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Analysis for Impurities in Helium Using the Helium Ionization Detector

By Charles A. Seitz



UNITED STATES DEPARTMENT OF THE INTERIOR



Report of Investigations 8941

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT			
°C	degree Celsius	MΩ	megohm
cm ³	cubic centimeter	mV	millivolt
cm ³ /min	cubic centimeter per minute	nA	nanoampere
ft	foot	pct	percent
in	inch	ppb	part per billion (by volume)
h	hour	ppm	part per million (by volume)
kΩ	kilohm	s	second
mCi	millicurie	V	volt
μF	microfarad	vol pct	volume percent
min	minute		
mm	millimeter		

ANALYSIS FOR IMPURITIES IN HELIUM USING THE HELIUM IONIZATION DETECTOR

By Charles A. Seitz¹

ABSTRACT

This Bureau of Mines report describes a chromatographic method for analyzing impurities in helium that utilizes a helium carrier gas containing 25 to 30 ppm Ne. An example of the effect of trace amounts of nitrogen, methane, and moisture on the detector's response is shown. The added neon in the carrier does away with irregularities of the analysis which were experienced when the carrier contained up to 3 ppm Ne. The addition of 25 to 30 ppm Ne causes a loss of sensitivity, but the remaining sensitivity is adequate for routine analyses. The high-neon carrier allows positive and more linear responses for eight impurities: neon, hydrogen, argon, oxygen, nitrogen, methane, carbon dioxide, and ethane. Neon concentration levels of 0.02 to 125 ppm in helium carrier gases were studied. The high-neon carrier has been in successful routine use in Bureau of Mines helium facilities since October 1981.

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INTRODUCTION

The purpose of this Bureau of Mines report is to publicize the use of a carrier gas containing 25 to 30 ppm Ne in a helium ionization detector (HID) (250-mCi-tritium activated detector) for gas chromatography. The high-neon carrier gas results in a positive and more linear analyzer response for each component normally found in Grade-A helium.² A positive peak response occurs when the detector cell is more conductive due to the presence of an impurity in the sample than for the background alone.

The sensitivity of HID's has been observed to be greatest when the carrier gas was purest. Seitz, Bodine, and Klingman (1)³ reported extreme sensitivity for an HID analyzer when using a special purifier to reduce impurities in the carrier gas to less than 2 ppb. The minimum detectable limit (MDL) for the analyzer was about 2 ppb each for neon, hydrogen, argon, and methane. Such extreme sensitivity, however, is not needed in routine analyses. They also reported total loss of the oxygen peak analytical capabilities due to chemisorption because of the high activity of the molecular sieve column when using carrier gas of that purity.

A commercial chromatograph with a so-called ion cross section detector was modified in 1969 to analyze for impurities in Grade-A helium; the name implies that the mechanism depends on the ionization cross section of each gas molecule. Others call this a helium ionization detector, paralleling a name given a similar detector described by Lovelock (2) as an argon ionization detector, where argon is used as the carrier to analyze for hydrocarbons. Several theories have been presented in the literature as to the mechanism of detector operation; none seem to fully explain anomalies observed.

²Grade-A helium means the grade of helium produced at the Bureau of Mines helium plants and is 99.9950 vol pct He.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

From 1969 to the present, it was assumed a pure helium carrier gas was needed to provide maximum sensitivity. The helium carrier gas normally contained less than 5 ppm total impurities; the major impurities were neon and moisture. The neon concentration varied between 0 and 3 ppm, which caused much of the variation in output of the HID analyzers. The output would swing from a negative to a positive peak, apparently without reason. Since a shift in peak polarity was observed, a point of zero sensitivity was also inferred, especially for hydrogen, argon, and nitrogen.

When the neon content of the carrier gas is less than 2 ppm, high sensitivities for impurities in the sample are observed. The 5-ppm N₂ sensitivity is reduced to essentially zero when the neon content of the carrier gas approaches 3 ppm.

The Bureau of Mines uses nine HID chromatographs in different phases of analysis and quality control; all except one are set up to use the "high neon" in helium carrier described in this study. The one exception is a chromatograph used to analyze for neon content at less than 1 ppm after a neon removal system. A low total impurity in helium carrier gas is used in this case. The anomalies above led to the study described in this paper, showing the characteristics of the responses to impurities normally found in a helium production facility.

Andrawes, Byers, and Gibson (3) described the addition of microscopic volumes of gaseous impurities to a helium carrier by a permeation tube technique to achieve a minimum background current. No concentration level of addition was given. The gases considered for addition were H₂, Ar, O₂, and N₂. When these components are added individually at an unknown concentration, that component is eliminated from the analytical scheme at the uncertain level of addition.

Bros and Lasa (4) described shifts in detector outputs as components were added to helium carrier gas. Their main study was made using a carrier gas spiked with

35 ppm H₂, and no mention was made of the neon content of any helium carrier gases or in any of the samples.

The method described in this report utilizes a carrier gas containing 25 to 30 ppm Ne. This "high neon" in helium is prepared by blending neon into the helium using a partial-pressure method in our laboratory. Each prepared carrier gas is then analyzed using a liquid helium

freezeout technique followed by mass spectrometer analysis (5). Typical minimum detectable limits (MDL) are less than 0.2 ppm for the normal impurities found in Grade-A helium except for neon. The MDL for neon is 1 ppm.

The effects on the sensitivities of neon, oxygen, nitrogen, and carbon dioxide due to minor amounts of moisture, nitrogen, and methane are also shown.

DESCRIPTION OF CHROMATOGRAPH

Each ionization chromatograph has special characteristics, but certain general statements or guidelines can be given that apply to acceptable operation when analyzed for eight impurities--neon, hydrogen, oxygen, argon, nitrogen, methane, and carbon dioxide--in helium. These conditions are--

1. Oven temperature is at 50° C.
2. A carrier gas is used with neon content of 25 to 30 ppm.
3. The column system uses a molecular sieve, a Porapak⁴ column, and two sample valves.
4. Special purge techniques are used when changing the carrier gas.
5. Precise column activation is used.
6. The detector cell is jacketed, and the jacket is constantly purged with discharge carrier gas from the detector.
7. The cell voltage is between 270 to 325 V when the detector cell electrodes are spaced about 1 mm apart, are 8 mm in OD, and contain 250 mCi tritium.
8. The pressure regulator diaphragms are purged free of air to prevent air permeation, or stainless steel diaphragms are used.

CARRIER PURGE

The following procedure is used to change the carrier gas cylinder without contaminating the chromatographic system. Valve B (fig. 1) is closed, the cylinder

valve is closed, and valve A is opened. The cylinder gas regulator is then moved to the new carrier gas cylinder, and the adapter is tightened. The cylinder valve is opened momentarily and closed until the low-pressure gage of the regulator has returned to near zero (gas vents through opened valve A), and then the cylinder valve is again opened and closed. This cycle is repeated not less than 10 times to ensure that the dead-end voids of the regulator and bourdon tubes of the gages have been pressure-purged free of air. The cylinder valve is then opened, valve A is closed, and valve B is opened. Carrier gas is supplied to the chromatograph during the purging time from the helium remaining in the two 500-cm³ surge tanks from the previous cylinder of carrier gas.

The regulator can be of the type having a permeable diaphragm that is jacketed and constantly purged by a stream of discharge carrier gas as shown in figure 1, or a stainless steel diaphragm can be used, requiring no purge.

COLUMN ACTIVATION

Column 1 contains 40/60-mesh molecular sieve 5A in a 15-ft-long stainless steel tube, 1/8 in in OD with a 0.020-in wall. For activation, this column is heated to 300° C for at least 3 h while using a helium flow. It is not unusual to observe liquid water and steam being driven off during activation. A "pigtail" tube is attached to the vent end of the column during activation to avoid back diffusion

⁴References to specific products does not imply endorsement by the Bureau of Mines.

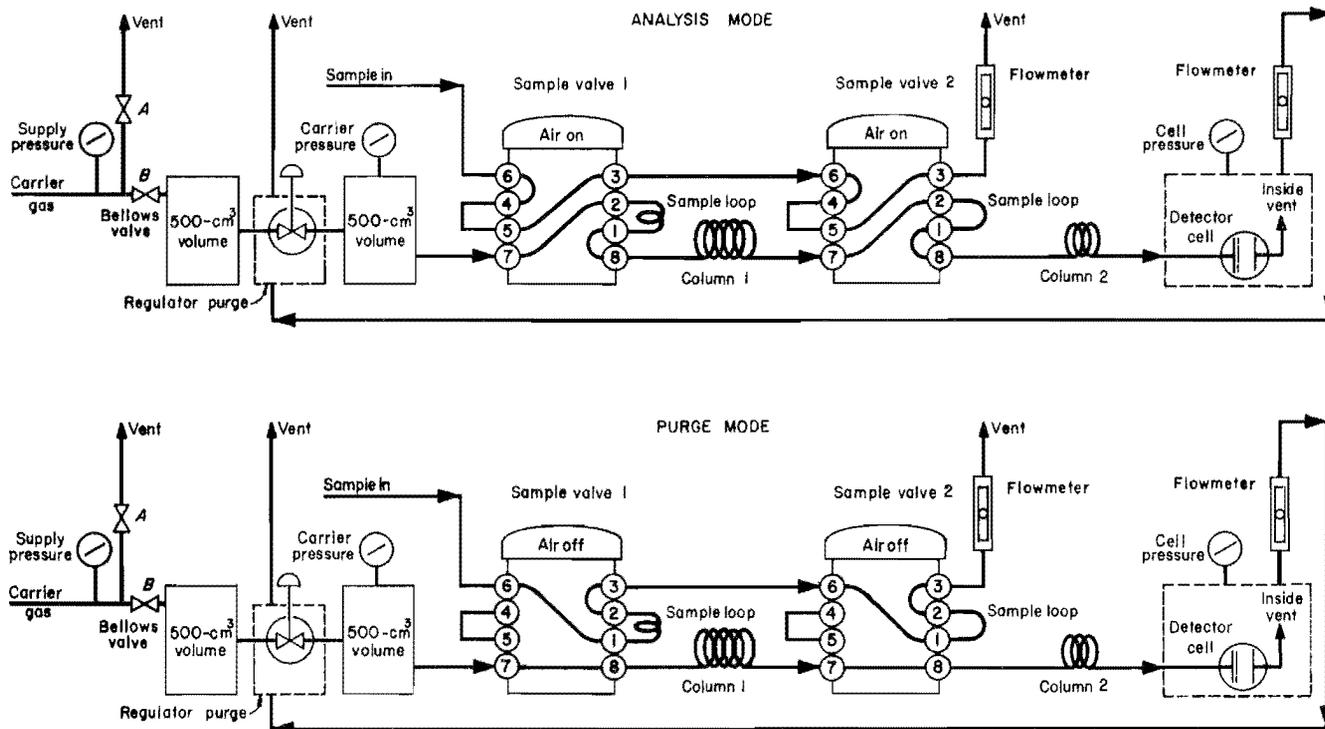


FIGURE 1. - Flow diagram of the chromatograph.

of air into the column and provide for flow measurement while allowing the entire column length to be in the activation oven. This column should be activated by using a flow of helium ($40 \text{ cm}^3/\text{min}$ at 300°C for 3 h) in the reverse direction to normal analytical use. This will ensure a longer column life in case some unknown contaminant was present that had only progressed a short distance into the column. When the column is heated overnight at 300°C , the separation of oxygen and argon can be made in addition to the normal use. The ability of the column to completely separate these two impurities will last approximately 3 to 5 weeks. Argon appears just before oxygen.

Column 2 contains 80/100-mesh Porapak T in a 3-ft-long stainless steel tube, 1/8 in in OD with a 0.020-in wall. For activation, this column is heated to 180°C for at least 2 h with reverse flow of helium at $40 \text{ cm}^3/\text{min}$.

ANALYSIS PROCEDURE AND COLUMN ARRANGEMENT

Two standard O-ring-type linear sample valves are used for the sampling system as shown in figure 1. Sample valve 1 provides the injection of a 1-cm^3 sample

into column 1 to analyze for neon, hydrogen, argon and/or oxygen, nitrogen, and methane. The sample flows through valve 2 as if it were a carrier, through column 2, and to the detector. The gas flowing from the detector is first used as a shield for the detector, then goes through a flowmeter into the atmospheric side of the regulator diaphragm, and is then vented.

The purpose of sample valve 2 is to provide a 0.2-cm^3 sample directly to column 2 to analyze for CO_2 . This is necessary because column 1 will not pass CO_2 . If the sample is wet, then the moisture will eventually exit column 2 (Porapak T) and cause interference with the next sample. Both sample valves can be operated simultaneously, and the order of components eluting from column 2 would appear as a composite of all components except CO_2 , then CO_2 , followed by the effluent from column 1 in the order of neon, hydrogen, argon and/or oxygen, nitrogen, and methane. Other components that would normally pass through Porapak would show up in the analysis at some point. The operator has the choice of using one or both valves at a time for component identification.

