

ANALYSIS OF NATURAL GAS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

**INTERIM REPORT
TFLRF No. 319**

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Under Contract to
U.S. Army TARDEC
Mobility Technology Center-Belvoir
Fort Belvoir, Virginia

Contract No. DAAK70-92-C-0059

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February 1996

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE February 1996	3. REPORT TYPE AND DATES COVERED Interim November 1994 to December 1995	
4. TITLE AND SUBTITLE Analysis of Natural Gas by Fourier Transform Infrared Spectroscopy			5. FUNDING NUMBERS DAAK70-92-C-0059; WD 37	
6. AUTHOR(S) Fodor, George E.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI) Southwest Research Institute P.O. Drawer 28510 San Antonio, Texas 78228-0510			8. PERFORMING ORGANIZATION REPORT NUMBER TFLRF No. 319	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Army Mobility Technology Center-Belvoir 10115 Gridley Road, Suite 128 Ft. Belvoir, Virginia 22060-5843			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A fast experimental protocol was established for the simultaneous determination of methane, ethane, propane, and butane in nitrogen from Fourier transform infrared (FT-IR) spectra. The method is based on correlations established between known gas compositions and their FT-IR spectra. The spectra were collected in the region of 4,000 to 400 cm ⁻¹ through KBr windows in a 100-mm pathlength gas sample cell operating at 100, 300, 500, 700, and 1,000 mm Hg pressure. Correlation between blending partial pressure or GC-based analysis and FT-IR data produced squared correlation coefficients (R ²) in excess of 0.98. Total required analytical time is less than 2 minutes.				
14. SUBJECT TERMS Natural gas Analysis Infrared spectroscopy FT-IR			15. NUMBER OF PAGES 43	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

EXECUTIVE SUMMARY

Problem: Traditionally, natural gas has been analyzed by relatively cumbersome and time-consuming gas chromatographic methods that are not conveniently adaptable to field use.

Objective: The objective of this program was to investigate and define the use of midband Fourier transform infrared (FT-IR) spectroscopy as a rapid and reliable means of estimating natural gas composition and derived properties in the field.

Importance of Project: This method provides a quick and simple way of estimating the concentrations of the major natural gas components and derived properties simultaneously. In comparison with the standard gas chromatographic procedure, the spectroscopic methods offer advantages in cost and time required per analysis and in their adaptability to perform analysis at remote locations.

Technical Approach: Since methane, ethane, propane, and butane each have distinct infrared spectra, the measurement of their individual concentration may be performed. Using standards, calibration files were constructed to correlate actual concentration of components with FT-IR spectra.

Accomplishments: A fast experimental protocol was established for the simultaneous determination of methane, ethane, propane, and butane in nitrogen from FT-IR spectra. Correlation between blending partial pressure or GC-based analysis and FT-IR data produced squared correlation coefficients (R^2) in excess of 0.98. Total required analytical time is approximately 1 to 2 minutes.

Military Impact: Improved analytical chemical speed and convenience facilitates obtaining compositional data on natural gas in the field.

FOREWORD/ACKNOWLEDGEMENTS

This work was performed by the U.S. Army TARDEC Fuels and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI), San Antonio, Texas, during the period November 1994 to December 1995 under Contract No. DAAK70-92-C-0059. The work was funded by the U.S. Army Tank-Automotive Research, Development and Engineering Center (TARDEC), Warren, Michigan. Mr. T.C. Bowen (AMSTA-RBFF) of Mobility Technology Center-Belvoir (MTCB) served as the contracting officer's representative and technical monitor.

The author would like to acknowledge the support provided by Messrs. S.J. Lestz, E.A. Frame, and S.A. Hutzler. Laboratory assistance provided by Ms. M.S. Voigt and Messrs. K.H. Childress and J.J. Dozier is gratefully appreciated. Also acknowledged is the support provided by Messrs. J.H. Marshall and J.W. Pryor and Mses. L.A. Pierce and M.M. Clark.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I. INTRODUCTION	1
II. OBJECTIVE	2
III. APPROACH	2
IV. EXPERIMENTAL	3
V. CHEMOMETRICS	4
VI. RESULTS AND DISCUSSION	6
VII. CONCLUSIONS	8
VIII. REFERENCES	8
APPENDICES	
A. Tables	11
B. Figures	17

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Schematic diagram of gas sampling system	4

I. INTRODUCTION

A recent survey showed that the composition of pipeline quality natural gas is not constant.(1)* King demonstrated that, as expected, the composition of natural gas will have a marked effect on the operational characteristics of engines burning natural gas as the fuel.(2) Kubesh and coworkers showed that gas composition has a significant effect on the octane number of natural gas blends used as fuel for internal combustion engines.(3) For these reasons and for determining values in product custody transfers, a reliable, quick, and accurate method was needed to determine gas composition that is more convenient and timely to perform than the commonly used gas chromatographic method.

Between 85 to 95 volume percent (vol%) of pipeline quality natural gas is methane. Generally, the balance of the gas, in decreasing order of concentration, is propane, ethane, butane, and inert gases. Although some studies have found measurable amounts of higher molecular weight hydrocarbons, it was shown that the components present in natural gas at concentrations of less than 0.2 mole percent (mol%) may be grouped as C_{5+} or C_{6+} components, and that they do not contribute significantly to the calorific value of the natural gas.(4) For this reason, a natural gas may be adequately described by the concentrations of the four lightest saturated hydrocarbons, i.e., methane through butane. From the concentrations of the major active ingredients, several pertinent gas properties, e.g., heating value, density, etc., may be easily calculated by built-in computers.

Near-infrared (near-IR) spectroscopy generally operates in the 900 to 2,000 nanometer (nm), or 0.9 to 2.0 micrometer (μm), wavelength region, while the range of midband Fourier transform infrared (FT-IR) spectroscopy may be extended to the 2.0 to 50 μm region and beyond. Due to limitations of optical window materials, FT-IR is usually used in the restricted spectral region from about 2.5 to 25 μm , corresponding to 4,000 to 400 cm^{-1} wavenumbers. In comparing near-IR with FT-IR, it may be noted that near-IR is the result of second and third overtones and combination tones of the fundamental frequencies that produce the directly measurable FT-IR

* Underscored numbers in parentheses refer to the list of references at the end of this report.

region of the infrared spectrum. Since FT-IR spectroscopy is based on the measurement of characteristic fundamental resonances, it produces specific, usually sharp, well-defined peaks at substantially increased extinction coefficients. Potentially, these facts lead to higher analytical specificity, accuracy, and sensitivity. The higher sensitivity manifested by FT-IR allows accurate measurement of the various natural gas components at substantially reduced pressures.

FT-IR and near-IR spectroscopies have the potential to meet the requirements for a transportable natural gas analyzer. Brown and Lo demonstrated the feasibility of near-IR in monitoring the energy content of natural gas.(5) The quartz optics and fiber-optic probes typically used with near-IR instruments allow the analyzer to be positioned remote to the measurement site and may be readily adaptable to field use.(6) Westbrook (7) used near-IR to analyze natural gas at 207 kPa (30 psig) in a flowing line. During the FT-IR analysis of such liquid fuels as gasolines and turbine and diesel fuels, Fodor et al. demonstrated that the use of infrared spectroscopic analyses, combined with multivariate calibration techniques, allowed the estimation of several pertinent fuel properties in which the accuracy of these measurements was comparable to measurements from techniques that were designed to directly measure the desired fuel properties.(8-10)

II. OBJECTIVE

The objective of this program was to explore the use of midband FT-IR spectroscopy as a rapid and reliable laboratory or field method to estimate natural gas composition and derived properties and to demonstrate the feasibility of FT-IR as an on-line natural gas analyzer.

III. APPROACH

Reference or calibration gases were blended according to compositions determined by statistical treatment of the natural gas compositional limits to maximize the expected correlational output using a minimum number of samples. These quantitatively blended reference gas mixtures were

also analyzed by gas chromatography (GC) to substantiate their composition. Using these data, calibration models were developed for methane, ethane, propane, and butane in nitrogen.

IV. EXPERIMENTAL

Compositions of 44 calibration gas mixtures were designed using the E-CHIP statistical program. The experimental design included the four C_1 - C_4 saturated hydrocarbons in nitrogen to provide the minimum number of standard samples to allow calibration within the expected concentration ranges for each component:

methane	50 to 100 vol%
ethane	0 to 10 vol%
propane	0 to 30 vol%
butane	0 to 5 vol%
nitrogen	0 to 35 vol%

To properly blend the various gas components, a four-port mixing manifold was fabricated, and on-off ball valves were installed at each port. Quantitative blending of mixtures of calibration gas standards was performed using a precision vernier "pressure volume controller" and a pressure regulator and monitor (Heise Models PTE-1 and HBC-1000). A schematic diagram of this sampling system is shown in Fig. 1. The calculated compositional data on these calibration standard mixtures are given in TABLE A-1 of Appendix A. Concentrations of components of the calibration gas standards were confirmed by GC using an instrument (Hewlett-Packard Model 5890 Series II) equipped with a gas sampling valve and a thermal conductivity detector. Operating parameters of the GC are given in TABLE A-2. To facilitate quantitative FT-IR analysis, pressure control was provided by the same precision pressure regulator that was used for the blending operations. Temperature control relied on the constant temperature environment of the spectrometer's internal sample compartment.

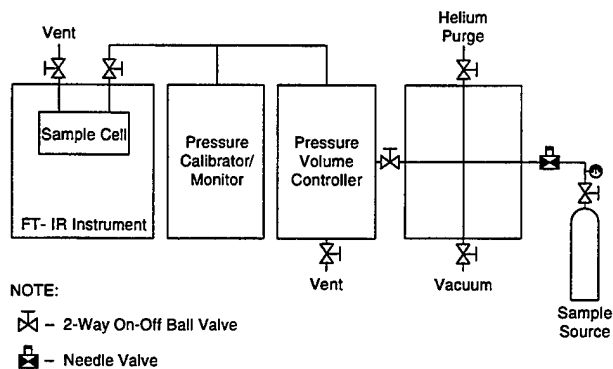


Figure 1. Schematic diagram of gas sampling system

FT-IR spectroscopic data were collected on a Nicolet Model 510 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector operating under OMNIC software. The 100 mm pathlength gas cell was equipped with KBr windows. Spectra of the average of 32 FT-IR scans of each gas sample were collected on all 44 calibration gas mixtures at a resolution of 2 cm^{-1} within the $4,000$ to 400 cm^{-1} wavenumber spectral region at 100, 300, 500, 700, and 1,000 mm Hg absolute cell pressure. The various applied gas pressures served to optimize FT-IR response to the vastly different concentration ranges of the several natural gas components.

V. CHEMOMETRICS

Spectroscopic data were correlated to fuel property values using Galactic Industries' PLSplus chemometric software package within the GRAMS/386 program. Since all gas components will exhibit only carbon-hydrogen bonds in their IR spectra, no regions were excluded from building the correlation models.

