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MONITORING NITROGEN PURITY BY GAS CHROMATOGRAPHY

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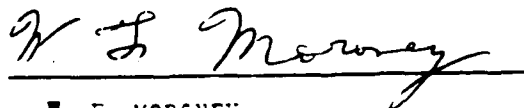
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A method had to be devised to check the purity of nitrogen to determine compliance with military specification BB-N-411C. A gas chromatographic technique using Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD) was developed for routine monitoring of nitrogen. An easy to follow step-by-step instruction is provided to analyze contaminants (parts per million) and to determine purity of nitrogen (percent by volume).					
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NADC-88136-60

CONTENTS

	Page
FIGURES	iv
TABLES	iv
ACKNOWLEDGEMENT	v
INTRODUCTION	1
PROPERTIES OF NITROGEN	1
EXPERIMENTAL PROCEDURE	2
EQUIPMENT	2
GASES	2
INSTRUMENT SET-UP PARAMETERS	5
TCD OPERATING PROCEDURE	5
FID IGNITING PROCEDURE	6
INTEGRATOR OPERATING PROCEDURE	7
GENERAL OPERATING PROCEDURE	8
SHUT-OFF PROCEDURE FOR DAILY USE OF THE GAS CHROMATOGRAPH	9
RESULTS	9

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NADC-88136-60

FIGURES

Figure		Page
1	GAS Chromatographic System for Analyzing Nitrogen Gas	3
2	TCD Analysis of Nitrogen Gas (Standard)	10
3	FID Analysis of Nitrogen Gas (Standard)	11

TABLES

Table		Page
1	Gas Flow Rates	4
2	Nitrogen Type II	4
3	Gas Chromatographic Analysis of Nitrogen	12

NADC-88136-60

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NADC-88136-60

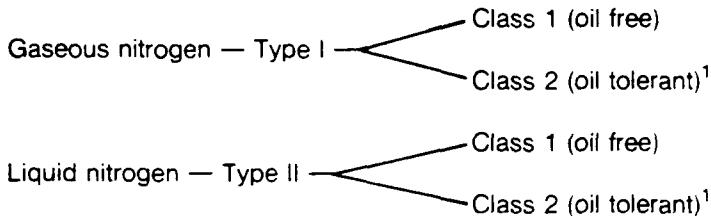
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INTRODUCTION

Liquid nitrogen is used for purging aircraft converters, pressurizing aircraft struts and purging, and pressurizing rocket engine propellant systems. It is also used as a cooling agent in low temperature processes and as an agent to shield against heat effects on temperature-critical apparatus. Liquid nitrogen is a source of gaseous nitrogen which is specifically intended for purging missile systems equipment.

According to military specification BB-N-411C, nitrogen (technical) is categorized into various types, grades, and classes. The classification depends on the physical state of nitrogen, its purity (percent by volume), and the amount of oxygen and other contaminants such as carbon monoxide, carbon dioxide and hydrocarbons present in it.



Liquid nitrogen is oil free, but contamination could be caused by contact with contaminated equipment or by improper container handling methods during transfer. Each type of nitrogen is required to meet certain performance criteria. The manufacturer/supplier is responsible for the performance of all inspection requirements specified as follows:

PROPERTIES OF NITROGEN

REQUIREMENTS

	Type II			Type I
	Grade A	Grade B		Grade C
Purity (minimum percent by volume) ²	99.95	99.50		99.50
Oxygen (maximum percent by volume)	0.05	0.50		0.50
Moisture (maximum 23ppm)	20ppm	20ppm		no limit characterized
Odor	none	none		none
Total hydrocarbons as methane	<50ppm	<50ppm		<50ppm

1. No tolerance value is available.
2. Purity is the percent nitrogen and trace quantities of argon, neon and helium.

Such inspections are deemed necessary to assure supplies and services conform to the prescribed requirements.