The porting of the linear O-ring valves is such that the carrier gas stream through the center portion of the valve is protected from air by the flow of the sample on each end of the valve porting, which allows the sample loop purging.

Permeation through the O-rings of these valves can be seen as a baseline shift when using a sample such as pure hydrogen, nitrogen, methane, or other than helium. The main reason for using this valve is its long service life at 50° C.

DETECTOR CIRCUIT

Figure 2 shows the detector circuit including the detector and an electrometer which uses three operational amplifiers. Each amplifier is set to a gain of 1. Operational amplifiers A and B are enclosed in a 16-pin 8043 integrated circuit plug-in and are used in the noninverting mode. The input to amplifiers A and B is protected from overvoltage with

diodes. The diodes FJT 1100 were chosen because of their low leakage current for the signal input from the detector.

Operational amplifier C is one section of an OP-07 which takes the difference of amplifiers A and B; the output is then used to drive an attenuator-recorder system. The output of amplifier C is diode (IN911) protected from any high-voltage spikes that could be picked up on the output line.

The method of zeroing uses the same voltage source as is supplied to the detector system to minimize any effect of minor voltage fluctuations of the B⁺ supply.

The signal to the electrometer system is developed across the 500-M Ω resistor by the current passed through the detector by the gas within the cell. The gas in the cell is activated and partially ionized by beta emission from radioactive hydrogen (tritium).

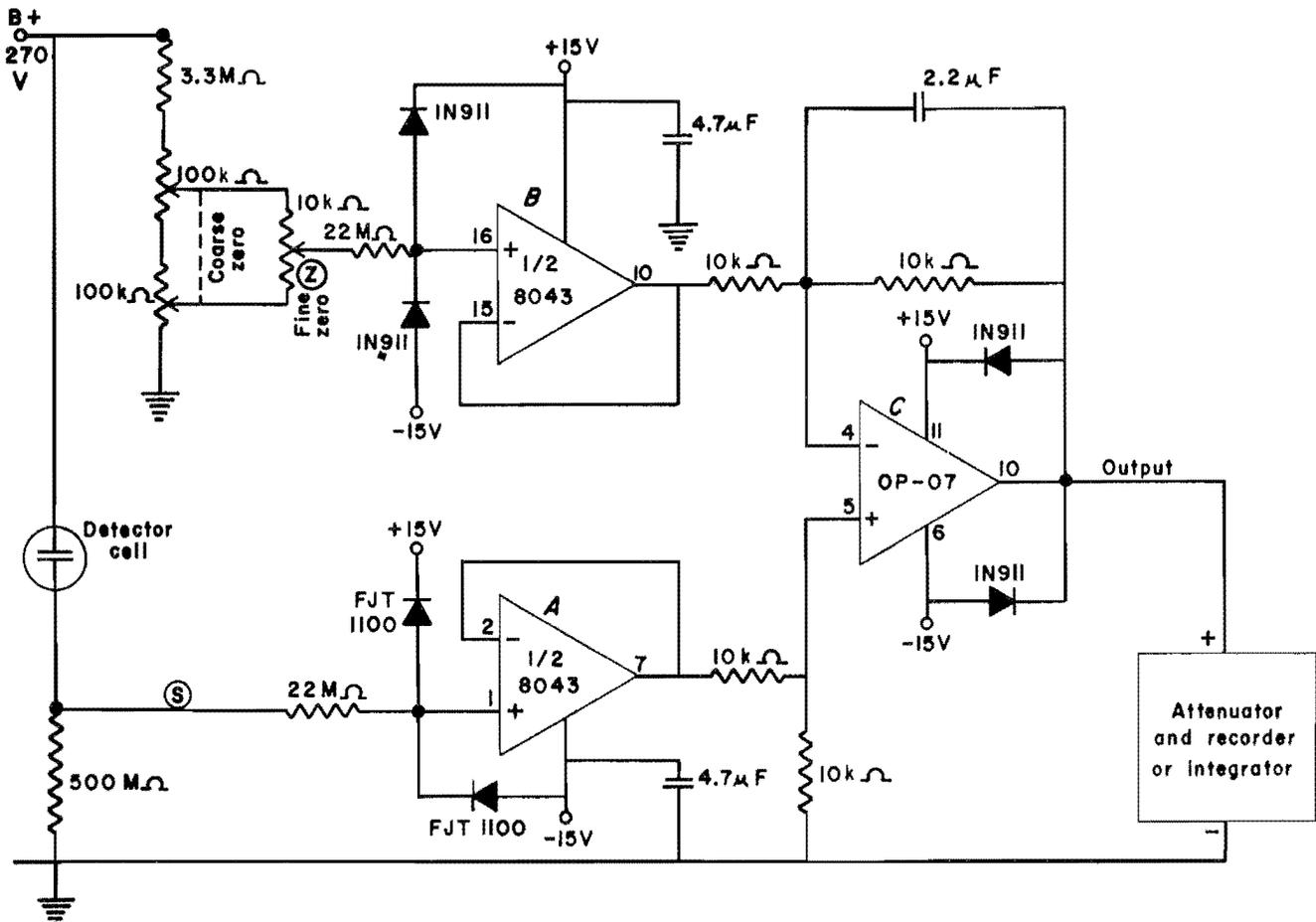


FIGURE 2. - Electrometer and detector system.

TABLE 3. - Results for sample 1 with various carrier gases, peak heights in divisions¹

Component and concentration	Neon concentration in helium carrier gas									
	0.02 ppm	1.2 ppm	2.0 ppm	3.3 ppm	7.1 ppm	10.4 ppm	27.4 ppm	32.5 ppm	59.8 ppm	125 ppm
32 ppm CO ₂ ...	48,000	49,000	48,500	49,000	45,000	45,000	40,000	36,000	31,000	25,000
37 ppm Ne....	-5,600	-4,900	-4,400	-4,000	-2,200	-1,700	-200	75	500	700
	3,400	3,400	3,100	3,200						
22 ppm H ₂	-9(8W)X200	-13(21W)X100	-10(21W)X100	-7(25W)X100	3,200	3,900	5,200	5,600	5,800	5,700
20 ppm O ₂	10,000	11,250	11,500	12,500	13,500	14,000	14,500	14,400	14,000	13,500
	760	900	975							
22 ppm N ₂	-19(19W)X20	-2(16W)X50	-5(19W)X50	1,250	2,150	2,400	2,900	3,000	2,900	3,900
27 ppm CH ₄ ...	15,000	16,000	16,750	16,000	13,750	14,000	12,000	11,400	9,000	6,700

¹Noise level approximately 15 divisions.

TABLE 4. - Results for sample 2 with various carrier gases, peak heights in divisions¹

Component and concentration	Neon concentration in helium carrier gas									
	0.02 ppm	1.2 ppm	2.0 ppm	3.3 ppm	7.1 ppm	10.4 ppm	27.4 ppm	32.5 ppm	59.8 ppm	125 ppm
10.9 ppm CO ₂ .	29,000	29,000	28,000	28,000	24,500	24,200	19,900	17,200	14,000	11,200
12.6 ppm Ne..	-3,400	-2,900	-2,400	-2,000	-650	-200	550	950	1,100	1,150
	1,800	1,400	1,200	380						
8.7 ppm H ₂ ..	18(F)X100	-13(1W)X100	-21(3W)X50	-14(5W)X20	800	1,300	2,200	2,250	2,300	2,350
	360	180	180							
7.6 ppm N ₂ ..	18(F)X20	-6(3W)X20	-2(7W)X20	300	820	950	1,110	1,180	1,050	1,100
9.4 ppm CH ₄ .	8,000	8,100	7,800	7,800	6,400	6,400	4,800	4,600	3,500	2,750

¹Noise level approximately 15 divisions.

TABLE 5. - Results for sample 3 with various carrier gases, peak heights in divisions¹

Component and concentration	Neon concentration in helium carrier gas									
	0.02 ppm	1.2 ppm	2.0 ppm	3.3 ppm	7.1 ppm	10.4 ppm	27.4 ppm	32.5 ppm	59.8 ppm	125 ppm
5.6 ppm CO ₂ ..	18,000	17,000	16,200	16,200	13,500	13,200	10,500	9,000	7,000	5,300
8.7 ppm Ne...	-2,600	-2,000	-1,625	-1,225	-120	310	1,300	1,260	1,350	1,200
4.8 ppm H ₂ ...	-1,700	-1,250	-1,025	-725	180	500	1,000	1,180	1,200	1,100
4.9 ppm N ₂ ...	-300	-5(1W)X20	-1(1W)X20	140	500	590	750	800	700	650
4.7 ppm CH ₄ ..	4,400	4,400	4,200	4,100	3,300	3,450	2,600	2,500	1,850	1,300

¹Noise level approximately 15 divisions.

The values shown in these tables are in divisions derived from the product of the peak height and the attenuator used for each peak; 1 division equals 0.05 mV or 0.0001 nA. The noise level was about 15 divisions.

When using the low-neon-content carrier gas, peaks for impurities in samples containing 5 ppm would result in a negative peak for neon, hydrogen, argon, and nitrogen. When the concentration of impurities increased to about 15 ppm, the initial portion of the peak would be negative, the high concentration portion of the peak would go to a positive output, and the trailing edge of the peak would be negative. This is termed a "foldover peak" or W-type peak."

The values in these tables shown as (e.g.) "-19(19W)X20" represent a W-type peak, as shown for nitrogen in figure 3, where the output first went negative 19 divisions (-19), next reversed direction for the higher concentration portion of the peak for 19 divisions (19W), and reversed at the apex to retrace the above for completion of the peak at an attenuator setting of 20 (X20). The positive portion is less sensitive than the negative part. Nitrogen gives all positive (no W) peaks for all carrier gases with neon concentrations above 3.3 ppm.

Hydrogen also undergoes a similar W-peak as seen in figure 3, and it responds with positive peaks for carriers above 7 ppm Ne.

Argon responds in the same manner as hydrogen and nitrogen with a positive response at 7 ppm Ne and above and a response of 4,800 divisions for 17 ppm when using a carrier helium with 27 ppm Ne.

Figure 3 shows the peaks for carbon dioxide at an attenuation of 1,000, neon negative at 200X, hydrogen a W-peak at 200X, oxygen positive at 500X, nitrogen a W-peak at 20X, and methane positive at 500X.

Figures 3-7 show the effect that a change in the carrier gas neon concentration has on the components of sample 1, and the peaks are shown tabulated in table 3. The nitrogen peak shown in figure 4 is mostly positive with a W-peak described as "-2(16W)X50."

A W-peak could be used in the calibration scheme by totaling the negative

portion and the center portion (positive going) to represent the peak height; in this case 18 divisions times 50 would equal 900 divisions. The use of the high-neon-content carrier gas eliminates the need for the W-peak consideration since all peaks are positive.

Figure 7 shows the chromatogram for sample 1 when the carrier gas contains 27.4 ppm Ne. The sample has a higher concentration of neon than the carrier, and its peak is negative. All other components show a positive response.

Figures 8-13 are used to show the type of peaks obtained for the components in sample gas 2 for varying neon concentrations in the carrier gases. The results of these chromatograms are shown in table 4.

Figures 14-19 show the type of peaks for sample gas 3 with varying neon content in the carrier gases; the summary results are shown in table 5. The loss in sensitivity for nitrogen with a carrier gas containing 2 ppm Ne is exemplified in figure 16, where the peak for 4.9 ppm is at the minimum detectable limit; this same nitrogen concentration in the sample gas yields a 750-division peak when the neon concentration in the carrier gas is 27.4 ppm, as shown in figure 19.

These chromatographic results show responses for a number of combinations of samples and carrier gas compositions. The responses shown are for values for samples of less than 40 ppm, but this chromatograph has been used to determine the concentration of nitrogen in helium to over 500 ppm.

MOISTURE EFFECT ON ONE SAMPLE

Any moisture in the sample that enters through sample valve 2 will pass through the Porapak column and will affect the detectors' response to other components. The normal operation of valve 2 is to allow only 2 s for injection of the sample to minimize the transfer of moisture within the sample loop into the Porapak column. Two experiments were made to illustrate the moisture effect. In both cases 27 ppm Ne in helium (carrier 7) was used as the carrier gas.