The PLS method creates a simplified representation of the spectroscopic data by a process known as spectral decomposition. Good summary treatises of PLS were published by Martens and Naes (11) and by Haaland and Thomas (12, 13). The PLS approach is based on a bilinear modeling method. A precursor to the PLS technique, which is closely linked to the bilinear framework used in PLS, is the latent root regression analysis, formulated in the 1970's by Webster, Gunst, and Mason.(14) The PLS algorithm initially calculates the concentration, or property value, weighted

average spectrum of all the spectra of the fuels in the calibration matrix. This calculation is followed by a computationally intensive procedure, accomplished by performing cross-validation calculations for all samples in the training set. In the cross-validation procedure, a given number of samples, in our case, two, are removed from the calibration data set, and a calibration model, calculated from the remaining samples in the training set, is used to predict the concentration (property value) of the removed samples. The residual errors, or the difference between the predicted and known concentration values, are squared and summed to determine the prediction error. Repeating this cross-validation process for the other samples in the training set results in a refined regression model useful in predicting the properties of unknown fuels. The results of spectral decomposition give one set of scores and one set of factors (loading vectors) for calibration for each component of interest. After a calibration model is established, it may be tested by validation experiments in which the calibration model is applied to similar fuels that were not part of the calibration training set. The predicted property values may then be compared with those derived by established ASTM procedures.

It is critical to establish the correct number of factors to be used in the correlation files, as the predicted fuel property values calculated from the model depend upon the number of factors used in the model. Too few factors will not adequately model the system, while too many factors will introduce noise vectors in the calibration, which will result in less than optimum prediction for samples outside the calibration set. The PLS program by Galactic Industries provides data for selecting the appropriate factor by plotting the prediction residual error sum of squares (PRESS) versus the factor. The factor may be selected for (a) the point at which the PRESS value is at a minimum, normally corresponding to a maximum in the value of the squared correlation coefficient, (b) the point at which the curve indicates that further increase in factors should have negligible effects (a rather arbitrary choice), or (c) a compromise as recommended by Haaland and Thomas. These authors advise the use of F -statistic to arrive at the best compromise in factors. The F -ratio can be calculated as the ratio of the minimum PRESS value to all PRESS values corresponding to fewer factors. As the difference between the minimum PRESS and other PRESS values becomes smaller, the probability, P , that each additional factor provides significant improvement to the model becomes smaller. Haaland and Thomas empirically determined that the optimum number of factors should be at the first PRESS value where the F -ratio probability

drops below 0.75. Initially we used factors corresponding to an F -ratio probability of 0.5, coinciding with a maximum for the squared correlation coefficients. However, to avoid possible overfitting, we standardized on using the compromise value of $P \leq 0.75$, as suggested by Haaland and Thomas.

VI. RESULTS AND DISCUSSION

The 44 synthetic blends of pure components were mixed, as described earlier, following the E-CHIP statistical design guidelines. Concentrations of the individual components, expressed in mole percent (mol%), were available by calculation from the blending partial pressure data and the supporting GC data. The FT-IR spectra were collected at gas sample cell absolute pressures of 100, 300, 500, 700, and 1,000 mm Hg.

The FT-IR spectra of the pure calibration gas components (methane, ethane, propane, and butane), obtained at absolute gas cell pressure of 100 mm Hg, are shown in Figs. B-1 through B-5 in Appendix B. Nitrogen has no active infrared resonance band.

The raw, unmodified spectroscopic data were correlated to both sets of concentration data (i.e., those derived from blending partial pressures and those obtained from GC analysis) for methane, ethane, propane, butane, and the IR-inactive inert diluting nitrogen, using Galactic Industries' PLSplus chemometric software package. Since all gas components exhibit only carbon-hydrogen bonds in their IR spectra, no spectral regions were excluded from building the correlation models. To maintain simplicity of operation without adverse effects on measurement capabilities, baseline segments were similarly not excluded from the calibration files.

Data derived from both the blending partial pressure information and from gas chromatographic data were used for the calibrations. Summary of the data from the pressure and GC-derived calibration experiments is summarized in TABLES A-3 and A-4, respectively. Since, as expected, these two data sets gave essentially identical results, further illustrations are given only for the pressure-derived data.

Figures B-6 and B-7 in Appendix B are barcharts derived from TABLES A-3 and A-4 using factors obtained at minimum PRESS and at $P \leq 0.75$, respectively. These figures show that R-squared data of all of the calibrations are above 0.95, and if the 700 mm Hg data are excluded, all R-squared data are above 0.98.

The excellent agreement between the calibration standards and FT-IR derived concentration data is illustrated in Figs. B-8 through B-12 for methane, ethane, propane, butane, and nitrogen, respectively, using factors at the compromise $P \leq 0.75$. Further information is given in the bracketed area of each figure for (a) the number of factors, F, (b) the sum of the absolute value of the error for all the samples, or total error, TE, (c) squared correlation coefficient, R^2 , and (d) root mean squared difference, RMSD, an indication of the average error in the analysis. Figures B-13 through B-17 show the relationship between the standard error of cross-validation, SECV, and the sample cell pressures for the five components using factors corresponding to (a) minimum PRESS and (b) $P \leq 0.75$ values. As expected, SECV increases with decreasing F. In the case of methane (and the inert, inactive diluent nitrogen), the SECV decreases with increasing pressure while remaining fairly constant with the C_2 - C_4 hydrocarbons. This fact suggests that improved analytical data may be obtained for methane at elevated pressures. However, using a 100-mm gas cell, at elevated pressures all these hydrocarbons displayed spectra with some peaks in the non-linear range of the absorbance, indicating detector overload. For instance, such detector overload may be observed in case of methane for each of the two characteristic resonance bands, i.e., at $3,014\text{ cm}^{-1}$ due to asymmetric stretching and at $1,303\text{ cm}^{-1}$, the result of asymmetric bending. Note, however, the reduced error (SECV) for methane at the higher calibration pressures (concentrations) in comparison with those of the other components.

As discussed earlier, to alleviate computational artifacts, it is desirable to use the smallest number of factors in the model that yields acceptable data. During our calibrations, we allowed the use of up to 20 factors. Factors associated with minimum in PRESS values or at $P \leq 0.75$ were lowest for all five components at sample cell pressures of 100 mm Hg. These data are shown in Figs. B-18 and B-19. Depending upon the outcome of future experiments, we are collecting our FT-IR spectra at 100 mm Hg absolute cell pressure and using the factors obtained at $P \leq 0.75$ to determine the C_1 - C_4 composition of natural gas.

It should be noted that computer output may also show composition related properties, e.g., the heat of combustion, carbon-to-hydrogen ratio, density, etc., that are key properties used for air/fuel ratio management in engines, or for gas custody transfer.

Following these calibration studies on synthetic natural gas compositions, the method will be validated by analyzing a large number of independently obtained and analyzed natural gas samples. In the unlikely event that the presented simplified model would be insufficient for the practical description of natural gas samples, further work may be performed to include the trace components, e.g., higher molecular weight hydrocarbons, carbon dioxide, hydrogen sulfide, in the calibration matrix, followed by new validation experiments.

VII. CONCLUSIONS

A fast experimental protocol was established for the simultaneous determination of methane, ethane, propane, and butane in nitrogen from Fourier transform infrared spectra. The method is based on correlations established between known gas compositions and their FT-IR spectra. The spectra were collected in the spectral region of 4,000 to 400 cm^{-1} in a 100-mm pathlength gas sample cell operating at 100 mm Hg pressure. Correlation between blending partial pressure or GC-based analysis and FT-IR data produced squared correlation coefficients (R^2) in excess of 0.98. Total required analytical time is approximately 1 to 2 minutes.

VIII. REFERENCES

1. Liss, W.E. and Thrasher, W.H., "Natural Gas as a Stationary Engine and Vehicular Fuel," SAE Paper No. 912364, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, 1991.
2. King, S.R., "The Impact of Natural Gas Composition on Fuel Metering and Engine Operational Characteristics," SAE Paper No. 920593, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, 1992.

3. Kubesh, J., King, S.R., and Liss, W.E., "Effect of Gas Composition on Octane Number of Natural Gas Fuels," SAE Paper No. 922359, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, 1992.
4. Skrbic, B.D. and Cvejanov, J.D., "Comparative Analysis of Methods for Determination of Calorific Values of Natural Gas Mixtures," *Fuel Processing Technology*, **28**, pp. 307-314, 1991.
5. Brown, C.W. and Lo, S-C., *Appl. Spec.*, **47**, No. 6, pp. 812-815, 1993.
6. Westbrook, S.R., "Army Use of Near-Infrared Spectroscopy to Estimate Selected Properties of Compression Ignition Fuels," SAE Paper No. 930734, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, 1993.
7. Westbrook, S.R., "The Feasibility of Using Near-Infrared Spectrometer to Estimate Selected Properties of Natural Gas," SAE Paper No. 940762, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, 1994.
8. Fodor, G.E. and Kohl, K.B., "Analysis of Middle Distillate Fuels by Midband Infrared Spectroscopy," *Energy & Fuels*, **7**, No. 5, pp. 598-601, 1993.
9. Fodor, G.E., "Analysis of Petroleum Fuels by Midband Infrared Spectroscopy," SAE Technical Paper No. 941019, Presented at the SAE 1994 International Congress & Exposition, Detroit, Michigan, February 28-March 3, 1994.
10. Fodor, G.E., Kohl, K.B., and Mason, R.L., "Analysis of Gasolines by FT-IR Spectroscopy," *Analytical Chemistry*, **68**, pp. 23-30, 1996.
11. Martens, H.A. and Naes, T., *Multivariate Calibration*, Wiley, New York, 1989.
12. Haaland, D. and Thomas, E.V., *Analytical Chemistry*, **60**, pp. 1193-1202, 1988.
13. Haaland, D. and Thomas, E.V., *Analytical Chemistry*, **60**, pp. 1202-1208, 1988.
14. Webster, J.T., Gunst, R.F., and Mason, R.L., *Technometrics*, **16**, pp. 513-522, 1974.

APPENDIX A

Tables

TABLE A-1. Calibration Gas Mixture Composition (mol%)

<u>Methane</u>	<u>Ethane</u>	<u>Propane</u>	<u>Butane</u>	<u>Nitrogen</u>
61.13	2.77	1.42	0.00	34.68
100.00	0.00	0.00	0.00	0.00
74.66	0.00	0.00	0.00	25.34
63.88	0.00	21.69	0.00	14.50
61.13	9.97	3.61	0.00	25.29
49.98	10.65	0.00	5.02	34.36
54.86	10.17	0.00	0.00	34.97
86.58	0.00	8.30	5.11	0.00
49.60	9.90	8.23	3.63	28.64
75.10	11.58	8.37	4.95	0.00
49.04	0.00	25.97	3.91	21.08
82.99	7.31	0.00	0.00	9.71
89.98	10.02	0.00	0.00	0.00
49.87	2.92	30.04	0.00	17.18
59.19	6.25	12.60	5.00	16.96
49.96	9.77	22.97	0.00	17.30
57.69	9.47	28.11	4.73	0.00
100.00	0.00	0.00	0.00	0.00
53.57	5.03	3.77	2.55	35.90
49.73	0.00	15.18	0.00	35.08
96.26	0.00	0.00	3.74	0.00
86.21	10.12	0.00	3.66	0.00
49.84	7.32	12.09	0.00	30.75
69.70	0.00	30.30	0.00	0.00
53.70	0.00	30.12	1.41	14.76
71.31	0.00	0.00	3.61	25.08
49.67	0.00	30.40	5.10	14.96
49.80	0.00	10.03	5.10	35.07
86.13	0.00	8.44	0.00	5.43
92.19	2.76	0.00	5.06	0.00
75.12	0.00	0.00	0.00	24.88
63.87	5.02	14.02	0.00	17.08
68.10	10.36	21.54	0.00	0.00
85.03	0.00	0.00	5.09	9.87
59.79	0.00	0.00	5.25	34.96
52.84	10.01	29.94	0.00	7.21
77.50	4.74	15.25	2.52	0.00
66.11	0.00	29.07	4.82	0.00
66.83	3.01	0.00	4.99	25.16
49.67	10.25	0.00	5.07	35.01
54.72	10.06	30.21	5.02	0.00
74.38	10.14	0.00	4.97	10.52
63.14	10.16	0.00	1.39	25.30
49.87	7.24	29.81	3.66	9.42

