yes	4.9.1
99.5 min	99.43	99.4	No	4.9.1
5 max	5.75	6	No	4.9.2
25 max	25.9	26	No	4.9.2
1 max	1.58	2	No	4.9.3
2 max	2.51	3	No	4.9.3
10 max	10.5	10	Yes	4.9.4
5 max	5.50	6	No	4.9.4

4.9.3 When the figures to the right of the last place to be retained are 5 followed by one or more nonzero digits, add 1 to the figure in the last place retained.

4.9.4 When the figures to the right of the last place to be retained are 5 alone or 5 followed by any number of zeros, add 1 to the figure in the last place retained if it is odd; do not change the figure in the last place retained if it is even.

5. DETAILED REQUIREMENTS

5.1 Typical Apparatus.

5.1.1 Infrared Spectrophotometer - A double beam, optical null, automatic recording spectrophotometer capable of making absorbance measurements through the range 2.5 to 15.5 μm utilizing a gas cell which has an optical pathlength of no less than 10 meters.

5.1.2 The infrared chart paper should have an abscissa scale in wave-numbers or wavelengths, and an ordinate scale in absorbance units.

5.1.3 Pump, high vacuum, Kinney KC-8 or equivalent. Use no oil; fill pump with tricresylphosphate. Other sources: Welch, Precision.

5.1.4 Manifold and Tubing - A manifold with suitable outlets to permit assemblage of the gas system.

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- 5.1.4.1 Valves, stainless steel, diaphragm packless, Matheson 939 series or equal. Other sources: Whitey, Robbins, Nu-Pro, Hoke.
- 5.1.4.2 Hose, flexible, stainless steel, teflon lines, braided, as needed.
- 5.1.4.3 Tubing, stainless steel, as needed.
- 5.1.4.4 Tube fittings, stainless steel, as needed.
- 5.1.5 Gauge, test, with minimum range of 0 to 150 psig in increments of one psi or less. Heise and Ashcroft are sources of satisfactory gauges.
- 5.1.6 Manometer, Mercury, Meriam Model 310EF10 or equivalent. Wallace and Tiernan is an alternate source.
- 5.1.7 Gauge, McLeod, Sargent-Welch P/N S-39798-10 or equivalent.
- 5.1.8 Regulators for compressed gases, as required. Air Products, Airco, and Matheson are sources.
- 5.1.9 Gas chromatography gas sampling valve (Perkin Elmer No. 154-0068 or equivalent) with 0.25, 1.0, and 5.0 ml sample loops. Carle and Barber Coleman are other sources of valves.
- 5.1.10 Syringe and needle 1.0 ml, 2.5 ml, 5.0 ml. Disposable types may be used. Hamilton and Precision are sources.
- 5.1.11 Wet test meter. Available from Precision.
- 5.1.12 Gas cell with optical pathlength of no less than 10 meters; suitable for pressurization to not less than 135 psig.
- 5.1.13 Water vapor saturation - Gas Washing Bottle, Sargent P/N S-39590 or equivalent.
- 5.1.14 Barometer, Mercury, Fisher Catalog No. 2-383 or equivalent.
- 5.1.15 Septum device suitable for absolute pressures of 1 mm Hg to 250 psi. Assemble as shown in figure 0. After seating the components, tighten the nut about two turns beyond finger tight.
 - 5.1.15.1 Tube fitting, male connector, stainless steel, 1/4 inch tube to 1/8 inch pipe, Swagelok P/N SS-400-1-2 or equivalent.
 - 5.1.15.2 Septum, gas chromatography, 3/8 inch in diameter by 1/8 inch thick, Applied Science Laboratories Type W-9 or equivalent.
 - 5.1.15.3 Washer. The diameter of the washer shall be such that it just fits inside the nut of the connector. The hole in the washer shall be 1/8 inch in diameter or less.

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5.2 Preparation and Assembly of Apparatus. All valves, fittings, hose, manifold blocks, mixing cylinders, and gauges must be cleaned with trichloroethane prior to assembling the gas system. After washing with this solvent and drying, all parts shall be assembled using teflon tape.

5.3 Gas Requirements.

5.3.1 Contaminant Gases. Following gases and chemicals are required for instrument calibration and must be at least 98.5% pure.

5.3.1.1 Methane.

5.3.1.2 Carbon Dioxide.

5.3.1.3 Nitrous Oxide

5.3.1.4 Ethylene.

5.3.1.5 Various Halogenated Refrigerants.

5.3.1.6 Ethane.

5.3.1.7 Acetylene.

5.3.1.8 Various Halogenated Solvents.

5.3.2 Dilution Gases. Following gases are required for instrument calibration and must meet the purity requirements of a zero grade gas.