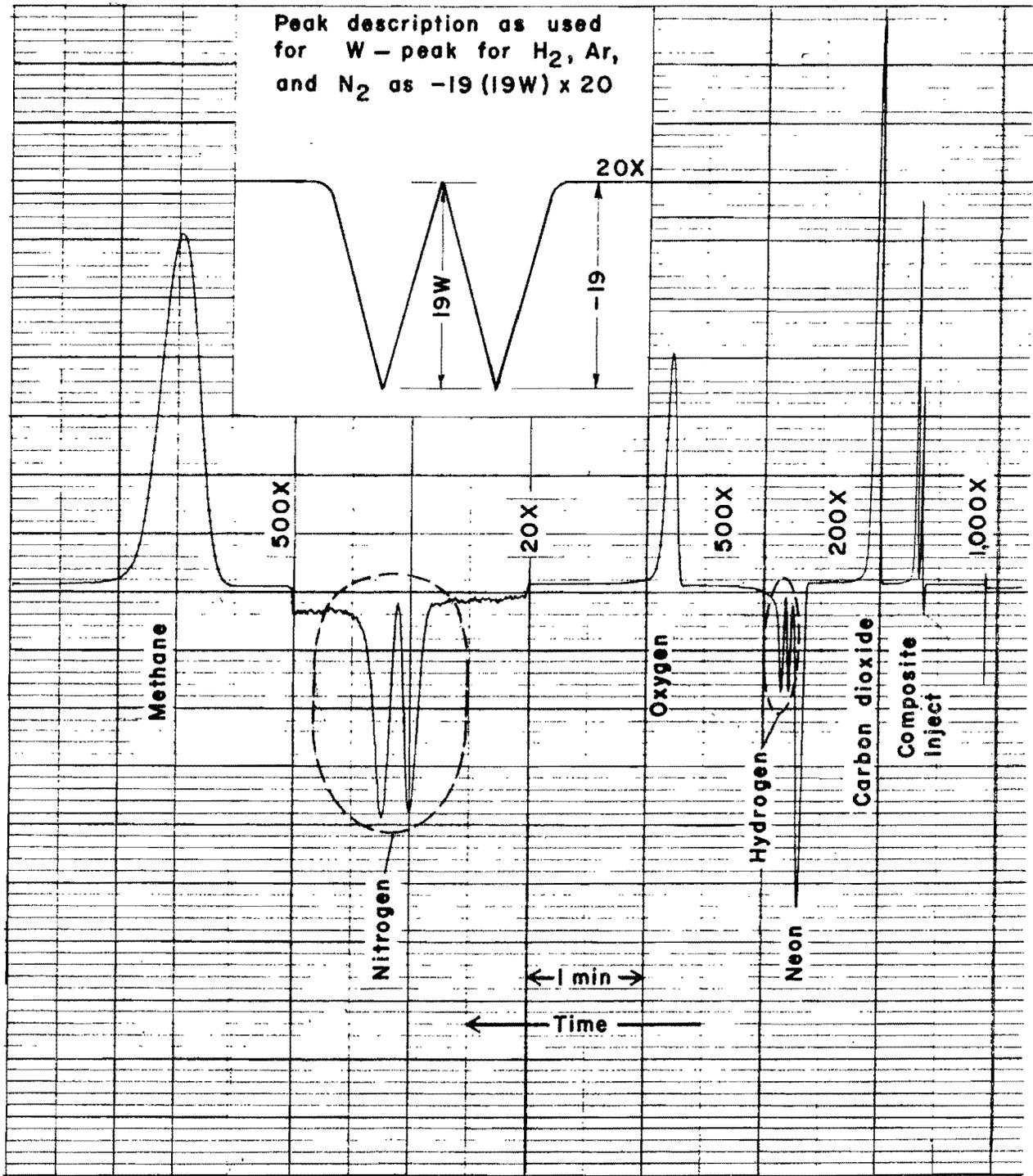


FIGURE 3. - Chromatogram of sample 1 using 0.02 ppm Ne carrier.

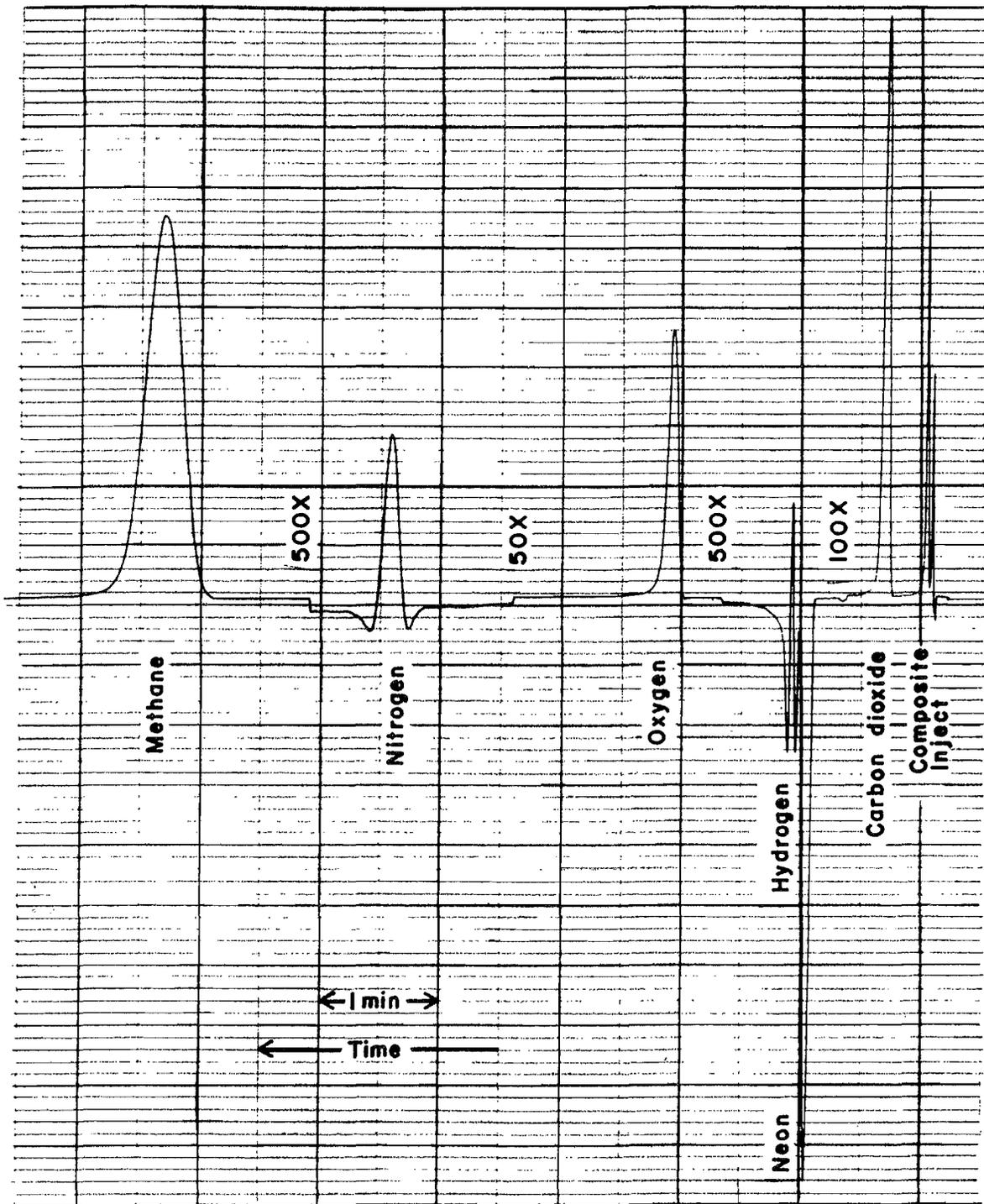


FIGURE 4. - Chromatogram of sample 1 using 1.2 ppm Ne carrier.

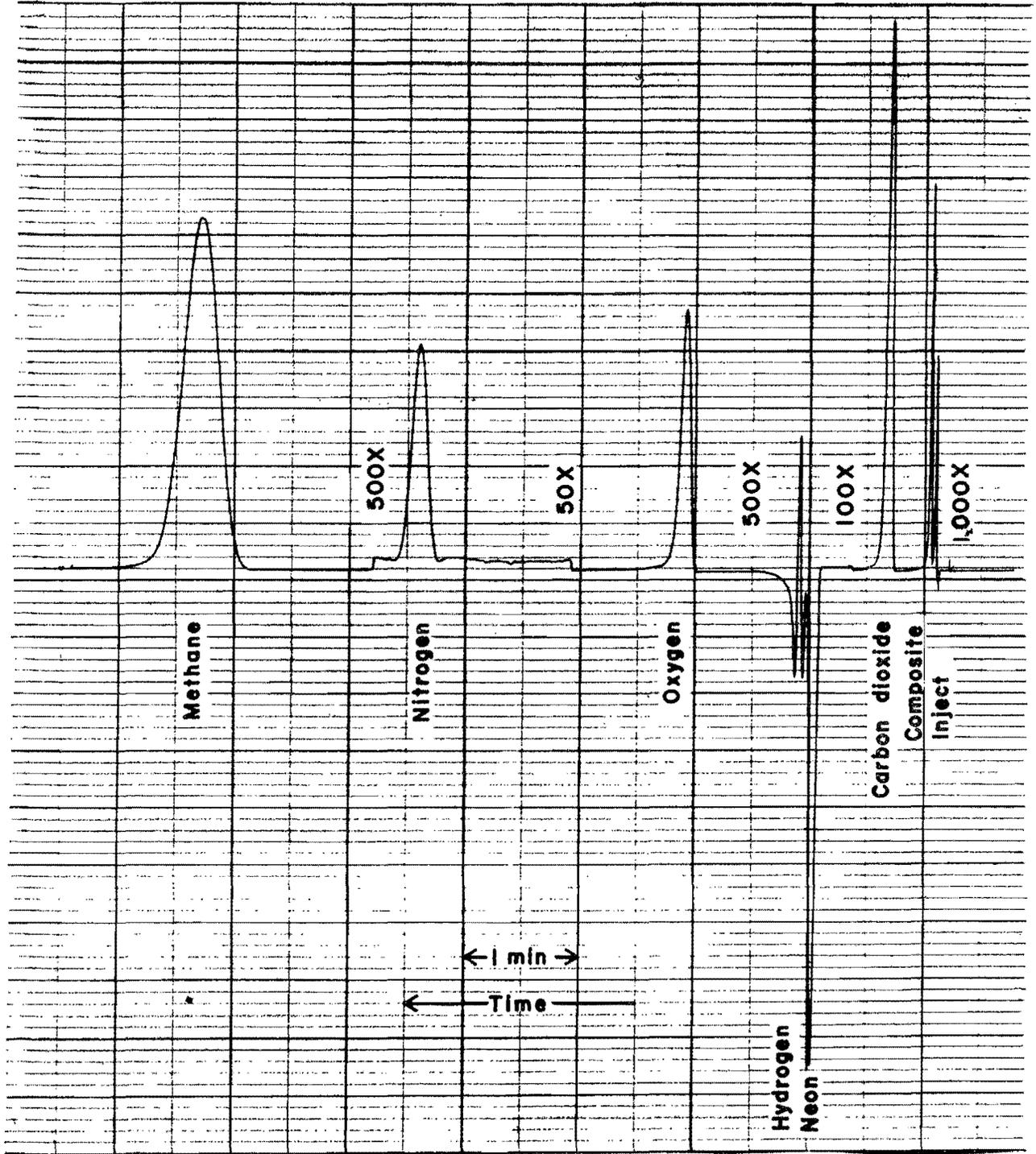


FIGURE 5. - Chromatogram of sample 1 using 2.0 ppm Ne carrier.

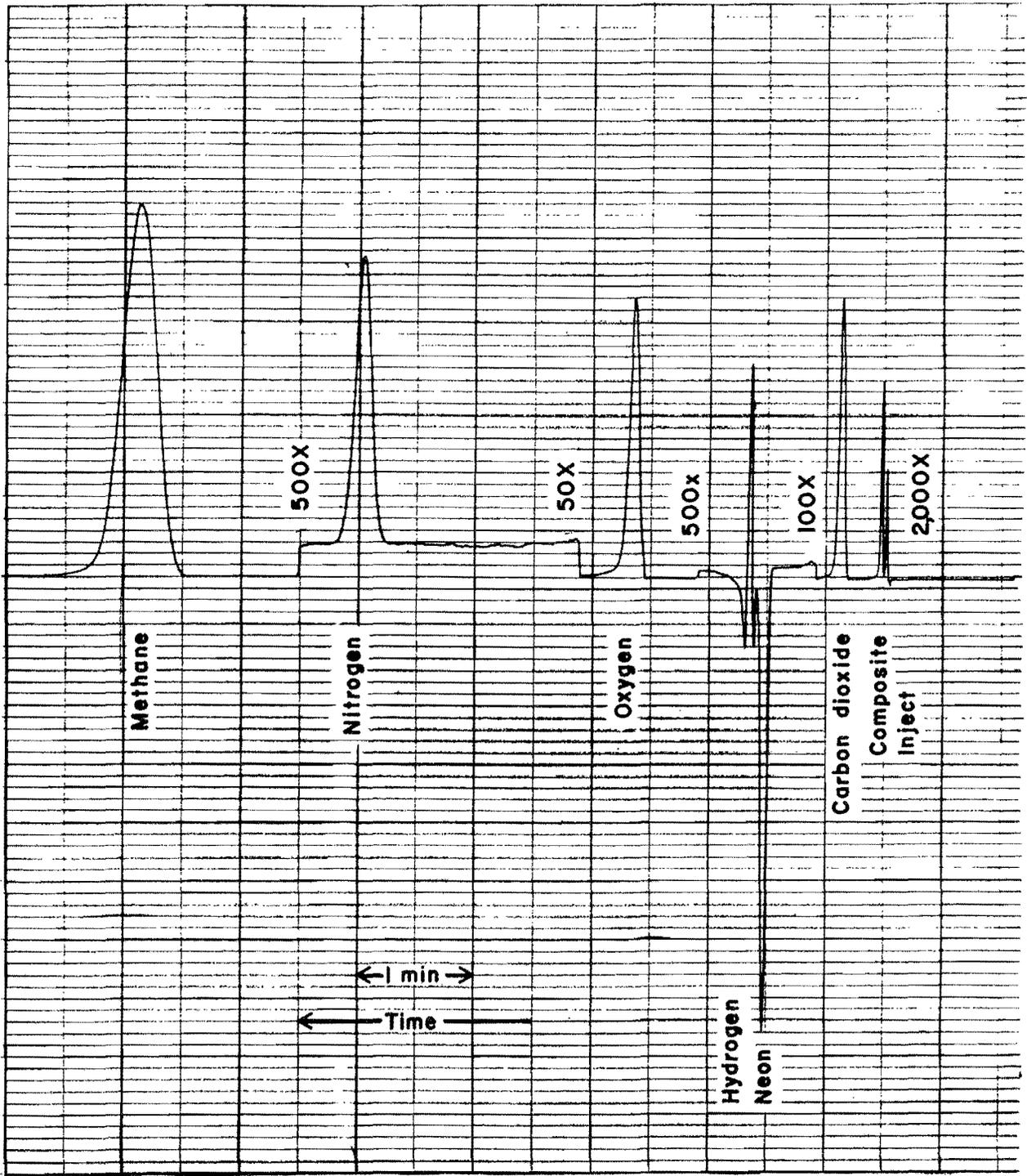


FIGURE 6. - Chromatogram of sample 1 using 3.2 ppm Ne carrier.