TABLE A-2. Gas Chromatographic Conditions

Instrument:	Hewlett-Packard model 5890 Series II
Detector:	Thermal conductivity, 250°C
Injector:	Gas sampling valve, 0.25 mL sample loop, 125°C
Column:	Porapak QS, 40/60 mesh, 4.6 m × 3.2 mm (15 ft × 1/8 in.) stainless steel packed column
Carrier Gas:	Helium
Flow Rates:	Analytical: 20 mL/min Reference: 30 mL/min
Column Program:	Initial temperature: 100°C Initial hold: 0 min Rate: 20°C/min Final temperature: 225°C Final hold: 4 min
Total Analytical Time Required:	Approx. 15 min

**TABLE A-3. FT-IR Calibration for Natural Gas Components
Based on Blending Partial Pressures of 44 Synthetic Standards**

Compound	P (abs) mm Hg	at min. PRESS			at P ≤ 0.75		
		F	SECV	R ²	F	SECV	R ²
methane	100	4	1.652	0.9891	3	1.804	0.9872
	300	7	1.350	0.9928	6	1.410	0.9922
	500	11	1.184	0.9944	8	1.301	0.9932
	700	11	1.138	0.9948	8	1.234	0.9940
	1000	13	0.664	0.9982	11	0.714	0.9980
ethane	100	8	0.179	0.9985	7	0.198	0.9981
	300	9	0.254	0.9969	7	0.268	0.9966
	500	9	0.193	0.9982	8	0.214	0.9978
	700	12	0.200	0.9981	10	0.218	0.9977
	1000	20	0.138	0.9991	18	0.151	0.9989
propane	100	11	0.350	0.9992	5	0.365	0.9991
	300	20	0.479	0.9984	19	0.522	0.9981
	500	20	0.376	0.9990	17	0.414	0.9988
	700	18	0.650	0.9971	15	0.711	0.9965
	1000	20	0.469	0.9985	17	0.509	0.9982
butane	100	13	0.152	0.9956	11	0.158	0.9952
	300	18	0.223	0.9906	17	0.228	0.9903
	500	20	0.257	0.9881	18	0.280	0.9861
	700	20	0.442	0.9627	17	0.477	0.9565
	1000	20	0.228	0.9906	18	0.251	0.9887
nitrogen	100	4	1.808	0.9818	4	1.808	0.9818
	300	7	1.400	0.9890	6	1.453	0.9882
	500	9	1.333	0.9901	8	1.405	0.9890
	700	10	1.077	0.9935	8	1.143	0.9929
	1000	8	0.856	0.9960	7	0.898	0.9958

Notes:

P	Absolute pressure, mm Hg
PRESS	Predicted Residual Error Sum of Squares
F	Factors in calibration model
SECV	Standard Error of Cross Validation
R ²	Squared correlation coefficient

**TABLE A-4. FT-IR Calibration on Natural Gas Components
Based on GC Analysis of 44 Synthetic Blend of Standards**

<u>Compound</u>	<u>P (abs) mm Hg</u>	<u>at min. PRESS</u>			<u>at P ≤ 0.75</u>		
		<u>F</u>	<u>SECV</u>	<u>R²</u>	<u>F</u>	<u>SECV</u>	<u>R²</u>
methane	100	4	1.545	0.9905	4	1.545	0.9905
	300	7	1.350	0.9928	6	1.410	0.9922
	500	10	1.230	0.9940	8	1.319	0.9931
	700	10	0.962	0.9964	8	1.032	0.9960
	1000	13	0.823	0.9973	8	0.899	0.9969
ethane	100	15	0.183	0.9984	12	0.202	0.9980
	300	9	0.254	0.9969	7	0.268	0.9966
	500	20	0.193	0.9982	16	0.205	0.9980
	700	16	0.224	0.9976	14	0.246	0.9971
	1000	10	0.227	0.9975	8	0.238	0.9973
propane	100	5	0.488	0.9983	4	0.524	0.9981
	300	20	0.479	0.9984	19	0.522	0.9981
	500	20	0.432	0.9987	17	0.467	0.9985
	700	20	0.709	0.9965	16	0.758	0.9960
	1000	19	0.498	0.9983	16	0.524	0.9981
butane	100	14	0.152	0.9957	11	0.158	0.9953
	300	18	0.223	0.9906	17	0.228	0.9903
	500	20	0.305	0.9828	14	0.335	0.9798
	700	20	0.470	0.9582	17	0.501	0.9526
	1000	19	0.282	0.9855	16	0.300	0.9836
nitrogen	100	4	1.775	0.9823	4	1.775	0.9823
	300	7	1.400	0.9890	6	1.453	0.9882
	500	10	1.263	0.9910	8	1.364	0.9895
	700	10	1.040	0.9940	8	1.075	0.9937
	1000	10	0.912	0.9953	7	0.959	0.9952

Notes:

P	Absolute pressure, mm Hg
PRESS	Predicted Residual Error Sum of Squares
F	Factors in calibration model
SECV	Standard Error of Cross Validation
R ²	Squared correlation coefficient

APPENDIX B

Figures

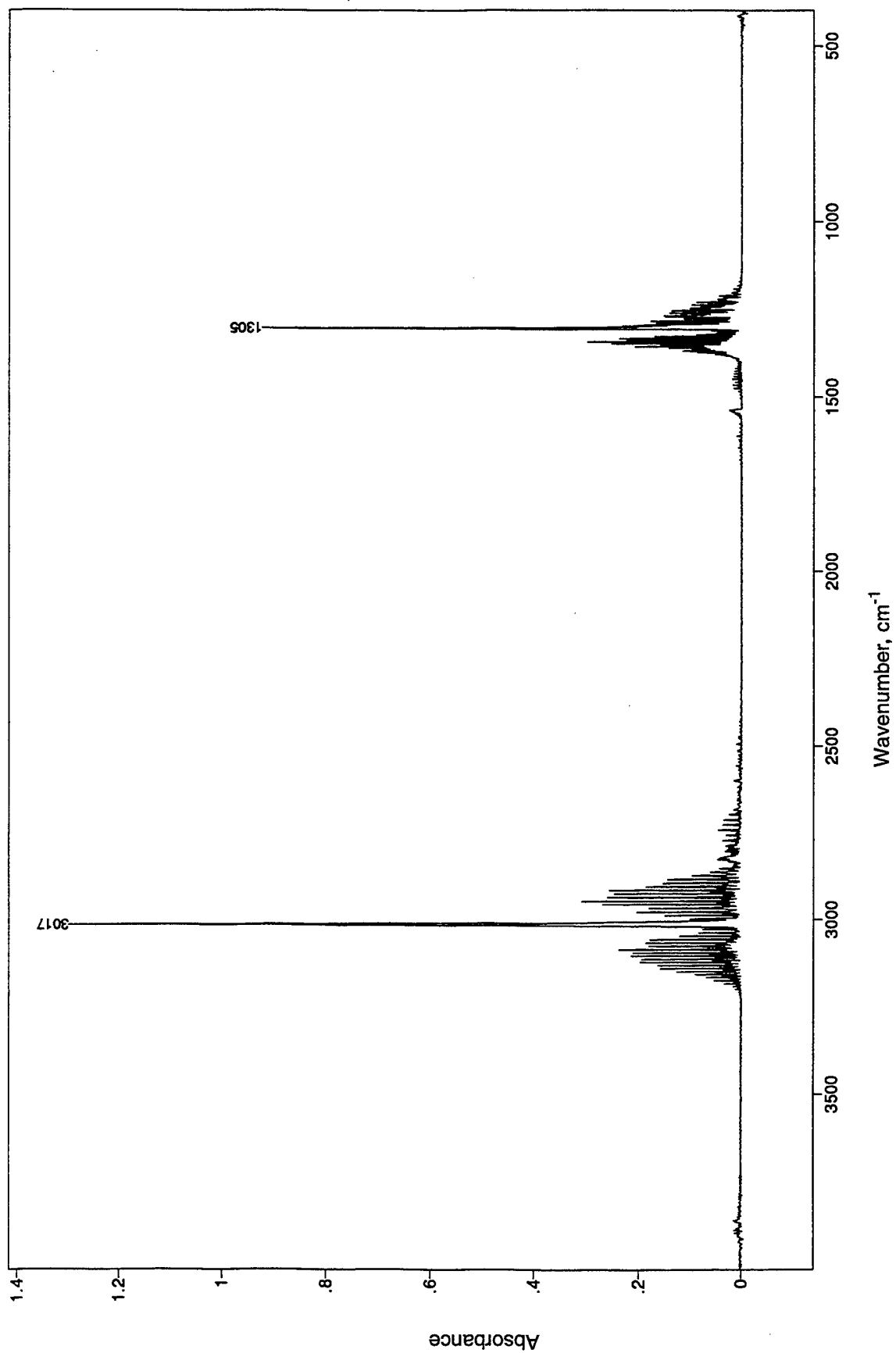


Figure B-1. FT-IR spectrum of methane ($P = 100$ mm Hg; Resolution = 2 cm^{-1})