5.3.2.1 Oxygen.

5.3.2.2 Nitrogen.

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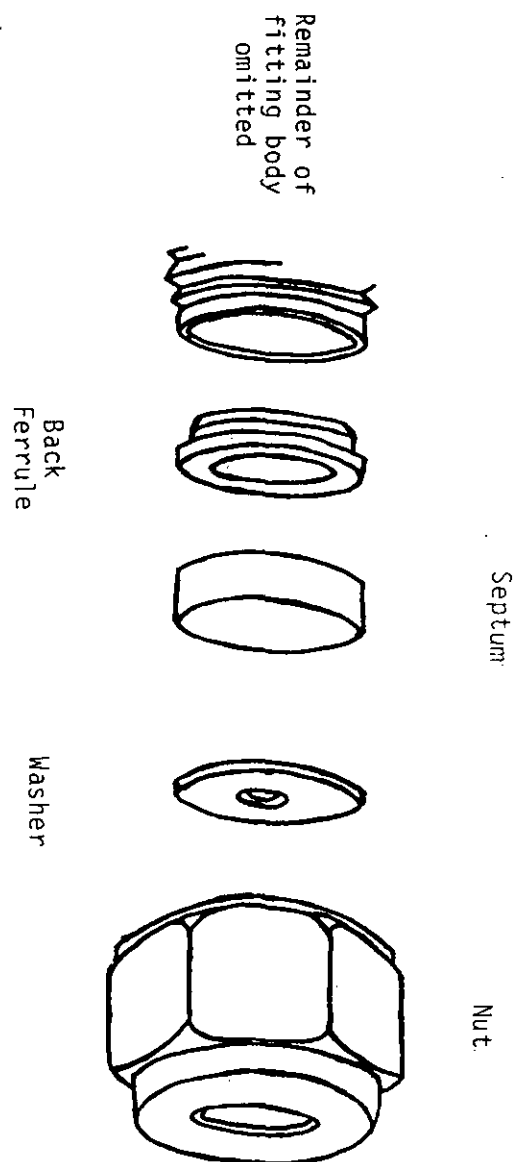


FIGURE 0. Septum Device.

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Where V_1 = Volume recorded by wet test meter in liters

P_b = Barometric pressure in mm Hg corrected for temperature and altitude

P_w = Vapor pressure of water in mm Hg

P_1 = Initial Pressure

P_2 = Final Pressure

K = 0.01934 psi/mm Hg

5.5.3 Purging of Gas System.

- a. Evacuate entire gas system. 1/
- b. Pressurize mixing cylinder to approximately 400 psig with dilution gas. Pressurize gas cell to 135 psig with gas from mixing cylinder. Let stand for 5 to 10 minutes. 2/
- c. Vent and evacuate entire system.
- d. Pressurize mixing cylinder to approximately 400 psig with dilution gas. Pressurize gas cell to 135 psig with gas from mixing cylinder.
- e. Run IR scan. If there is no observable absorbance, blank values are zero. Proceed to 5.5.5.
- f. If there is observable absorbance repeat procedure "c" and "d" above.
- g. Run IR scan. If absorbance is observed again repeat procedure "c" and "d" until IR scans show no absorbance or the absorbance remains constant. Retain final scan for blank determination (5.5.4).

1/ The effectiveness of purging is enhanced by evacuating the system to low pressures. Evacuating to higher pressures may increase the number of purge cycles required. No maximum pressure of evacuation is specified because the final criteria of no observed or constant absorbance determines when purging is complete.

2/ Pressurization of system may cause high boiling impurities to condense on interior surfaces. Five to ten minutes should be sufficient time to allow these impurities to vaporize and thereby be detectable. This stand time should be followed whenever the gas cell is pressurized.

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h. Vent gas cell to 50 psig. Run IR scan and save for blank determination(5.5.4).

5.5.4 Determination of Blank Values. Reproducible absorbance indicates either the presence of contaminants in the dilution gas or inherent characteristics of the instrument (see also 4.3). These measurable absorbances must be included as blank values when determining absorbance values for the calibration curves. Using the wavelengths or wavenumbers of typical contaminants listed in Table II, evaluate the spectra saved from 5.5.3. Record these absorbance values for use in preparing the calibration curves.

5.5.5 Addition of Contaminant Gas; Dilution; Scanning. Known quantities of contaminant gas shall be transferred to the mixing cylinder by use of a gas chromatograph (GC) gas sampling valve or by use of a syringe and septum device.

5.5.5.1 GC Gas Sampling Valve Method. Assemble GC valve and lecture bottle of contaminant gas into gas system as shown in figure 2. Evacuate gas cell, mixing cylinder, manifold, and hoses back to dilution gas cylinder valve. Cut off pump, close all valves and start contaminant gas flowing through gas sample valve loop and out to the atmosphere. Start dilution gas flowing and immediately turn handle on gas sampling valve so that the standard sample loop is coupled to the dilution gas stream. Turn off the flow from the lecture bottle and pressurize the mixing cylinder and manifold to a predetermined pressure with dilution gas. This pressure shall be as described in 5.5.5.2.m. Pressurize the cell with gas from the mixing cylinder. Check instrument zero and scan through the absorption band of interest for the contaminant gas in the cell. Vent gas cell to 50 psig and rescans. Dilutions are made by repressurizing with dilution gas after venting operation. Calculate concentration of standard in accordance with paragraph 5.5.5.3.

5.5.5.2 Syringe and Septum Method. Assemble two septum devices. See 5.1.15. One septum device shall be placed in the gas system as shown in figure 2. The other shall be fitted to the lecture bottle of contaminant gas via a regulator.

- a. Evacuate mixing cylinder, manifold, and septum device.
- b. Insert syringe of appropriate volume into septum connected to lecture bottle.
- c. Adjust pressure regulator of lecture bottle so that pressure is sufficient to move the plunger out of the syringe barrel.
- d. Remove plunger to allow purging of the septum device and regulator. Purging will be aided if the lecture bottle valve is turned off, and the pressure to the regulator and septum device is allowed to

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