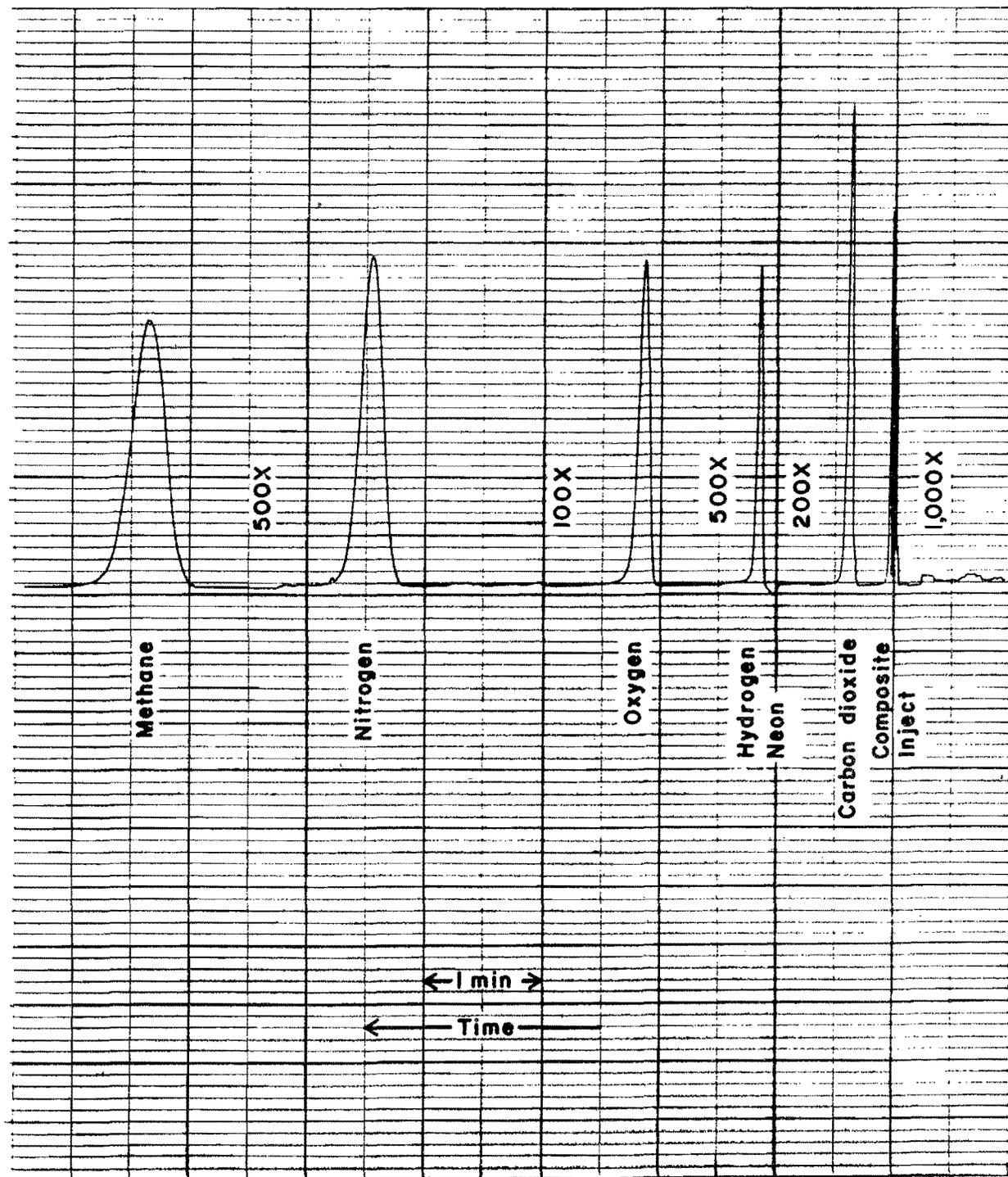


FIGURE 7. - Chromatogram of sample 1 using 27.4 ppm Ne carrier.

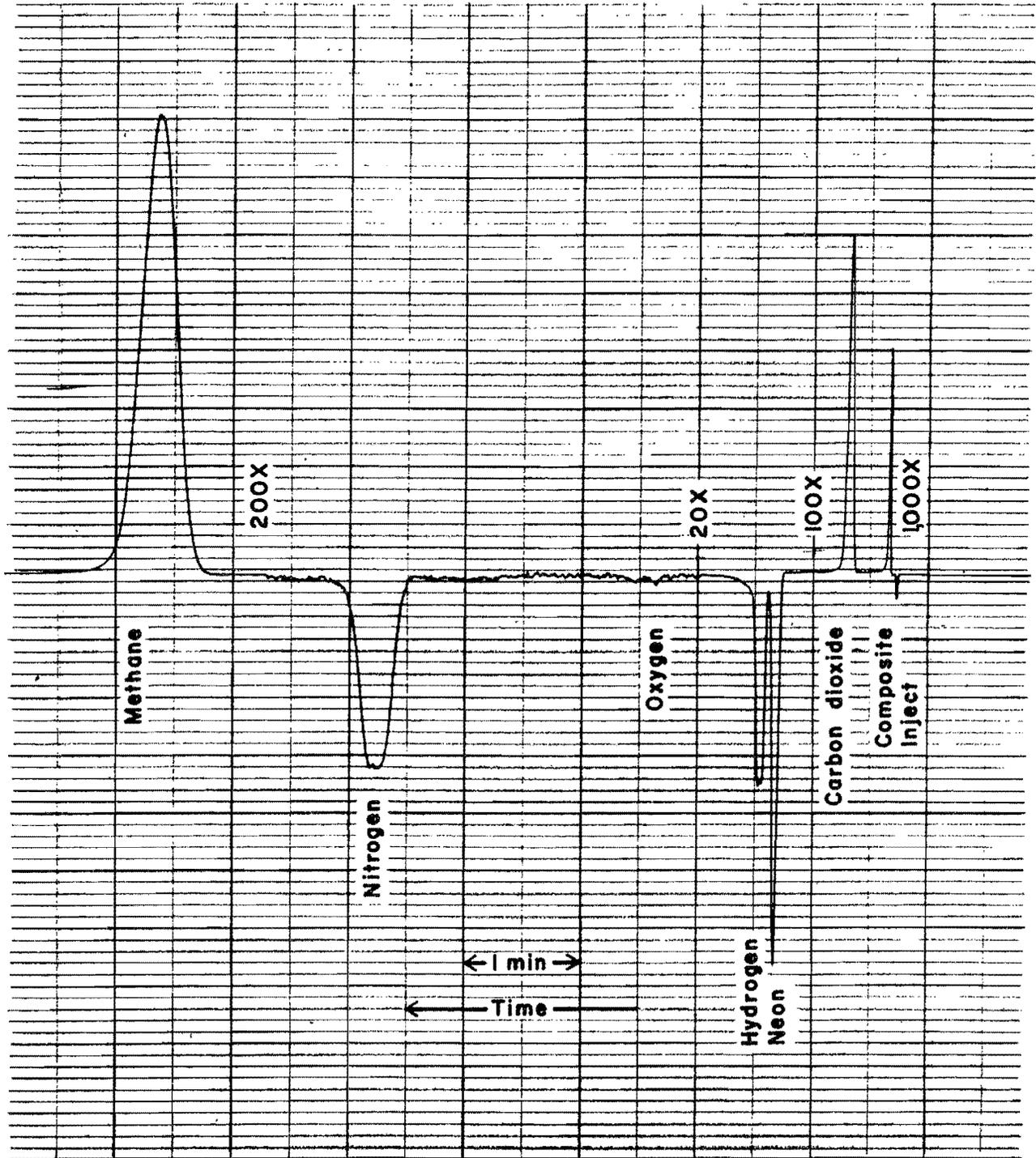


FIGURE 8. - Chromatogram of sample 2 using 0.02 ppm Ne carrier.

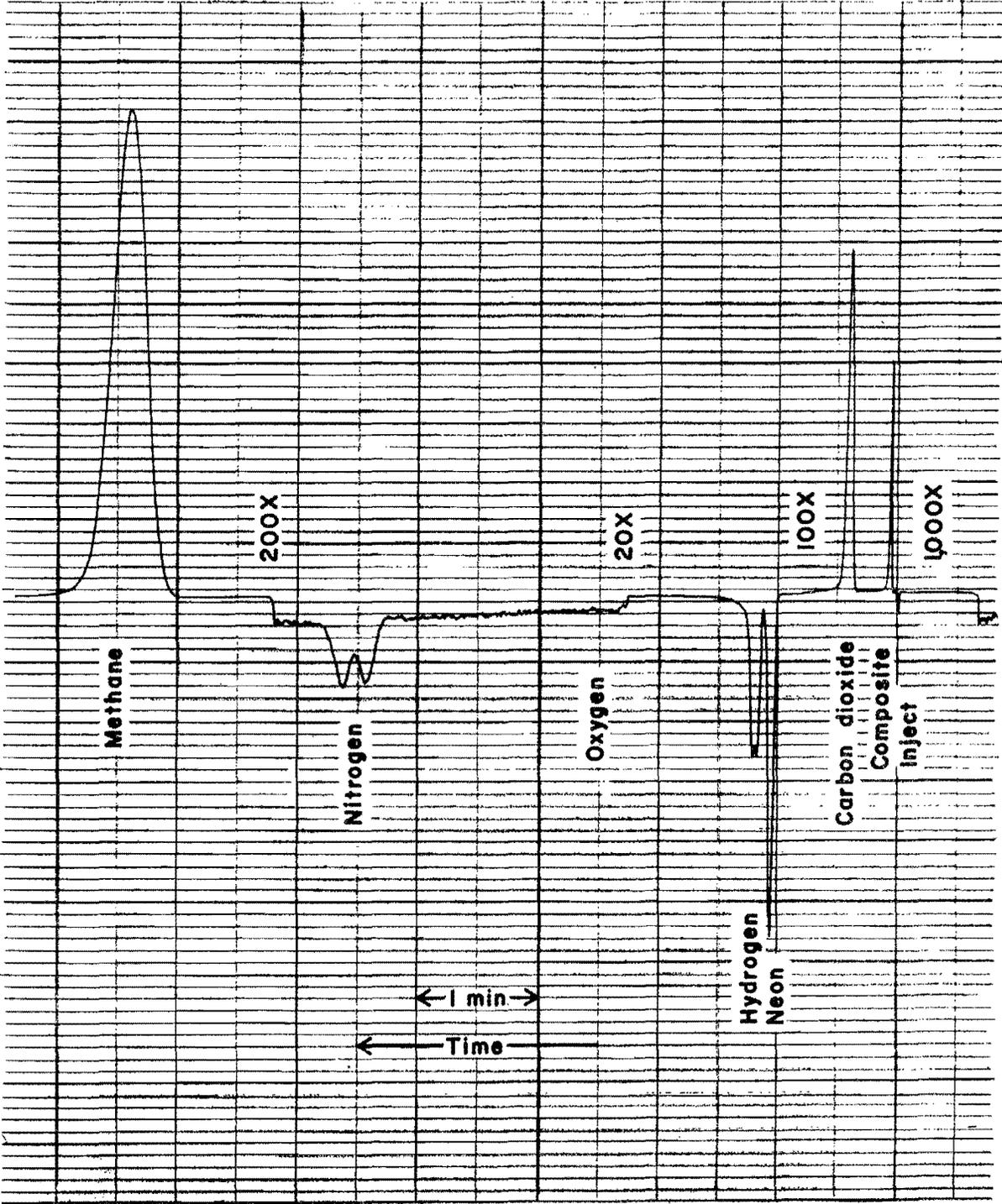


FIGURE 9. - Chromatogram of sample 2 using 1.2 ppm Ne carrier.