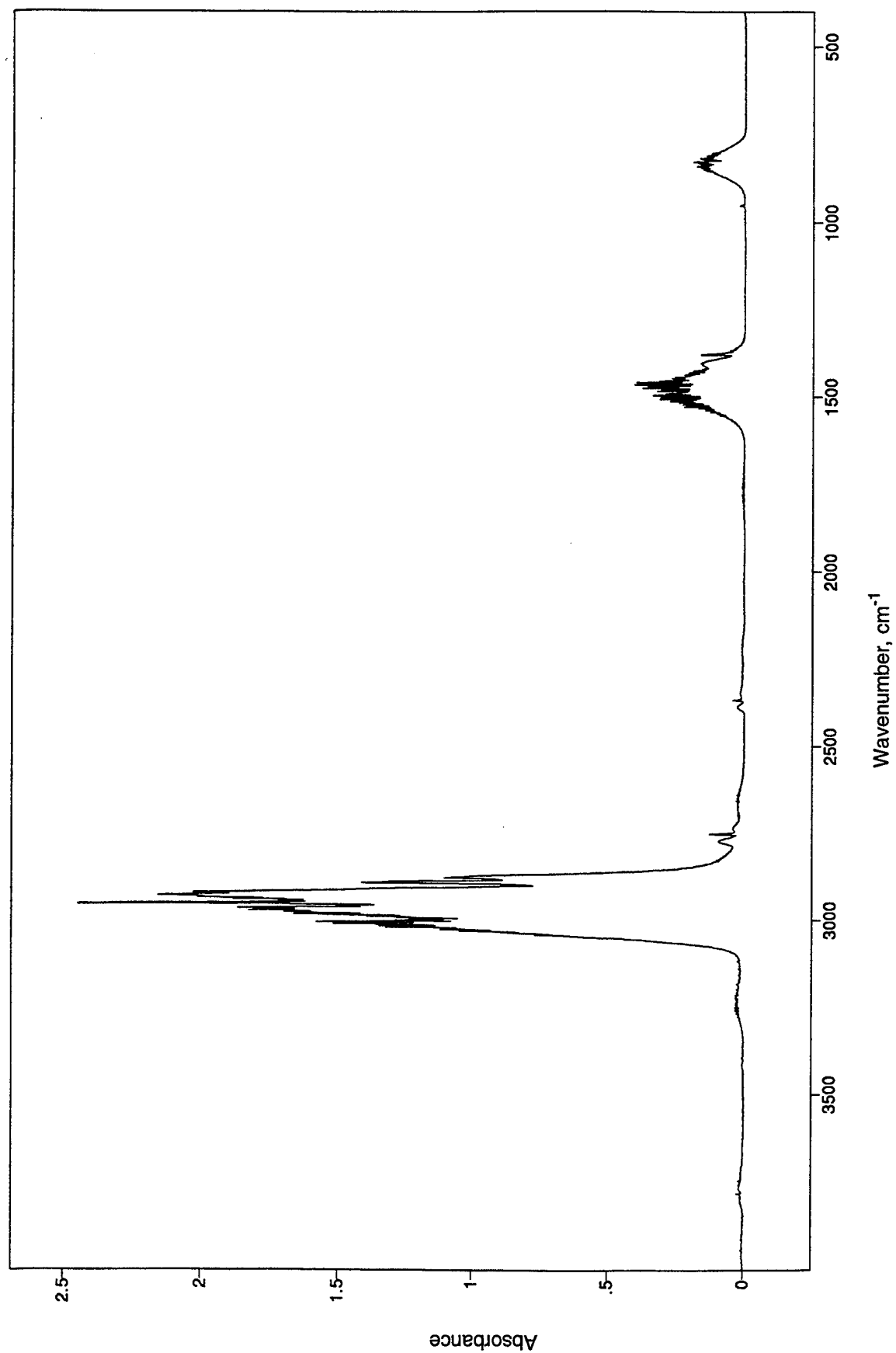


Figure B-2. FT-IR spectrum of ethane ($P = 100$ mm Hg; Resolution = 2 cm^{-1})

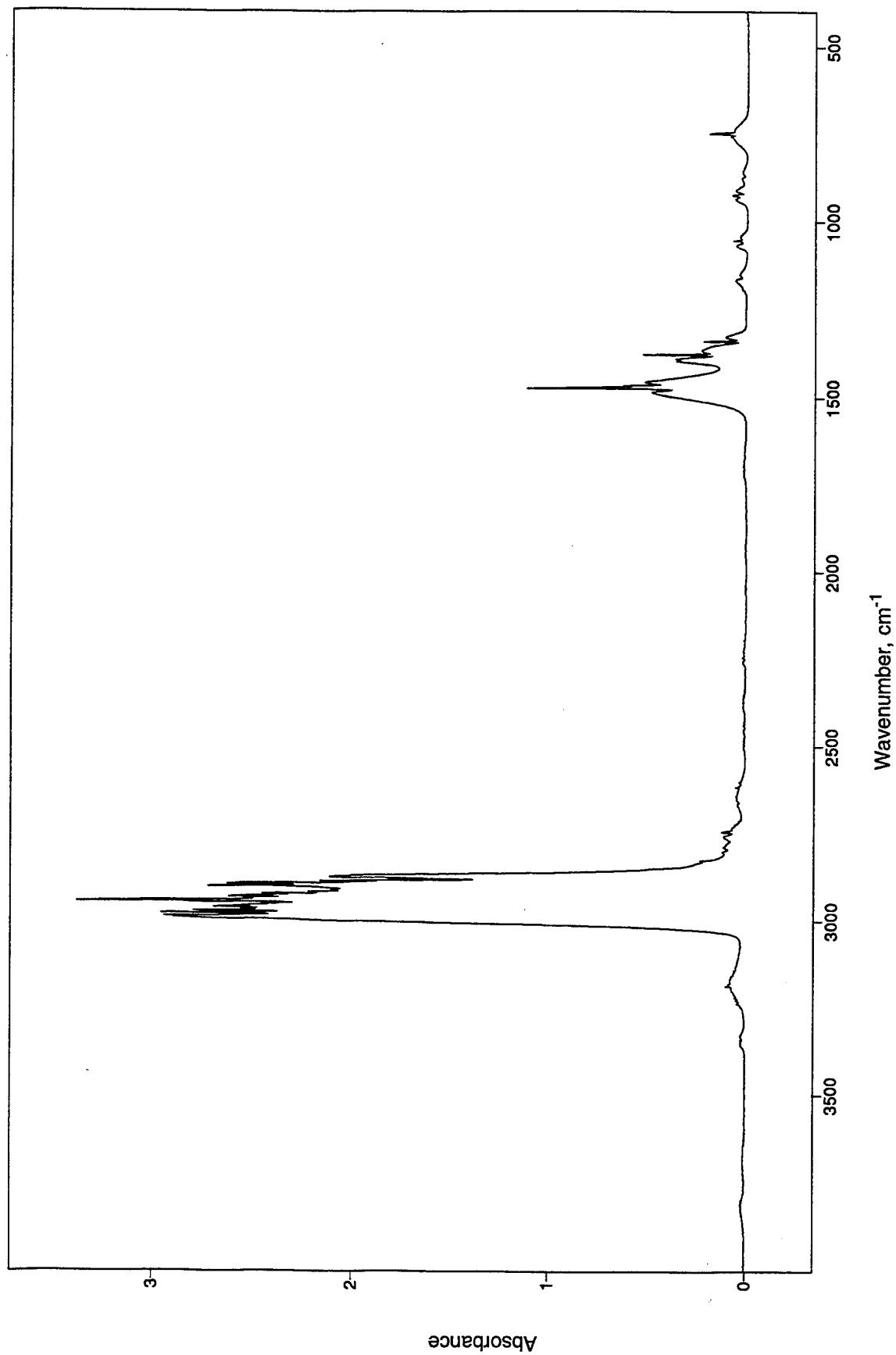


Figure B-3. FT-IR spectrum of propane ($P = 100$ mm Hg; Resolution = 2 cm^{-1})

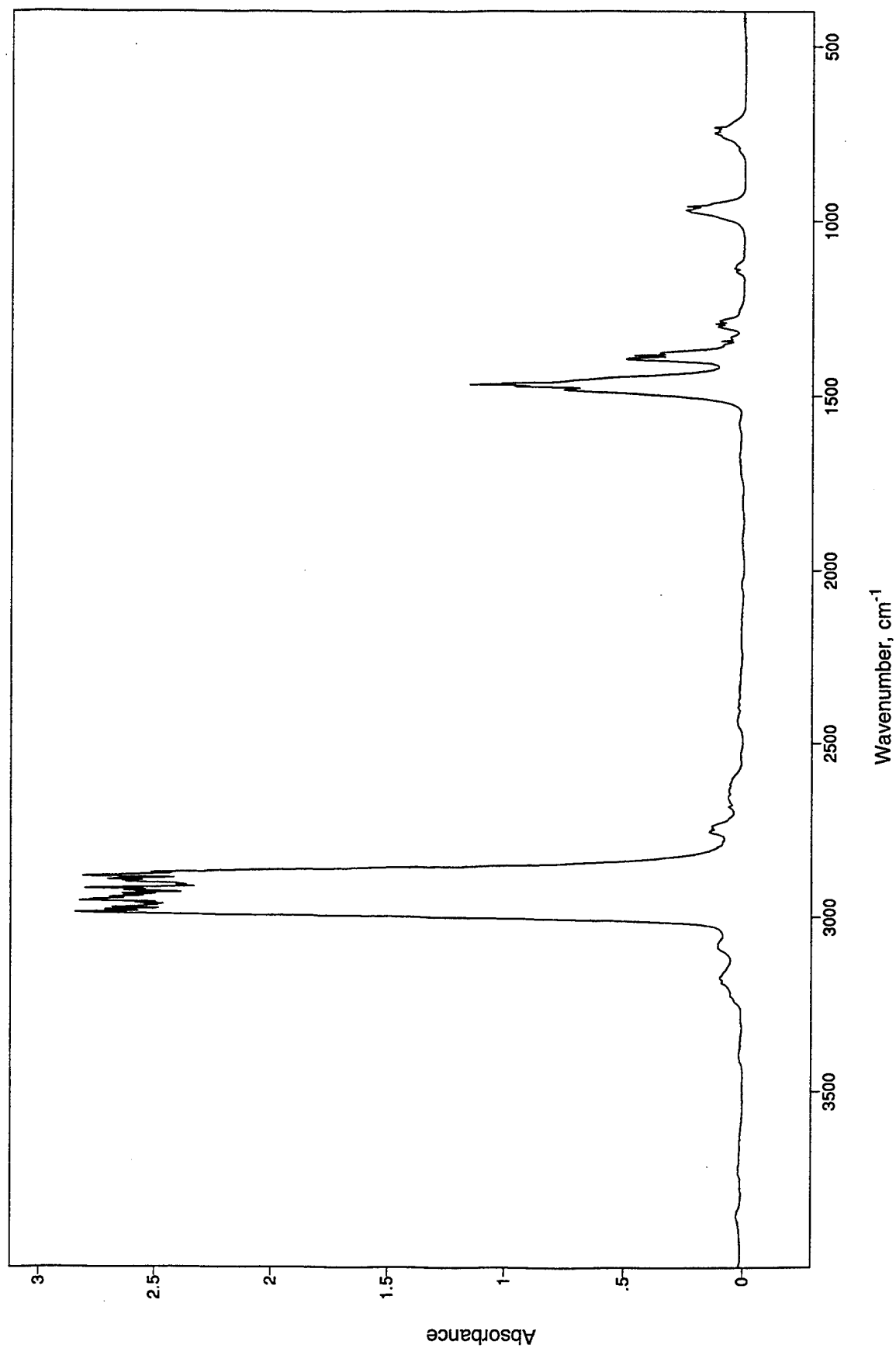


Figure B-4. FT-IR spectrum of butane ($P = 100$ mm Hg; Resolution = 2 cm^{-1})