It became necessary to analyze nitrogen samples in-house due to a conflict between manufacturer and the inspector, which resulted in refusal to ship supplies to the Naval Air Development Center. Therefore, a method was developed to provide a rapid routine analysis of contaminants and to determine the purity of nitrogen delivered to the Naval Air Development Center. There are no specific details available in the literature or in the military specifications for the contaminant limits (carbon monoxide, carbon dioxide etc.) in nitrogen. Therefore, a limit was set for these contaminants based on military specifications BB-N-411C and aviator's breathing oxygen MIL-O-27210-E

EXPERIMENTAL PROCEDURE

EQUIPMENT

1. Gas chromatograph equipped with a:
 - a) Thermal Conductivity Detector (TCD)
 - b) Flame Ionization Detector (FID)
 - c) Gas sampling valve
 - d) 12' x 1/8" molecular sieve 5A column for TCD
 - e) 6' x 1/8" carbosieve S column for FID analysis
2. A strip chart recorder or an integrator.
3. Two-stage gas regulators for air, hydrogen, helium and nitrogen gases.
4. Flow meters with a glass, teflon, steel ball or flow check gauge

Figure 1 shows the gas chromatographic system used in the present studies. It includes two GOW-MAC GC, a 550 IUP and a 750 FID interfaced with a Spectraphysics SP 4290 integrator.

GASES

High purity gases are required, especially when a flame ionization detector is used for the analysis. Table 1 provides detailed information on gases used for the nitrogen analysis. Two nitrogen standards required for contamination and purity analysis were provided by the Matheson Gas Co. The maximum tolerance limits for each component were set according to military specifications BB-N-411C and MIL-O-27210-E. These set values are presented in Table 2.



Figure 1. Gas Chromatographic System for Analyzing Nitrogen Gas

NADC-88136-60

TABLE 1. Gas Flow Rates

Gas name	Pressure,psig	Flow rate, mL/min.
Hydrogen	30	30 for FID ignition 25-30 during operation
Helium	40	30
Air	50	400 for FID
	60	to activate the valves
Nitrogen	<5	40

TABLE 2. Nitrogen Type II

Components	Grade A		Grade B	
	Conc. required mg/L	Manufact. anal. value mg/L	Conc. required mg/L	Manufact. anal. value mg/L
Carbon monoxide	10.0	10.5	10.0	10.0
Carbon dioxide	10.0	10.5	20.0	20.0
Methane	50.0	53.0	50.0	54.0
Oxygen*	450.0	449.0	4500.0	4700.0
Nitrogen	Balance	Balance	Balance	Balance

* Specification requirements are 500 and 5000 mg/L for grade A and B respectively.

NADC-88136-60

INSTRUMENT SET-UP PARAMETERS

1. Thermal Conductivity Detector (TCD) settings:

Column	Molecular sieve 5A
Column temperature	50°C
Injection port temperature	80°C
Detector Temperature	100°C
Current	150 mA
Sample size	1 mL
Instrument warm-up	15 minutes
Gases	Helium, air and nitrogen (purge and standards)

2. Flame Ionization Detector (FID) settings:

Column	Carbosieve S
Column temperature	85°C
Injector temperature	155°C
Detector temperature	300°C
Sample size	2 mL
Instrument warm-up	35-40 minutes
Gases	Helium, hydrogen, air and nitrogen (purge & standards)

TCD OPERATING PROCEDURE

1. Turn carrier gas (helium) ON and adjust flow rate approximately at 30 ml/min.
2. Turn air ON to activate valves.
3. Turn GC power ON and make sure that detector is off.
4. Check carrier flow rate at the exit ports of the two detectors. It should be 30 mL/min, if not, indication is that there is a leakage in the system.