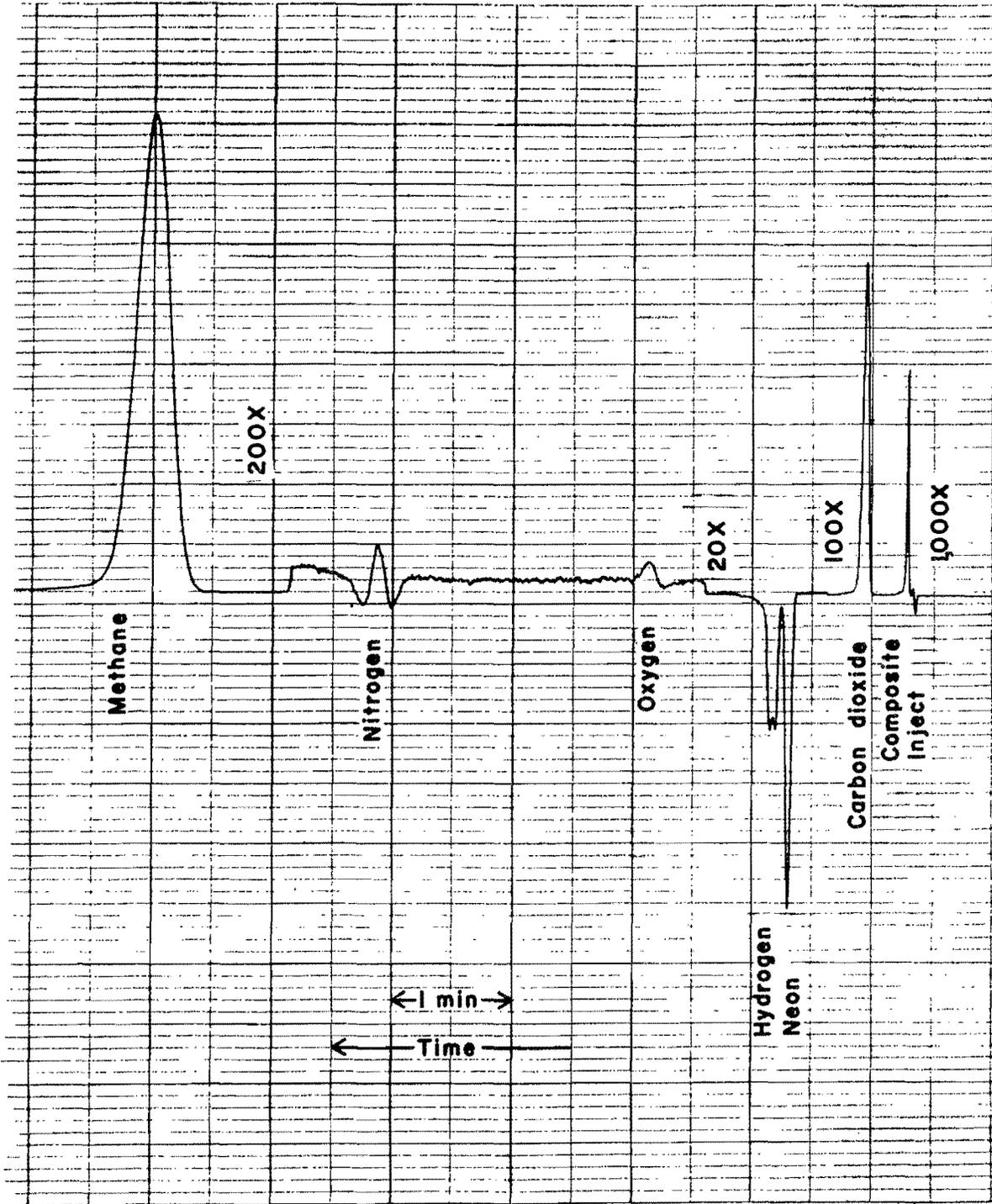


FIGURE 10. - Chromatogram of sample 2 using 2.0 ppm Ne carrier.

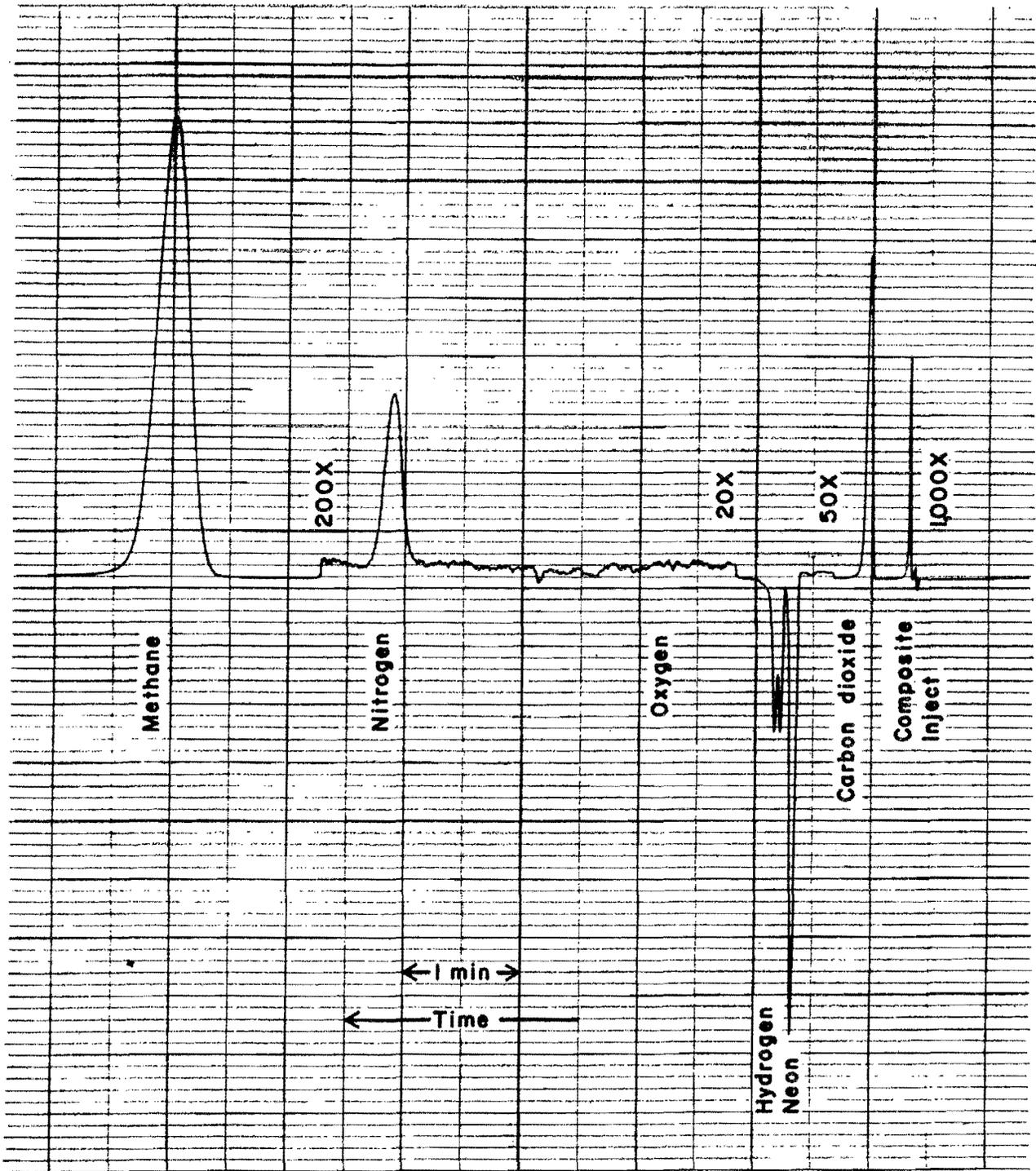


FIGURE 11. - Chromatogram of sample 2 using 3.2 ppm Ne carrier.

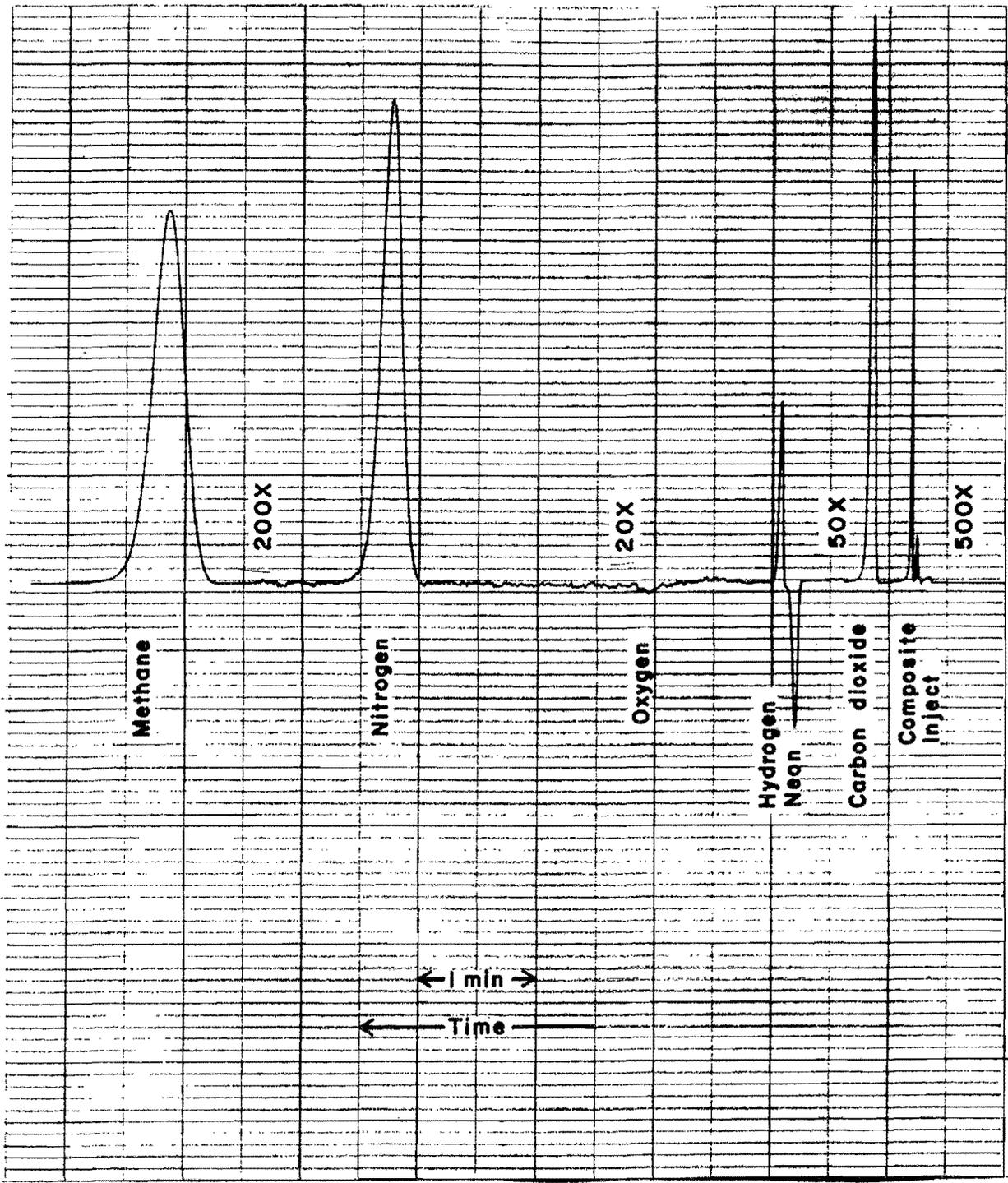


FIGURE 12. - Chromatogram of sample 2 using 7.1 ppm Ne carrier.