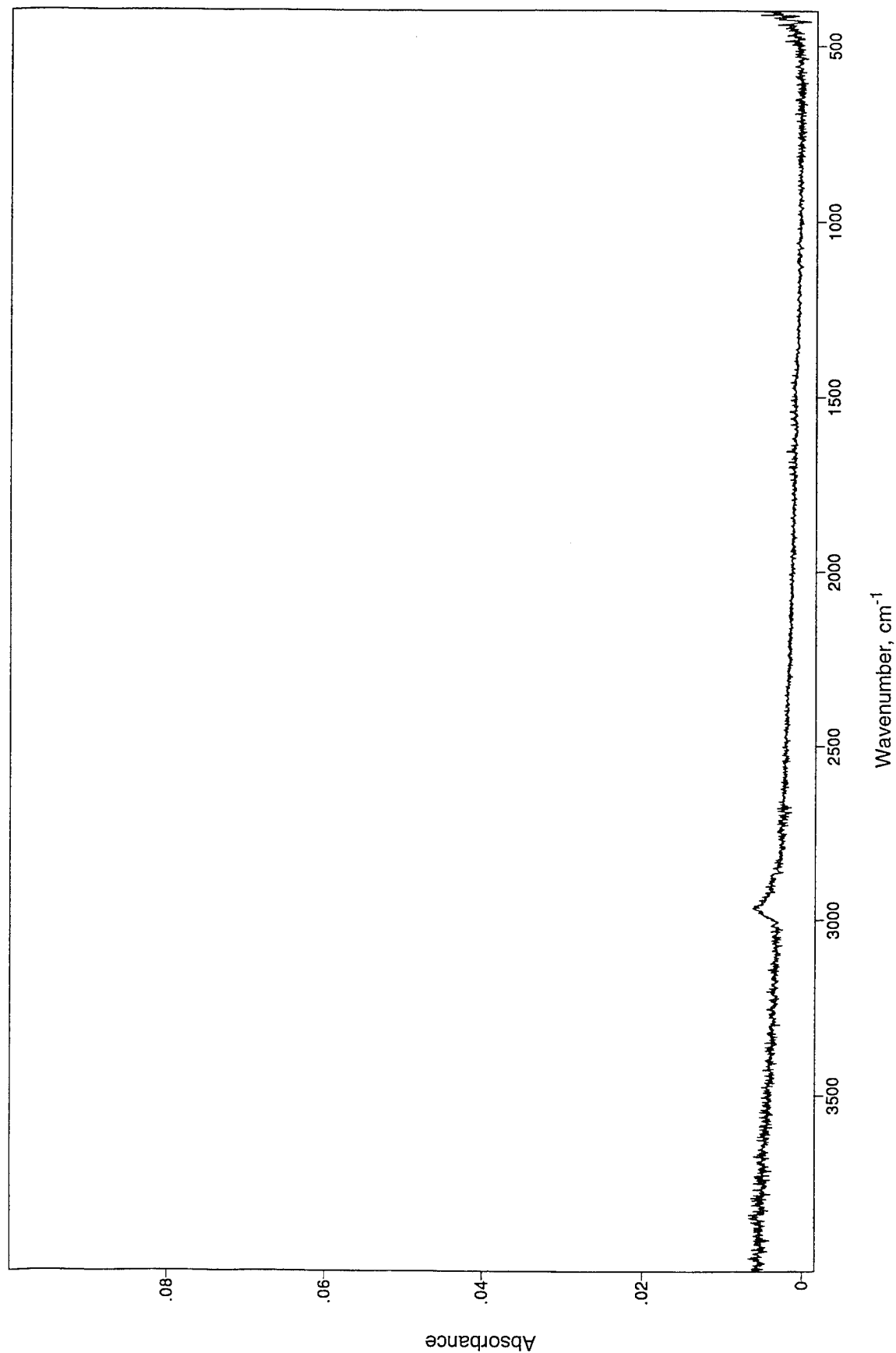


Figure B-5. FT-IR trace of nitrogen (P = 100 mm Hg; Resolution = 2 cm⁻¹)

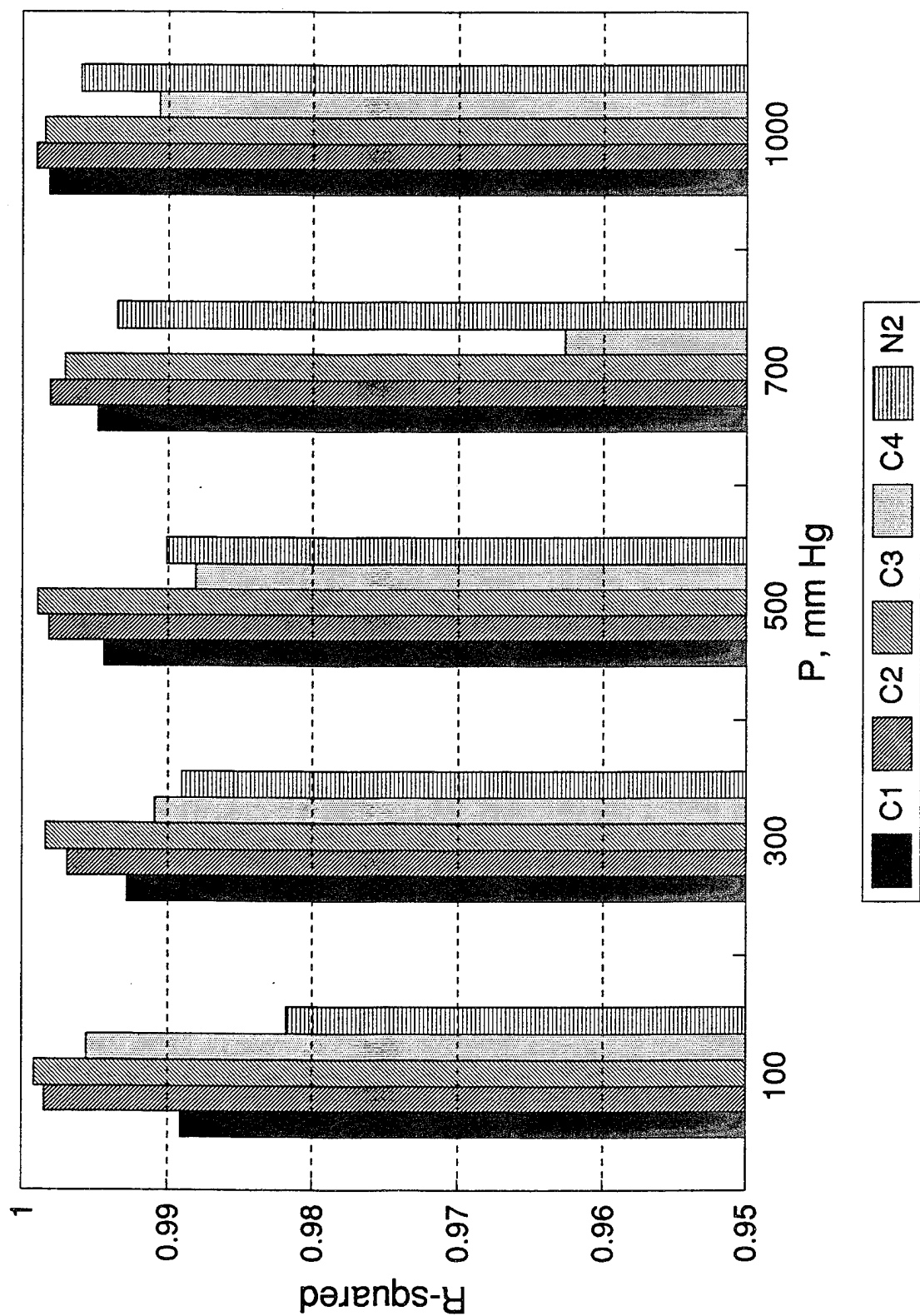


Figure B-6. Effect of cell pressure on correlations with measured natural gas component concentrations
(F at min. PRESS; pressure-based)

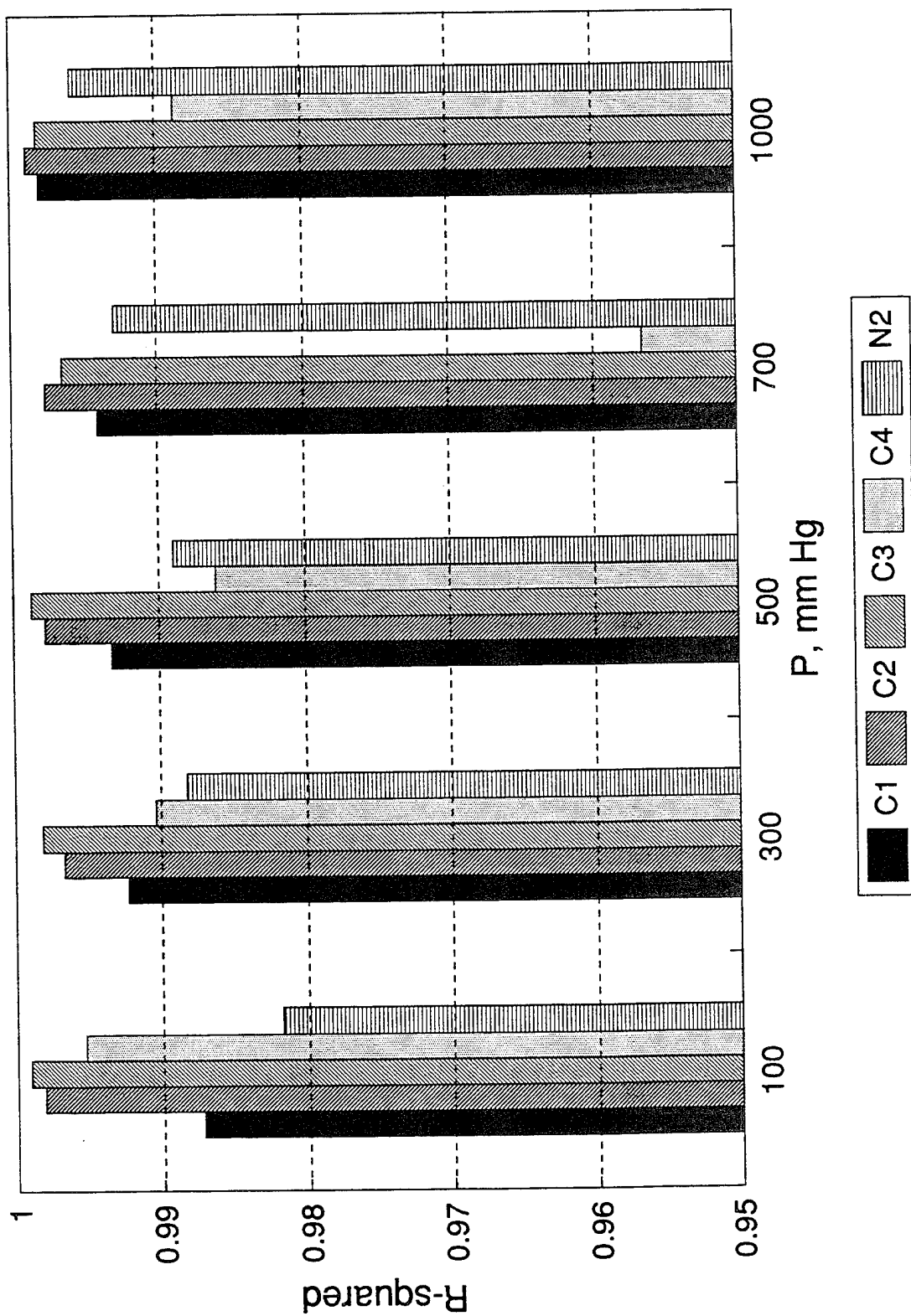


Figure B-7. Effect of cell pressure on correlations with measured natural gas component concentrations
 (F at $P \leq 0.75$; pressure-based)