NADC-88136-60

5. Set all the parameters according to the previously mentioned TCD settings. Press ABORT to actuate the set conditions (this option may not be available in every GC or it may be called by a different name).
6. Set GC (GOW-MAC) settings as follows:
 - a. switch Auto/Manual to Manual,
 - b. switch Hold/Advance to Advance.
 - c. switch Fan heater ON,
 - d. set polarity at negative.
7. Turn detector ON.
8. Purge nitrogen for 10 minutes at the rate of 40 mL/min.
9. Press RUN on GC, and immediately START the recorder or integrator.
10. A normal chromatogram will have two peaks one for oxygen and another for nitrogen as shown in Figure 2. If the baseline is noisy, adjust it by turning the Zero knob in clockwise (pen moves to left) or counterclockwise (pen moves to right) direction.
11. A chromatogram with more than two peaks indicates contamination of column. Purge for 5-10 minutes and then make next run. If contamination persists, change the column. Usually, if the instrument is not in use or in standby condition without carrier gas flowing through, purge the system for another 10 minutes. Make several runs with the purge nitrogen until no more contamination can be detected.

FID IGNITING PROCEDURE

1. Open air and hydrogen gas tank valves and adjust flow rates:

air at 400 mL/min.

hydrogen at 30 mL/min.

helium at 30 mL/min.

The combined hydrogen and helium flow rates should not exceed 60-70 mL/min.
2. Allow air and hydrogen to flow for 1 minute and then ignite the flame. Press ignition and hold for 10 seconds. A slight "pop" indicates ignition. Place a watch glass or a shiny stainless steel plate against the FID exhaust port, if condensation appears, the flame is lit.
3. If, no ignition takes place after 2 or 3 trials, check all the gas flows. Turn hydrogen OFF for 10-15 minutes, reduce air flow rate to 300 mL/min and carrier flow rate at 25 mL/min. Turn hydrogen ON and ignite. After ignition, readjust the flow rates for operation as follows.

NADC-88136-60

air 400 mL/min.

hydrogen 25-30 mL/min.

helium 30 mL/min.

4. Recorder baseline will drift until all temperatures and flows are stabilized. Lack of noise will indicate a "flame-out".
5. Purity of all the gases will have an effect on baseline drift and noise.
6. Excess hydrogen flow will result in noise.
7. Precautions:
 - a) Insufficient air flow is dangerous and can cause explosion.
 - b) Do not leave hydrogen ON for more than 3 minutes without ignition.
 - c) Do not allow hydrogen to accumulate in detector, because on ignition it can explode.
 - d) Turn hydrogen OFF for 10-15 minutes in case of hydrogen/air flow ignition failure.

INTEGRATOR OPERATING PROCEDURE

SP4290 Integrator

Parameters for FID and TCD detectors

<u>Parameter</u>	<u>FID</u>	<u>TCD</u>
Run Time (min)	18	7
Attenuation	2	1
Chart Speed (cm/min)	0.25	0.50

To set run time:

1. Press "DIALOG"
2. In time function section enter run time desired for TT = prompt, enter "E" "R" for TF = prompt and enter "I" on TV= prompt.

Note: To change a run time that has already been entered you must delete the previous dialog.

To activate peak markers:

1. Press "TFN" "P" "M" "ENTER" "1" "ENTER"

NADC-88136-60

To zero base line:

1. Press "LEVEL", a value of 1000 ± 2 is obtained.
2. Adjust zero control on GC and then press "level" until a value of 10000 ± 2 indicates a zero baseline.
3. Press "ENTER"
4. Press "ZERO"

To set attenuation:

1. Press "ATTEN"
2. Enter the value
3. Press "ENTER"

To set chart speed:

1. Press "CHT SP"
2. Enter the value
3. Press "ENTER"
4. Press "ZERO"

GENERAL OPERATING PROCEDURE

1. Turn carrier gas (helium) ON flow rate at 30 mL/min at 40 psig.
2. Turn power ON to the gas chromatograph (GC).
3. Turn gases ON and adjust flow rates for TCD and FID operations accordingly.
4. Turn FID and TCD detectors ON only after the selected temperature values for column and injection ports are achieved.
5. Turn recorder/integrator ON.
6. Purge the gas chromatograph with nitrogen for 10 minutes.
7. Make a GC run with the purged nitrogen to check the baseline and performance of the chromatograph.
8. A chromatograph obtained for purged nitrogen on TCD indicates two peaks. The first peak is for oxygen and the second one is for nitrogen.
9. A chromatogram obtained on FID for the high purity purged gas indicates two peaks for oxygen and carbon dioxide.