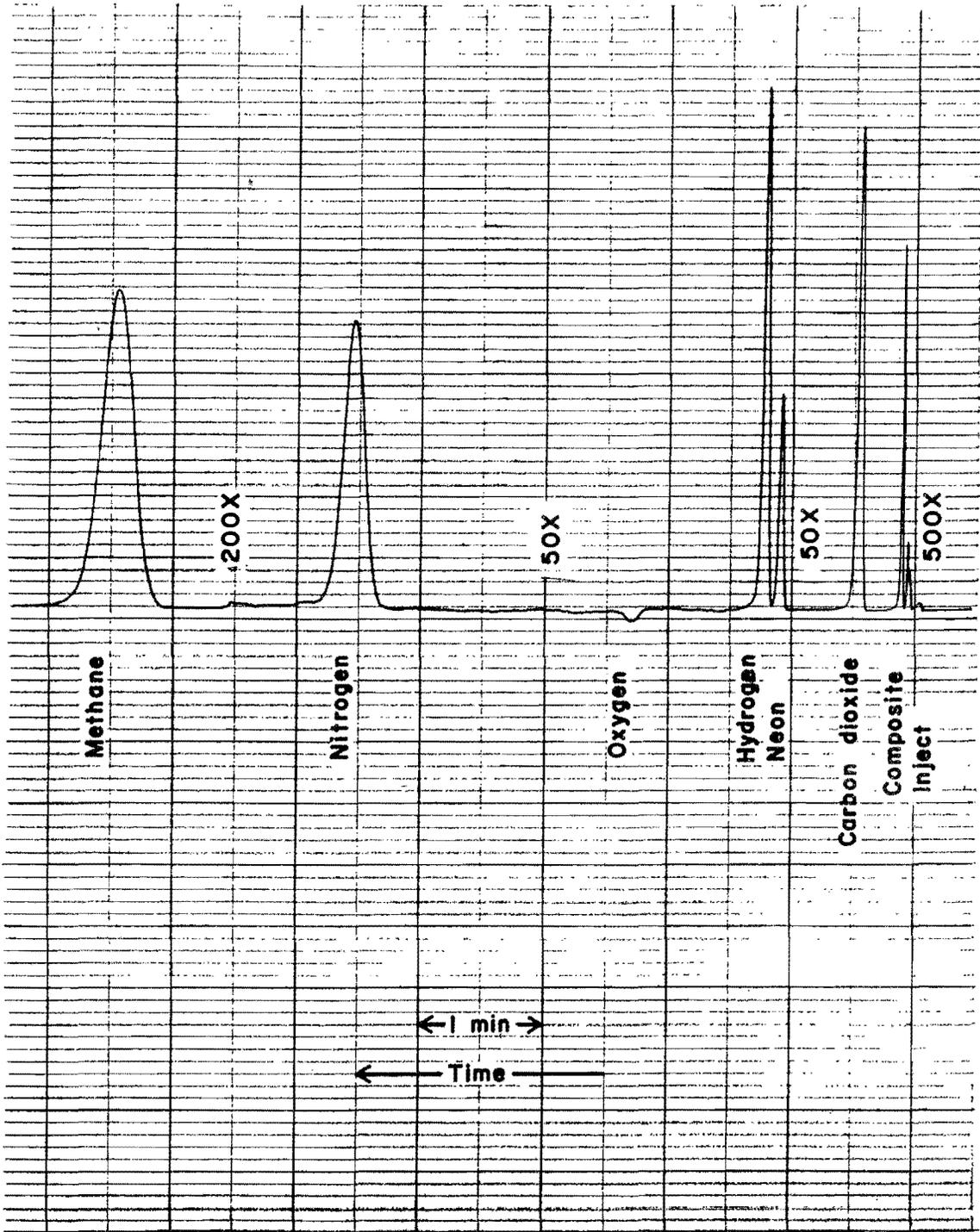
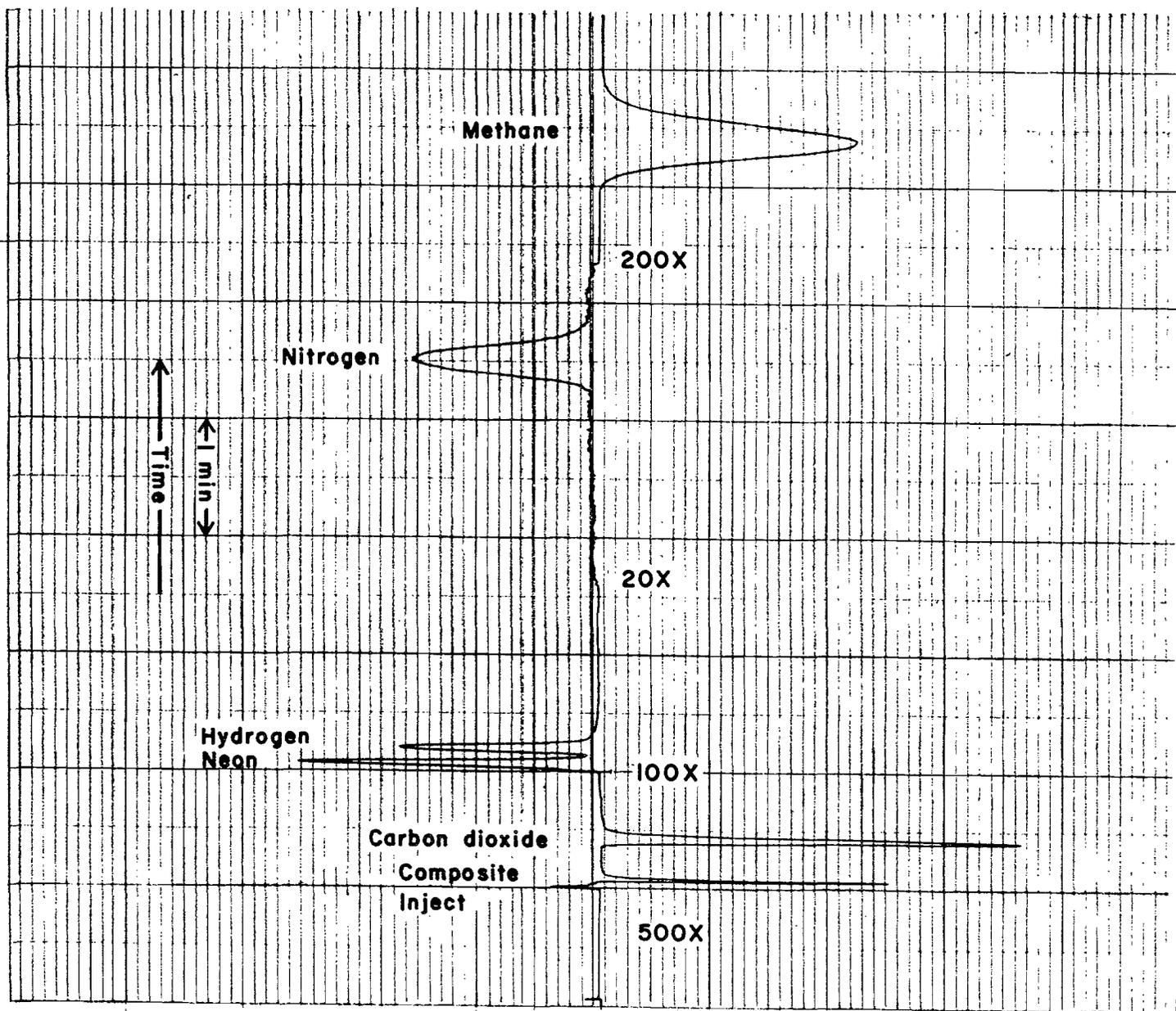


FIGURE 13. - Chromatogram of sample 2 using 27.4 ppm Ne carrier.

FIGURE 14. - Chromatogram of sample 3 using 0.02 ppm Ne carrier.



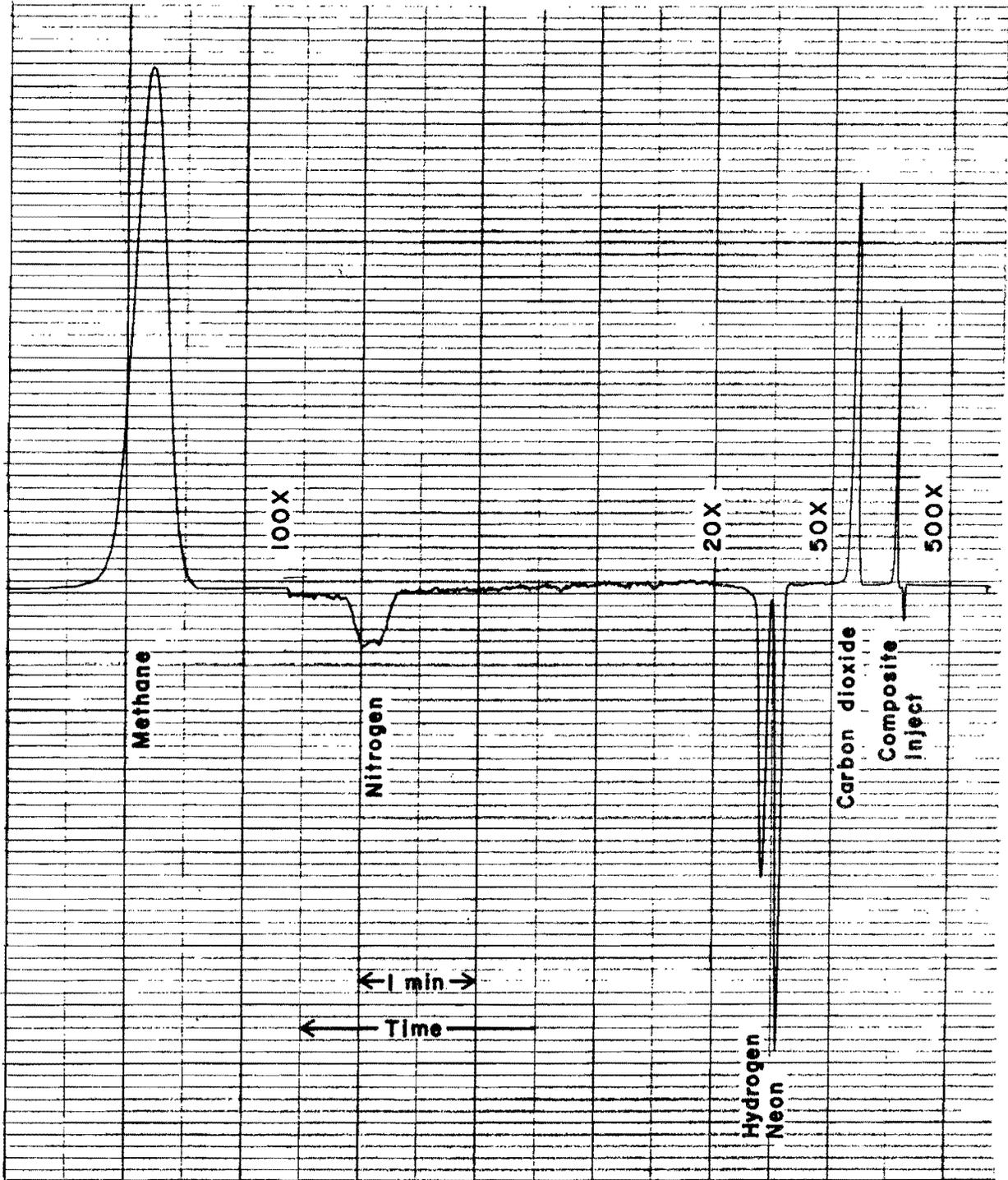


FIGURE 15. - Chromatogram of sample 3 using 1.2 ppm Ne carrier.

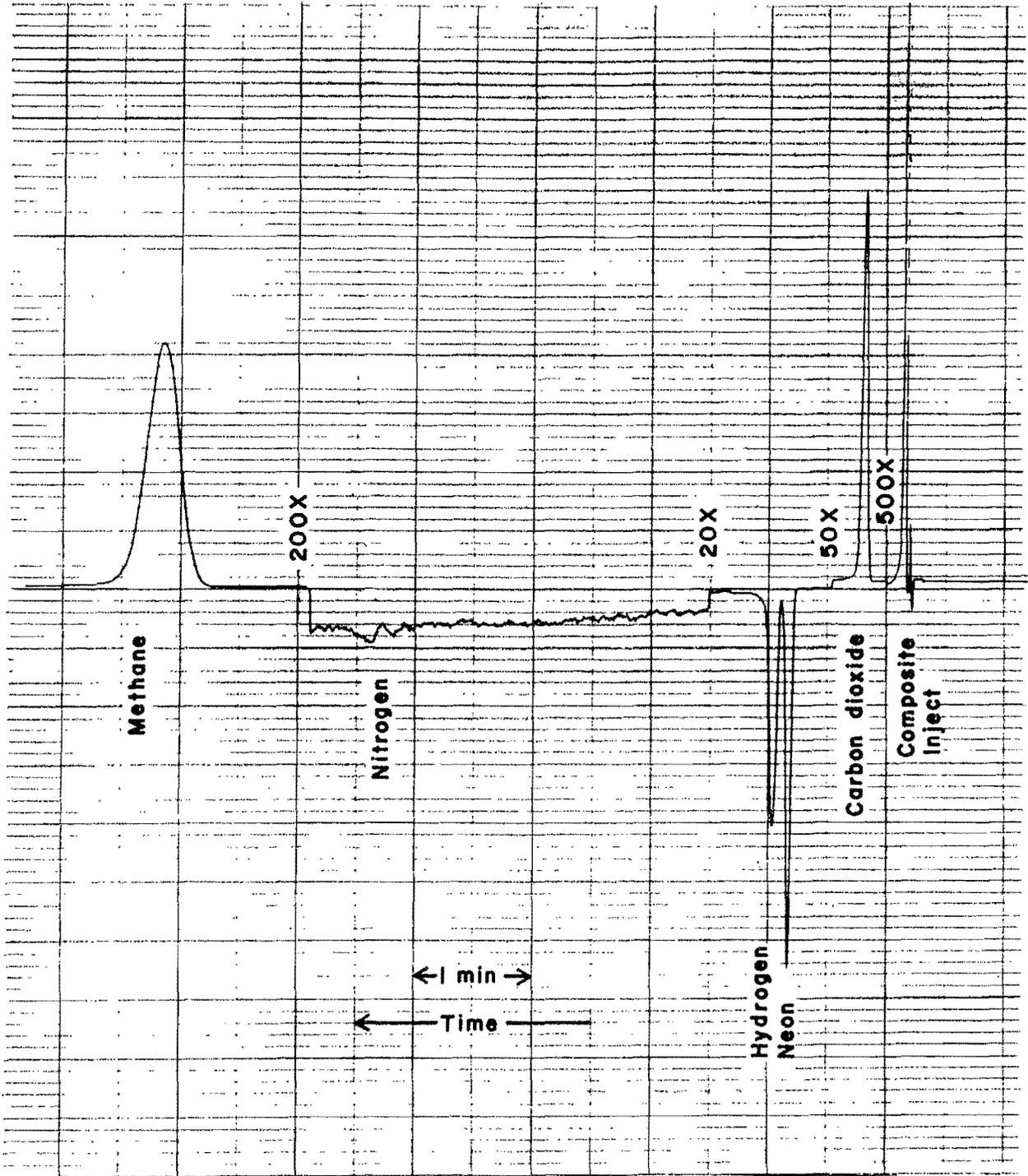


FIGURE 16. - Chromatogram of sample 3 using 2.0 ppm Ne carrier.