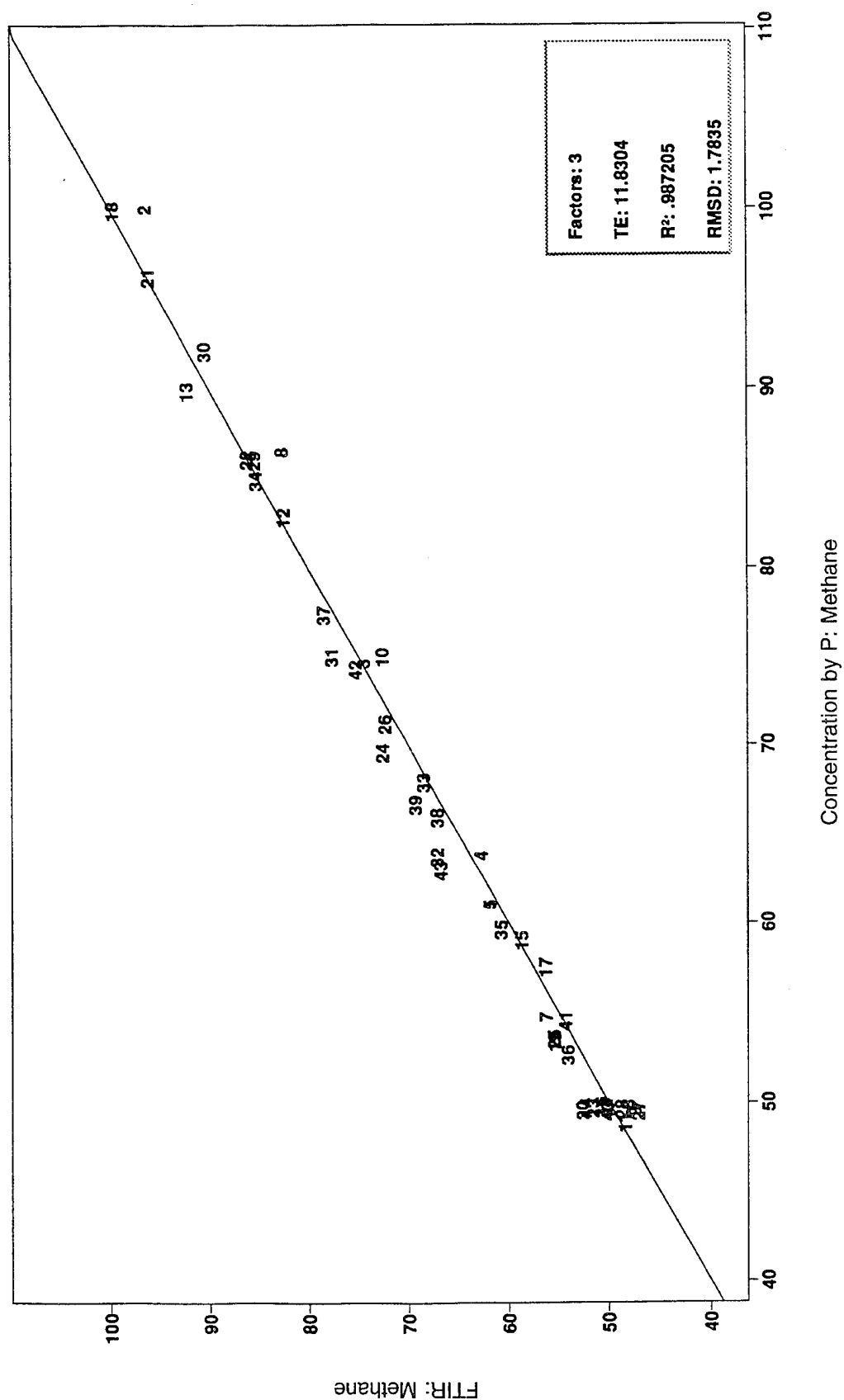


Figure B-8. Calibration for methane at cell P = 100 mm Hg (pressure-based analysis)

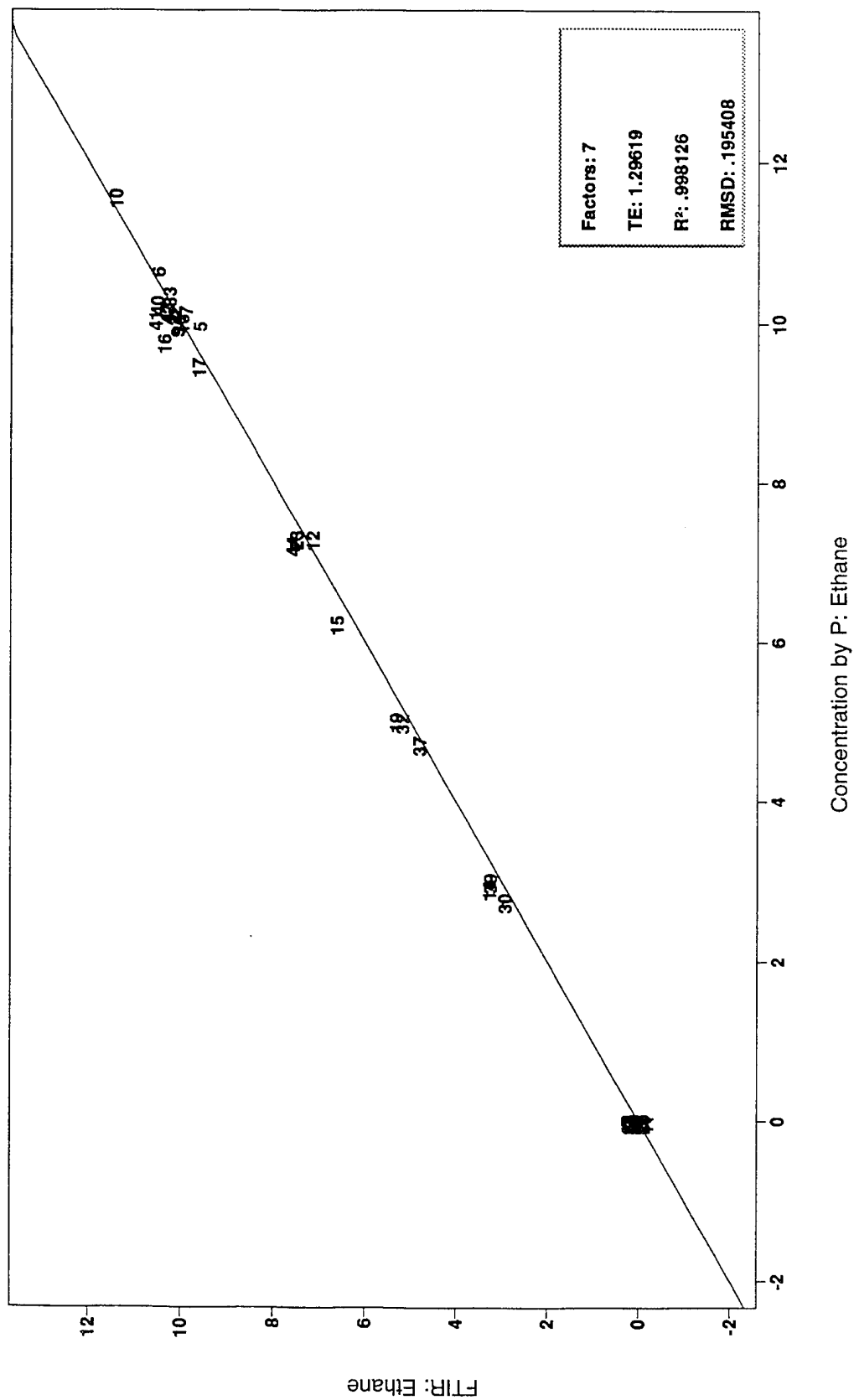


Figure B-9. Calibration for ethane at cell P = 100 mm Hg (pressure-based analysis)

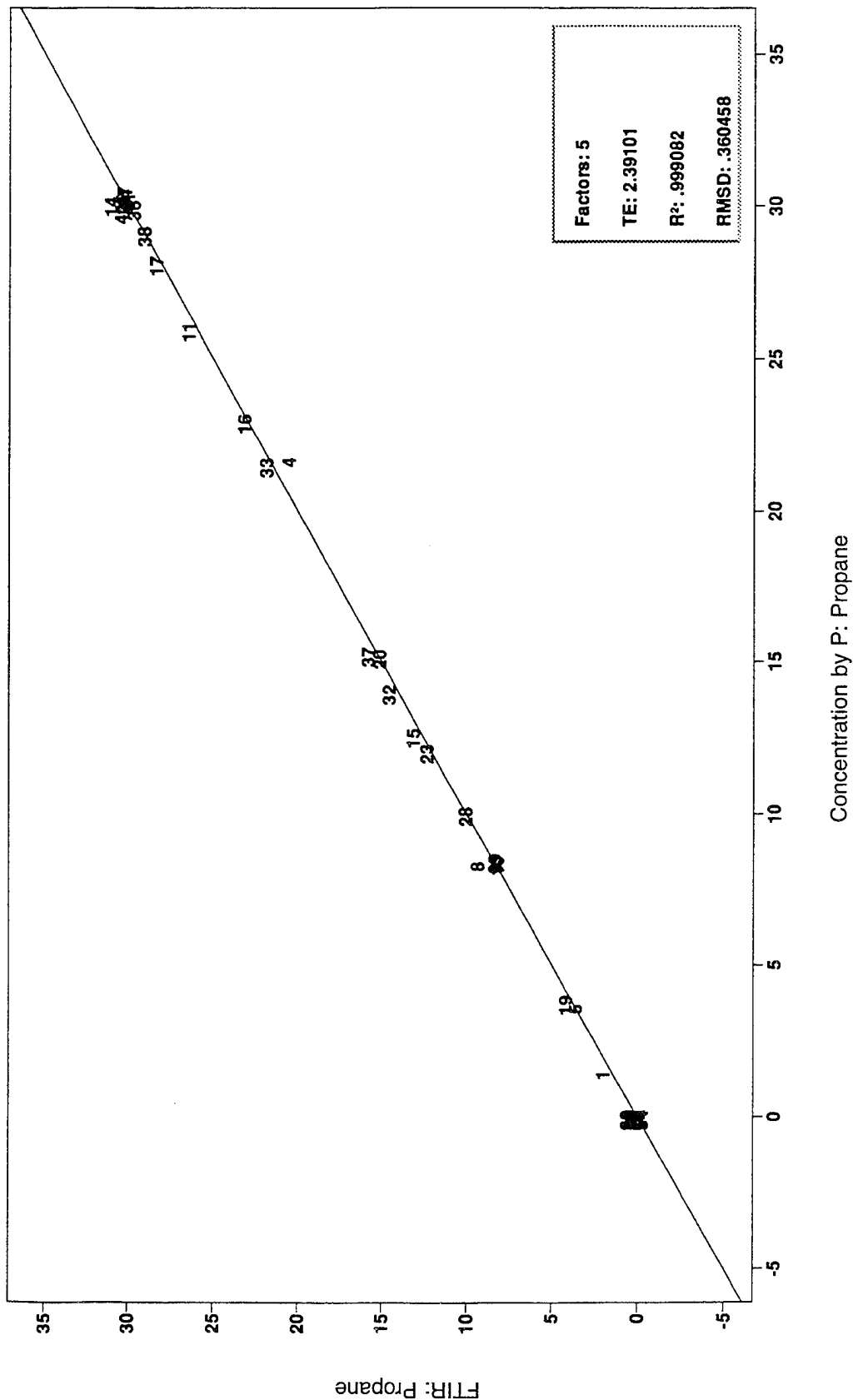


Figure B-10. Calibration for propane at cell P = 100 mm Hg (pressure-based analysis)