NADC-88136-60

10. The gas chromatograph is now ready for the standard and the sample analysis. Follow the analysis procedures for TCD and FID analyses as described for the purge nitrogen. Make at least 3 runs for each sample standard.
11. A gas chromatogram obtained for the standard nitrogen by TCD will have two peaks (See Figure 2).
12. A gas chromatogram obtained for the standard nitrogen by FID will have 5 peaks as shown in Figure 3. The components will elute in this order: moisture, oxygen, carbon monoxide, methane and carbon dioxide.

SHUT-OFF PROCEDURE FOR DAILY USE OF THE GAS CHROMATOGRAPH

1. Turn detectors OFF (TCD or FID).
2. Turn hydrogen and air gases OFF.
3. Turn column and injection port heating OFF or leave it at room temperature settings.
4. Reduce helium flow to a minimum to prevent column contamination and waste of the gases.

RESULTS

The peaks obtained were sufficiently sharp for the determination of oxygen, carbon monoxide and hydrocarbons. Therefore, the peak height was used in lieu of peak area. A direct comparison was made between the peak height or peak area of the sample chromatogram and that of a standard containing a known concentration of contaminants. Both the sample and the standard were analyzed under identical experimental conditions. The percent amount of oxygen in a sample was calculated from the equation.

$$\text{Percent volume O}_2 = \frac{\text{Peak height of O}_2 \text{ in sample}}{\text{Peak height of O}_2 \text{ in standard}} \times \text{Percent volume O}_2 \text{ (in standard)}$$

The amount of other contaminants were calculated by simply substituting the percent values with the parts per million (ppm) values (from the standard) in the above equation. If peak area has to be used, a graph of integration units versus concentration can be plotted for a standard and then the concentration of an unknown can be obtained from this calibration curve.

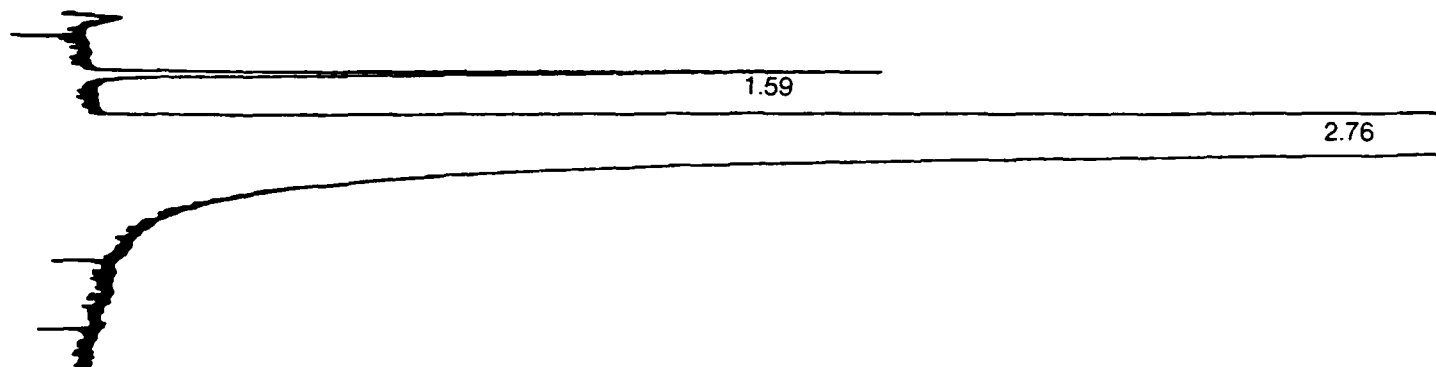
Nitrogen samples obtained from the fuel farm were analyzed using TCD and FID methods. Results obtained are shown in Table 3. Only a small amounts of contamination of carbon dioxide was found in most of the samples during the ten months period of routine monitoring.