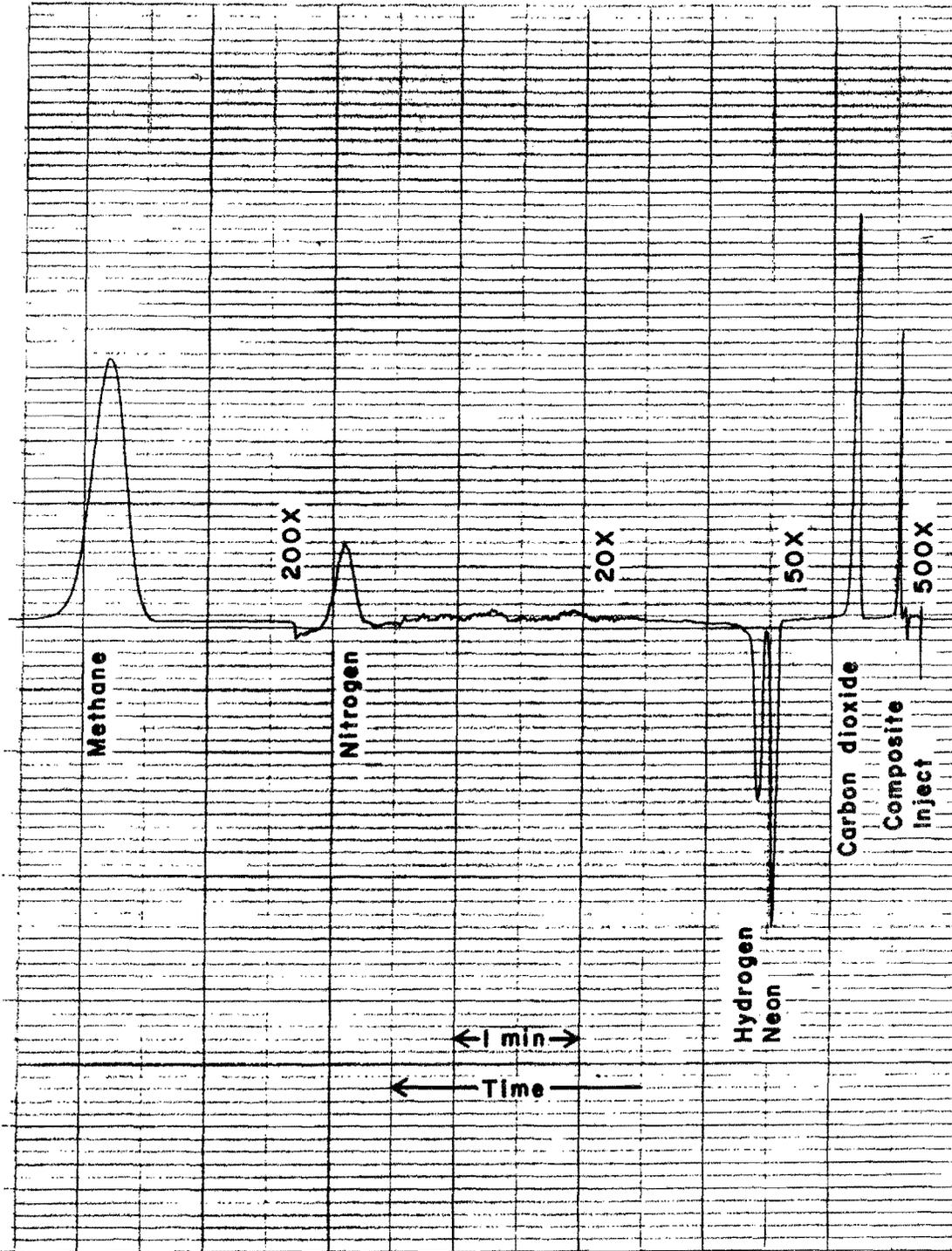


FIGURE 17, - Chromatogram of sample 3 using 3.2 ppm Ne carrier.

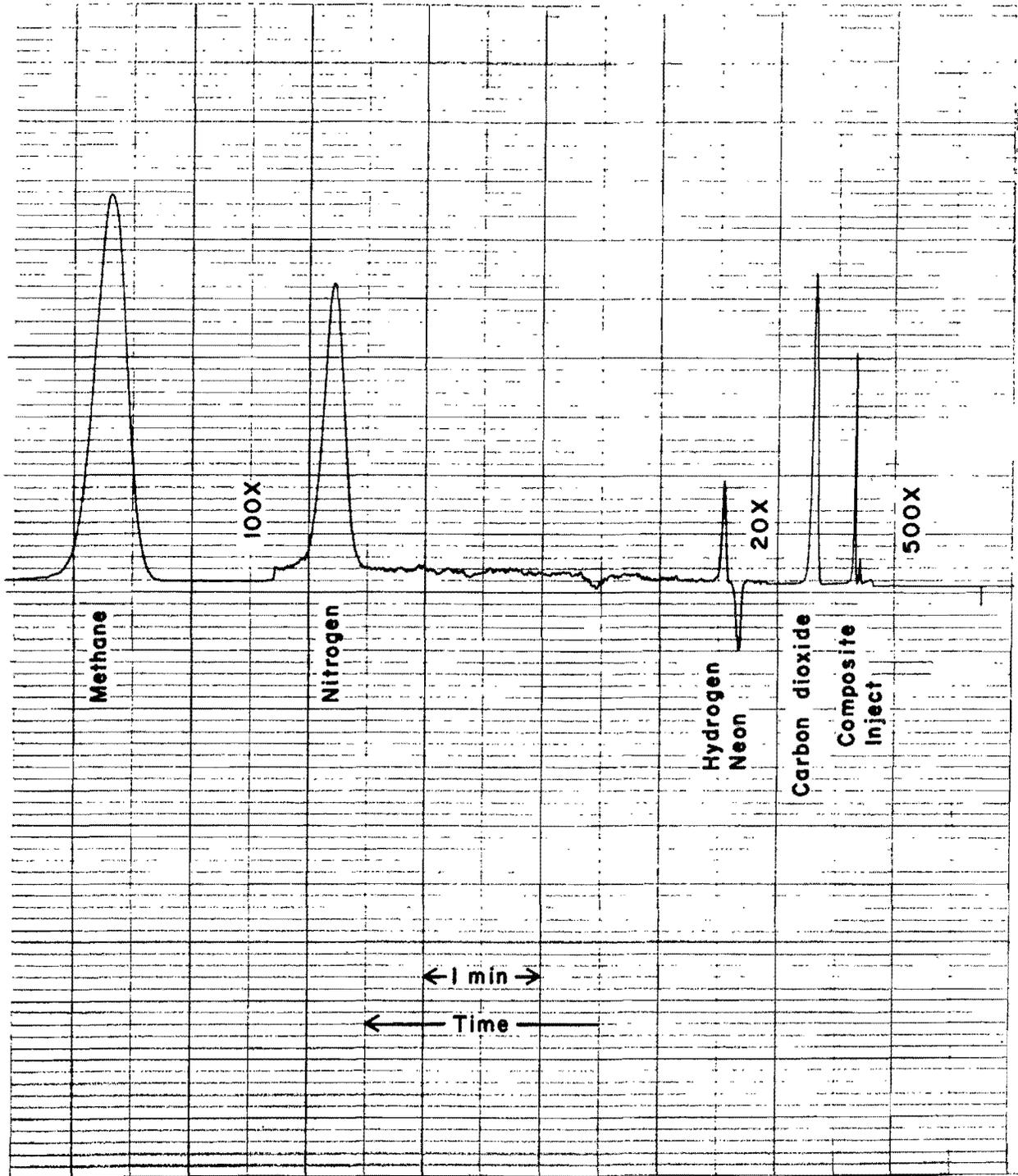


FIGURE 18. - Chromatogram of sample 3 using 7.1 ppm Ne carrier.

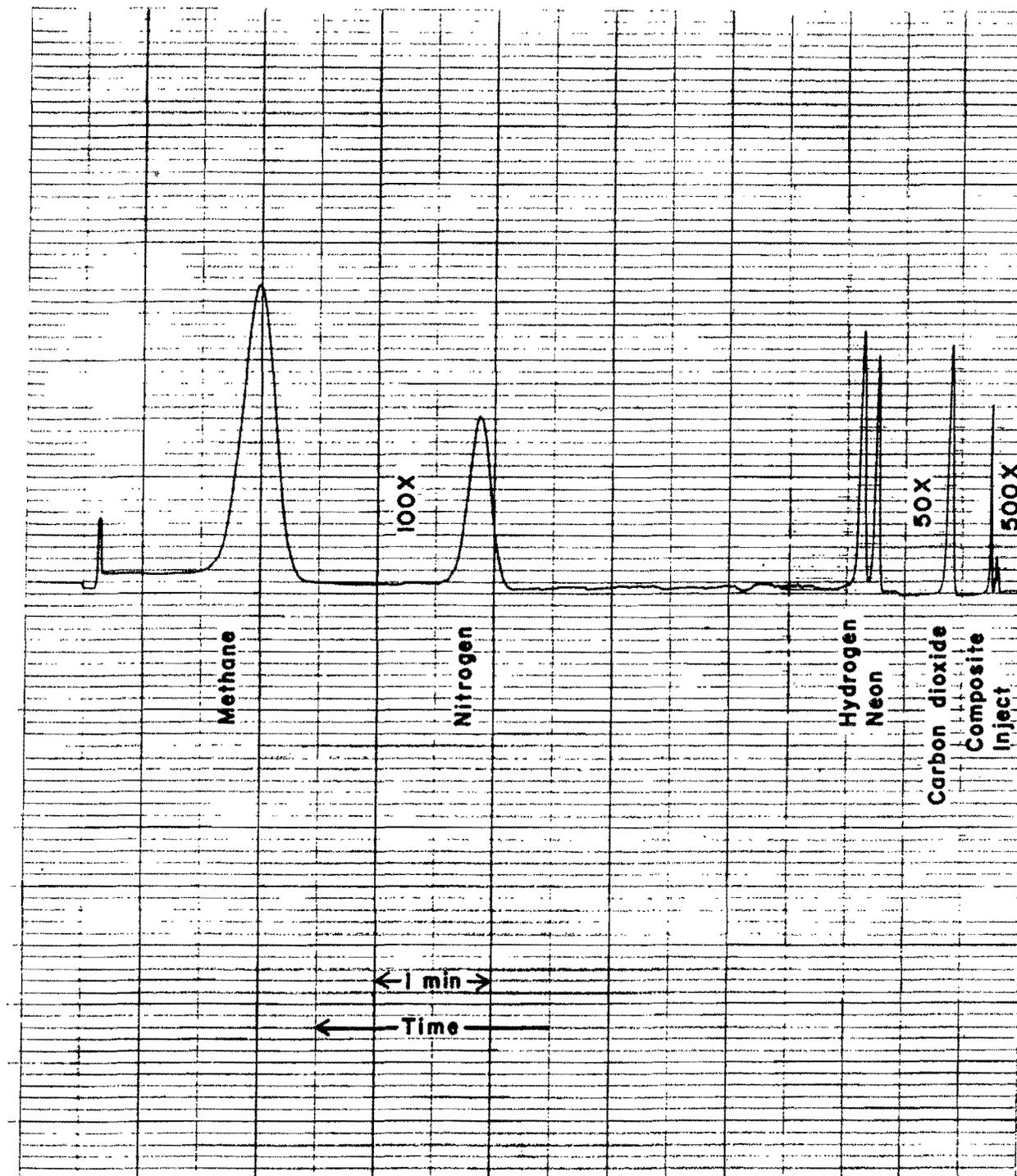


FIGURE 19. - Chromatogram of sample 3 using 27.4 ppm Ne carrier.