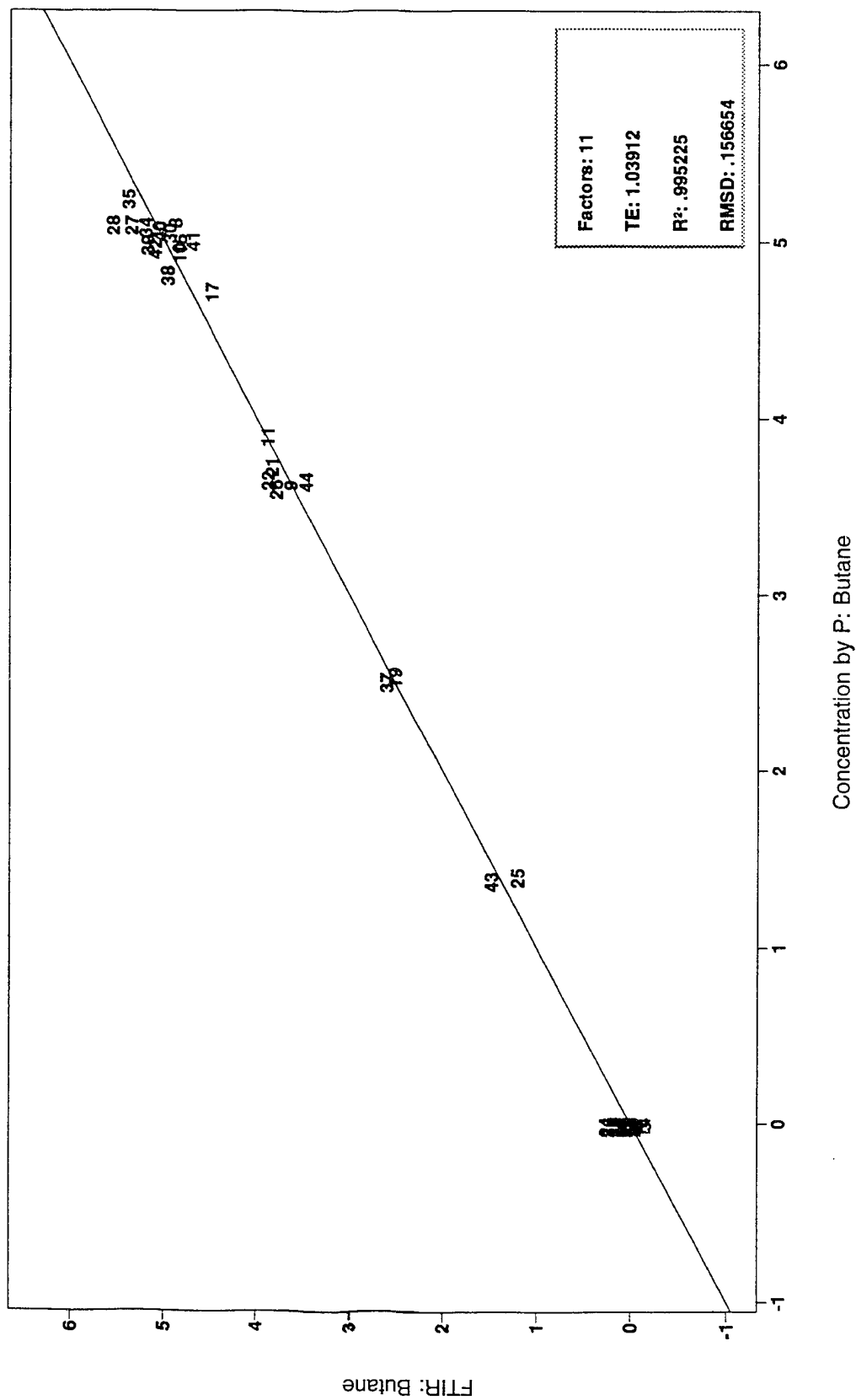


Figure B-11. Calibration for butane at cell P = 100 mm Hg (pressure-based analysis)

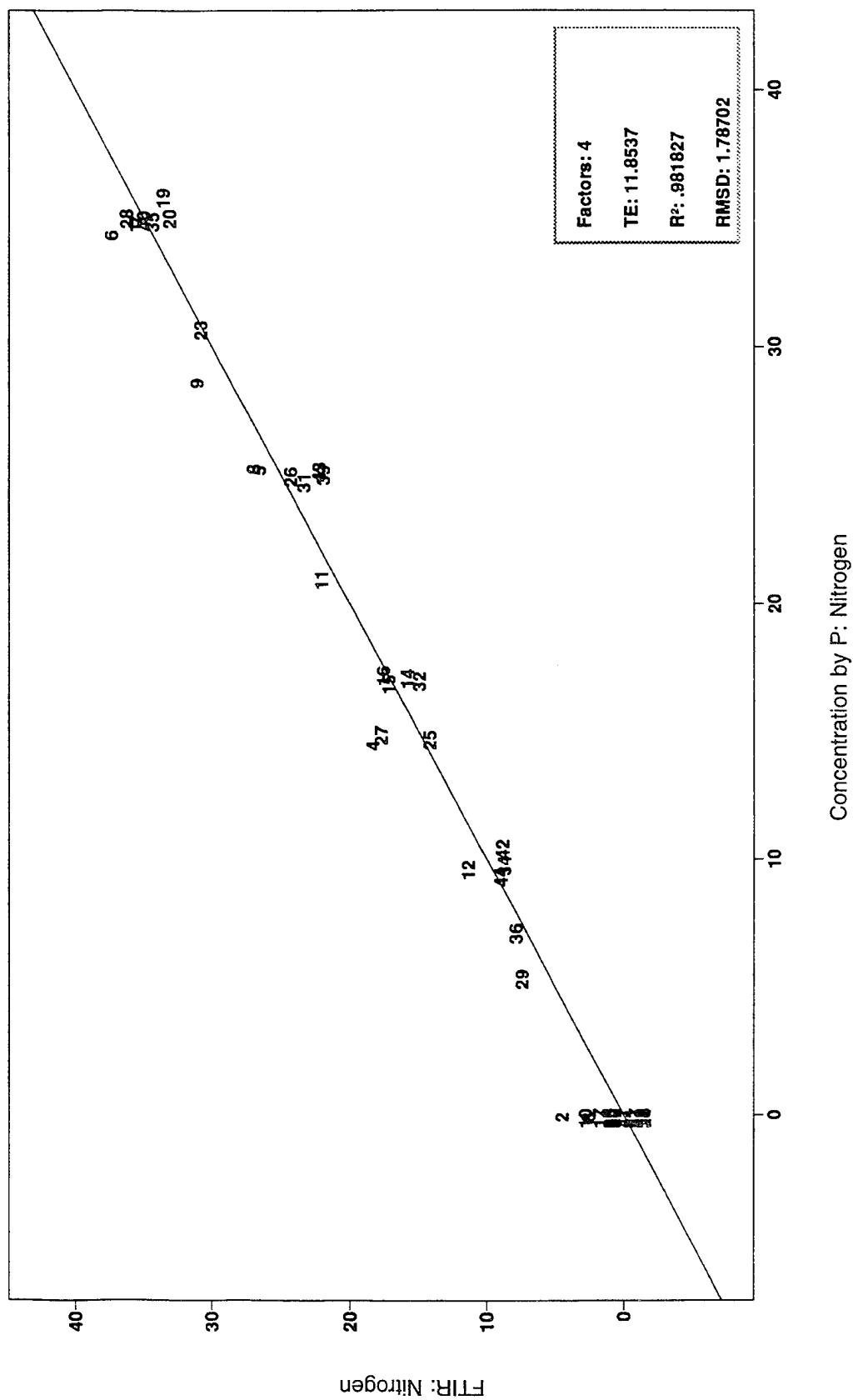


Figure B-12. Calibration for nitrogen at cell P = 100 mm Hg (pressure-based analysis)

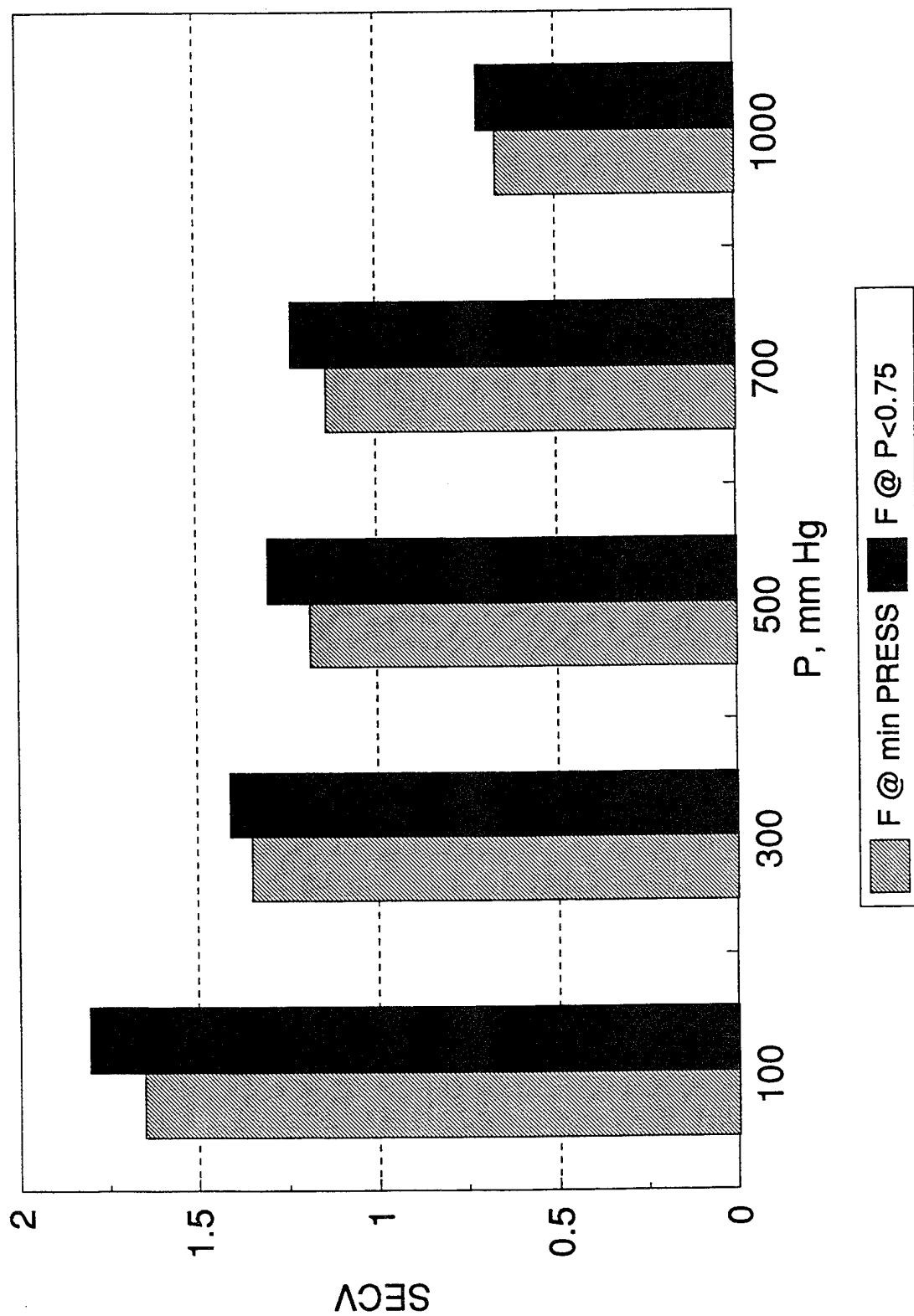


Figure B-13. Effect of cell pressure on the standard error in the analysis for methane (pressure-based calibration data)