Figures 2 and 3 show standard nitrogen analysis chromatograms obtained by TCD and FID methods.

Best results were obtained when a standard nitrogen was analyzed each day before testing the sample. Since it is not possible to produce identical experimental conditions such as temperature, flow rate etc. every time the analysis is performed, the retention time (RT) for each elute may vary slightly. So long as the RT values are consistent, results will be reproducible.

NADC-88136-60

CHANNEL A INJECT 12/12/85 10:42:18



FILE 1.	METHOD 0.	RUN 23	INDEX 23
PEAK#	AREA%	RT	AREA BC
1	0.006	0.12	617 01
2	0.048	1.59	4557 01
3	99.946	2.76	9575621 01
TOTAL	100.		9580795

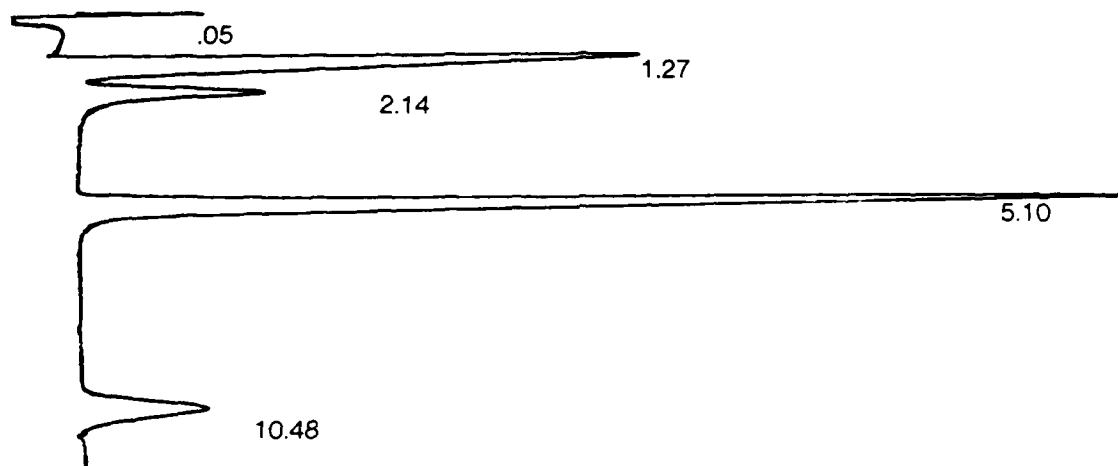
Figure 2. TCD Analysis of Nitrogen Gas (Standard).

NADC-88136-60

PLOT "B" AUTO

998

CHANNEL B INJECT 12/12/85 10:06:37



12/12/85 10:06:37 CH= "B" PS= 1.

FILE 1.	METHOD 0.	RUN 8	INDEX 8
PEAK#	AREA%	RT	AREA BC
1	1.367	0.05	691. 01
2	31.733	1.27	16040. 02
3	9.306	2.14	4704. 03
4	47.885	5.1	24204. 01
5	9.708	10.48	4907. 01
TOTAL	100.		50546

Figure 3. FID Analysis of Nitrogen Gas (Standard).

NADC-88136-60

TABLE 3. Gas Chromatographic Analysis of Nitrogen

500 Gallon Sample Numbers	TCD Method		FID	
	Nitrogen,%	Oxygen,%	Oxygen%	Carbon dioxide, ppm
1.	99.95	0.040	0.038	7.65
2.	99.96	0.041	0.042	8.81
3.	99.96	0.036	0.036	8.65
4.	99.96	0.042	0.040	7.89
5.	99.58	0.440	0.460	15.21
6.	99.58	0.441	0.453	15.77
7.	99.56	0.444	0.463	17.67
8.	99.59	0.393	0.390	19.58
9.	99.95	0.038	0.036	7.52
10.	99.58	0.440	0.461	15.31

This method provides step-by-step instructions to non-technical personnel to perform the simultaneous analysis of nitrogen for purity and contamination.