One experimental test of the moisture effect involved the addition of moisture with the sample of ambient air by first purging the sample loops with wet compressed air (service-station-type air compressor with no drier), followed by injecting a sample using valve 2 and holding it in the inject mode for 10 s, thereby giving moisture a better chance of being desorbed from the sample loop into the carrier stream and the column 2 Porapak. The volume of the sample loop for valve 2 is about 0.2 cm³. The sample supply was then changed to sample 6 with the first injection using valves 1 and 2, 2 min after the air sample, and the samples were taken every 5 min thereafter.

The peak height results as a function of time are shown in table 6. The sensitivity for the neon increased (vacancy peak), and sensitivity for all other components decreased as the injected moisture eluted from column 2. The column of table 6 labeled "Before" gives the peak height before the air injection. The column labeled "2" shows the results after 2 min, which are lower for all components due to the trace components remaining (other than moisture) resulting from the air sample. The major effect was

seen at 7 min, which is about the time for the major portion of the broad moisture to be eluted from column 2 into the detector. The greatest change in response was for the hydrogen peak, which exhibited a W-peak at the 7-min sample. The response for all components returned to normal in about 1 h.

A second experiment was set up to demonstrate the effect of moisture. Moisture was added to column 2 by repetitive operation of valve 2 only, while sample 6 was again used as the moisture source, even though it contained only 1.7 ppm H₂O. Valve 2 was cycled on to off to on, at 6 s on 6 s off, for 20 min, which resulted in a nearly constant amount of moisture being added for a short time period but long enough to demonstrate the moisture effect. Some sample 6 was injected, using both valves 1 and 2, 2 min after stopping the repetitive injection; this time the first sample (at 2 min) shows the effect of moisture, which is essentially the same as seen for the results of the sample taken at 7 min. After that, the response returns toward normal. These results are shown in table 7.

TABLE 6. - Sample 6 with addition of moisture from an air sample (using carrier gas 7), peak heights in divisions

Component and concentration	Time after air sample injected					
	Before	2 min	7 min	12 min	17 min	22 min
6 ppm CO ₂	11,200	8,000	7,500	8,900	9,900	10,200
19 ppm Ne....	300	200	700	700	600	500
19 ppm H ₂	4,100	3,200	-1(2W)X200	1,300	2,500	2,900
17 ppm O ₂	10,000	9,000	6,000	7,300	8,300	8,700
24 ppm N ₂	3,000	2,600	1,600	1,900	2,200	2,300

TABLE 7. - Sample 6 with addition of moisture by repetitive injections (using carrier gas 7), peak heights in divisions

Component and concentration	Time after addition				
	Before	2 min	7 min	22 min	27 min
6 ppm CO ₂	11,200	8,600	8,600	9,500	10,300
19 ppm Ne....	300	800	900	700	600
19 ppm H ₂	4,100	-1(3W)X200	-1(3W)X200	1,700	2,600
17 ppm O ₂	10,000	6,200	6,000	8,000	8,600
24 ppm N ₂	3,000	1,200	1,100	2,000	2,300

The detector output due to the moisture added by the repetitive injections begins to fall off at about 8 to 10 min. If one assumes that the addition of the sampling for 6 s transfers the moisture from the sample into the analytical stream, then the sampling at 6 s on 6 s off would cause the moisture level of the carrier to be increased by a calculated amount of 0.1 ppm, which appears to have a much greater effect on the component peaks than one would expect.

The effect of moisture, should it be present in the sample, is minimized by a short sample injection time (2 s). If a moisture peak is observed as a peak of long duration (almost as a drift), it could have an effect on sequential samples. The most general use of this type of chromatograph in production quality control is to show the absence of the components rather than the determination

of the level. With a little operational finesse, major upsets due to moisture and moisture interferences can be avoided even if it means waiting for a high-moisture sample to clear before the next sample injection.

EFFECT OF MINOR CONCENTRATIONS OF NITROGEN AND METHANE IN THE HELIUM CARRIER GAS

Carrier gases 11 and 12 contained essentially the same concentrations of all components as carrier gas 7 except for nitrogen in No. 11 and methane in No. 12. The results of the use of these gases are shown in table 8, 9, and 10. These are used to show how small concentrations of other "nonrelated" impurities affect calibration curves, emphasizing the need for recalibration, especially when carrier gases are replaced.

TABLE 8. - Results for sample 1 with minor concentrations of nitrogen (gas 11) and methane (gas 12) in neon-spiked helium carrier gas, peak heights in divisions

Component and concentration	Gas 7	Gas 11	Gas 12
32 ppm CO ₂	41,000	37,400	39,000
37 ppm Ne.....	-200	-200	-300
22 ppm H ₂	5,400	5,080	4,600
20 ppm O ₂	14,000	12,750	13,500
22 ppm N ₂	2,950	2,240	2,600
27 ppm CH ₄	12,500	9,750	11,500

TABLE 9. - Results for sample 2 with minor concentrations of nitrogen (gas 11) and methane (gas 12) in neon-spiked helium carrier gas, peak heights in divisions

Component and concentration	Gas 7	Gas 11	Gas 12
10.9 ppm CO ₂	20,500	18,250	19,750
12.6 ppm Ne.....	900	790	1,225
8.7 ppm H ₂	2,250	2,050	1,840
7.6 ppm N ₂	1,250	825	1,025
9.4 ppm CH ₄	5,600	5,000	5,100

TABLE 10. - Results for sample 3 with minor concentrations of nitrogen (gas 11) and methane (gas 12) in neon-spiked helium carrier gas, peak heights in divisions

Component and concentration	Gas 7	Gas 11	Gas 12
5.6 ppm CO ₂	10,700	9,600	10,500
8.7 ppm Ne.....	1,260	1,100	1,800
4.8 ppm H ₂	1,090	960	825
4.9 ppm N ₂	770	420	625
4.7 ppm CH ₄	2,800	2,500	2,550

The results when using carrier gases 11 and 12 are noticeably reduced by 5 to 10 pct as compared to results when using carrier gas 7. All three carrier gases contained essentially the same concentration of neon, 27.5 ppm.

It is noted that in the case of these added minor components, should the sample be free of these components, reverse peaks will exist, and in the examples given above, the peaks would go negative for nitrogen and methane. An absence of a peak would indicate the concentrations of the components in the sample to be equal to those of the carrier when the sample has the same common major component.

EFFECT OF VOLTAGE ON RESPONSE FOR COMPONENTS OF SAMPLE 2

Table 11 shows the responses for the components of sample 2 when using carrier 1 with 0.02 ppm Ne. Sample 2 was chosen because both hydrogen and nitrogen were at a concentration that exhibited near W-peaks.

Hydrogen exhibited a W-peak at 90 V and a flat-top peak (near W) for all other voltages (220 to 300 V). Nitrogen showed a small positive peak at 90 V and a flat-top peak (near W) for all other

voltages (220 to 300 V). The sensitivity of all components increased as the voltage was increased without a significant increase in the noise level, thereby increasing the signal-to-noise ratio, which allows for a lower minimum detectable limit (MDL). The MDL for methane at 90 V would be 0.40 ppm and at 270 V 0.08 ppm. An erratic baseline started above 300 V with major noise spikes, which is assumed to be near arc conditions. A voltage of 270 V was chosen as a good operating range.

BACKGROUND CURRENT AS A FUNCTION OF APPLIED VOLTAGE

The background current through the cell was determined indirectly by measuring the voltage at the point marked Z (fig. 2) when the zero circuit had been adjusted to a null at the output. This is the point where the voltage supplied by the zero circuit at Z is equal to the signal voltage level due to the current through the cell, which develops across the 500-M Ω resistor at the point marked S. The background current values are shown in table 12 as calculated from the indirectly measured voltage and divided by the 500-M Ω resistor.

TABLE 11. - Results from sample 2 with cell voltage changes from 90 to 300 V using carrier gas 1, peak heights in divisions

Component and concentration	90 V	220 V	260 V	270 V
11 ppm CO ₂	920	9,000	23,000	29,000
13 ppm Ne.....	-125	-1,300	-2,900	-3,400
8.7 ppm H ₂	-7(4W)X5	-13(F)X50	-16(F)X100	-18(F)X100
7.6 ppm N ₂	+20	-10(F)X10	-15(F)X20	-18(F)X20
9.4 ppm CH ₄	300	2,700	6,400	8,000
Noise.....divisions..	7	10	15	15
	280 V	290 V	300 V	
11 ppm CO ₂	36,000	45,000	55,000	
13 ppm Ne.....	-4,100	-4,800	-5,700	
8.7 ppm H ₂	-23(F)X100	-28(F)X100	-33(F)X100	
7.6 ppm N ₂	-21(F)X20	-27(F)X20	-35(F)X20	
9.4 ppm CH ₄	9,400	11,500	13,500	
Noise.....divisions..	15	15		

TABLE 12. - Background current as a function of neon in carrier gases and applied voltages, nanoamperes

Applied volts	Neon concentration in helium carrier gas							
	0.02 ppm	1.2 ppm	2.0 ppm	3.3 ppm	10.4 ppm	27.4 ppm	32.5 ppm	59.8 ppm
40			1.96					
50				2.00				
60	2.02		2.04		2.00	2.00		
90	2.06		2.08	2.06	2.04	2.04	2.04	2.06
220	2.66	2.64	2.62	2.60	2.46	2.40	2.38	2.38
230	2.80	2.76	2.76	2.72	2.56	2.48	2.44	2.44
240	2.96	2.90	2.90	2.86	2.66	2.58		2.50
250	3.14	3.08	3.06	3.06	2.78	2.68	2.60	2.58
260	3.34	3.26	3.24	3.14	2.90	2.78	2.70	2.68
270	3.60	3.46	3.44	3.38	3.02	2.90	2.80	2.76
280	3.82	3.68	3.66	3.58	3.18	3.04		
300	4.44							

USE OF 25 TO 30 PPM NEON IN THE HELIUM CARRIER GAS

When the concentration in the sample is less than the concentration in the carrier gas, the peak for neon is positive and can be considered a vacancy peak. The concentration of neon in the carrier gas should be greater than the concentration expected in the helium sample to be analyzed. This method provides adequate sensitivity even though a loss in sensitivity is observed when compared to using a carrier gas with about 0.02 ppm Ne. This loss is not important since there remains 2 to 10 times more sensitivity than required. This sensitivity loss is also a function of the operating temperature and voltage applied to the detector. It varies from one chromatograph to the next. Typical MDL's for this method are shown in table 13, which are interpreted values equal to 2 times the noise level (15 divisions) for results from sample 4. The limit of the uncertainties of the MDL is generally due to the limit of the uncertainties of analysis of these impurities in the carrier gas. The chromatograph is responsive and more linear for each component. The change to the high-neon carrier gas was made in October 1981 in all of the chromatographs used for routine analysis of the impurities in production-grade helium in the Bureau of Mines facilities. No unforeseen difficulties have arisen because of the change in carrier gas.

TABLE 13. - Minimum detectable limit (MDL) calculated for a noise level of 15 divisions when using 270 V, carrier gas 7, and sample 4

Component and concentration	Peak height, divisions	MDL, ppm
0.95 ppm CO ₂	3,400	0.008
6.5 ppm Ne.....	1,570	.39
0.93 ppm H ₂	225	.12
1.3 ppm O ₂	575	.07
1.9 ppm N ₂	275	.21
0.96 ppm CH ₄	575	.05

Maximum sensitivity for most impurities in the sample was observed when the carrier contained 0.02 ppm Ne. The detector output for each component normally responding negatively (a decrease in cell conductivity) went through a point of zero response (transition point) when the neon carrier content was below 8 ppm. The transition point for nitrogen was between 2 and 3 ppm Ne in helium carrier, as was shown in figure 16. The response for methane and carbon dioxide was positive for all neon carrier levels tested (0.02 to 125 ppm).

A 25- to 30-ppm Ne carrier gas was used for this method so that the response for all components was positive for concentrations encountered except for neon. The response for neon is positive when the neon concentration of the sample is lower than that of the carrier (a vacancy peak). Should the sample be anything other than helium, the vacancy peak no longer exists.

CONCLUSIONS

A chromatographic system has been described that gives reliable analysis for impurities in helium. The use of 25 to 30 ppm Ne in the carrier gas provides positive peaks for the normal impurities found in Grade-A helium and improves interpretation of the data. This change eliminates the foldover W-peaks and inconsistencies previously observed.

The ionization chromatograph system has been used successfully for quality control analysis since 1969 by the Bureau of

Mines, Division of Helium Field Operations. Improved reliability has been obtained with the use of the high-neon carrier.

When traces of nitrogen and methane are in the carrier gas in addition to the high neon, the response to components is further reduced, but the results are still usable after recalibration. The effect of moisture in the sample is minimized by using a short injection time (2 s).

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