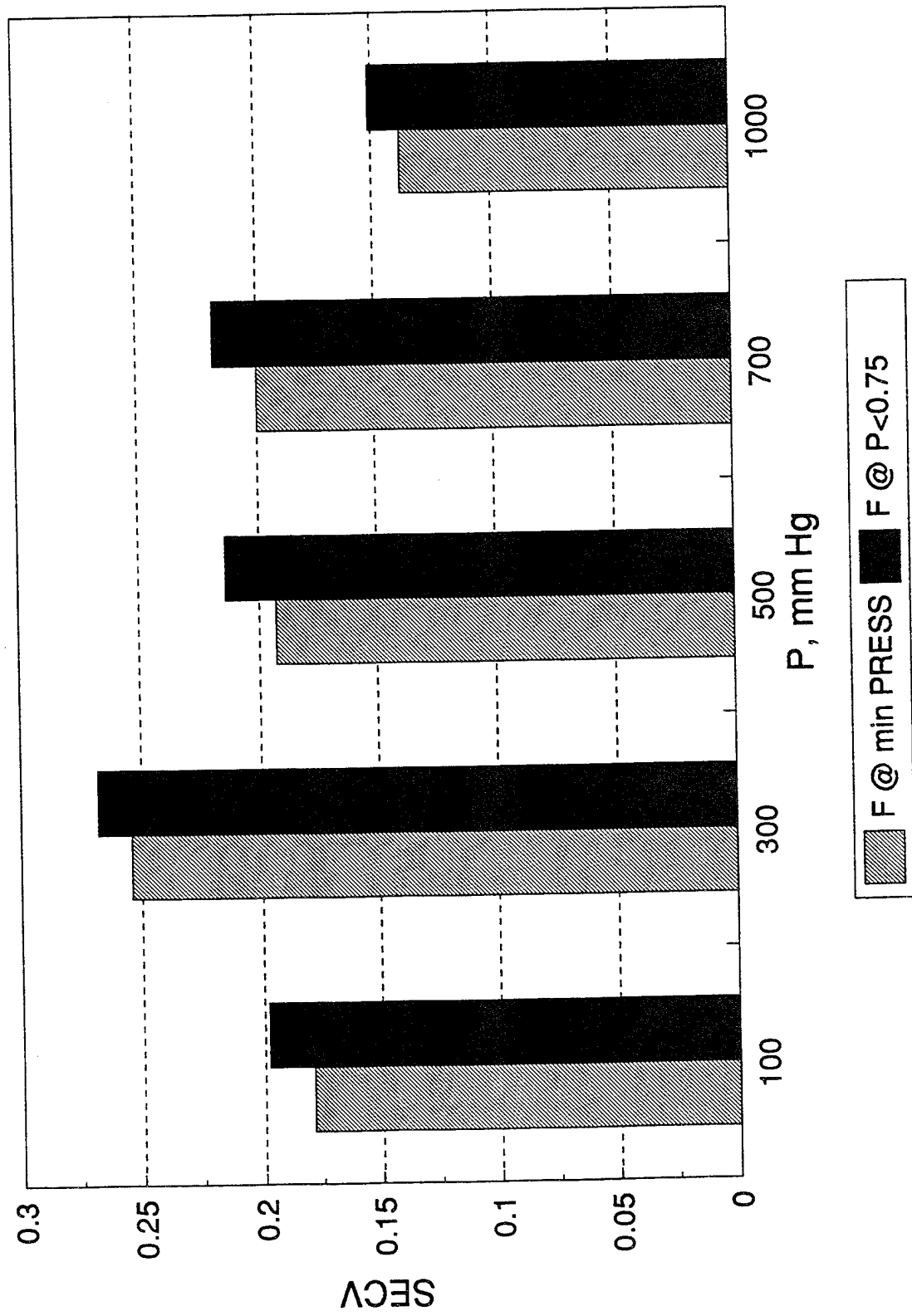


Figure B-14. Effect of cell pressure on the standard error in the analysis for ethane (pressure-based calibration data)

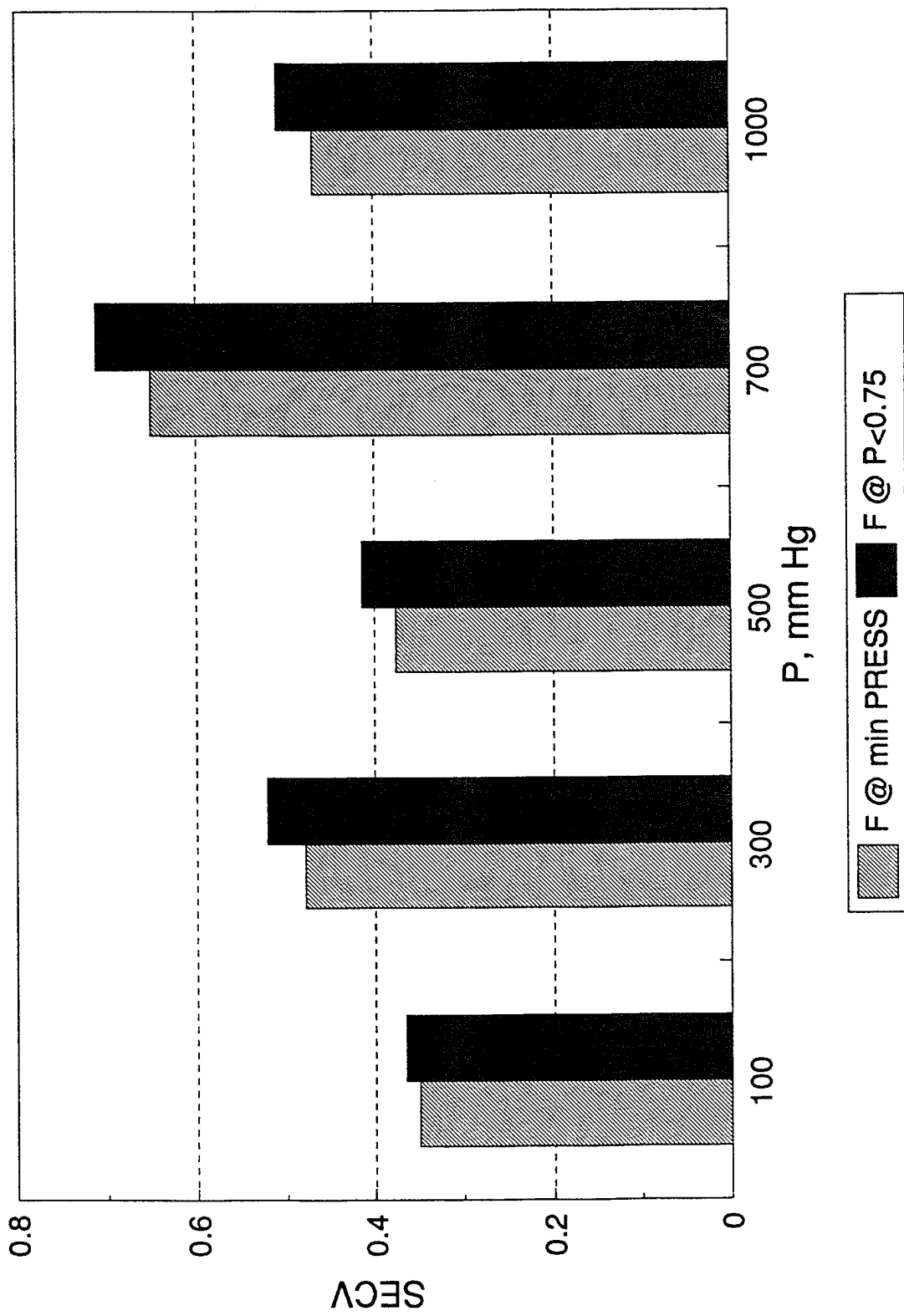


Figure B-15. Effect of cell pressure on the standard error in the analysis for propane (pressure-based calibration data)

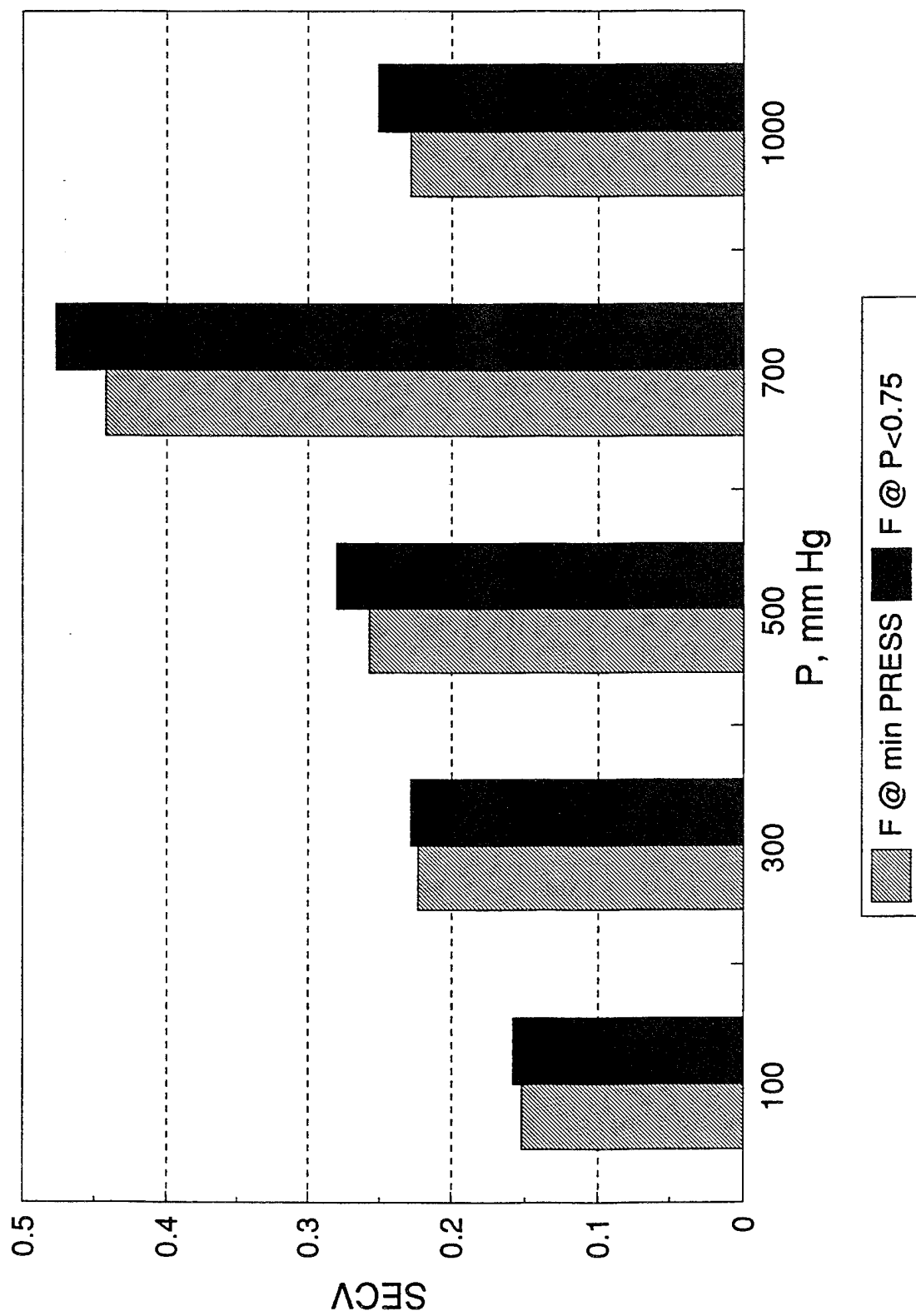


Figure B-16. Effect of cell pressure on the standard error in the analysis for butane (pressure-based calibration data)

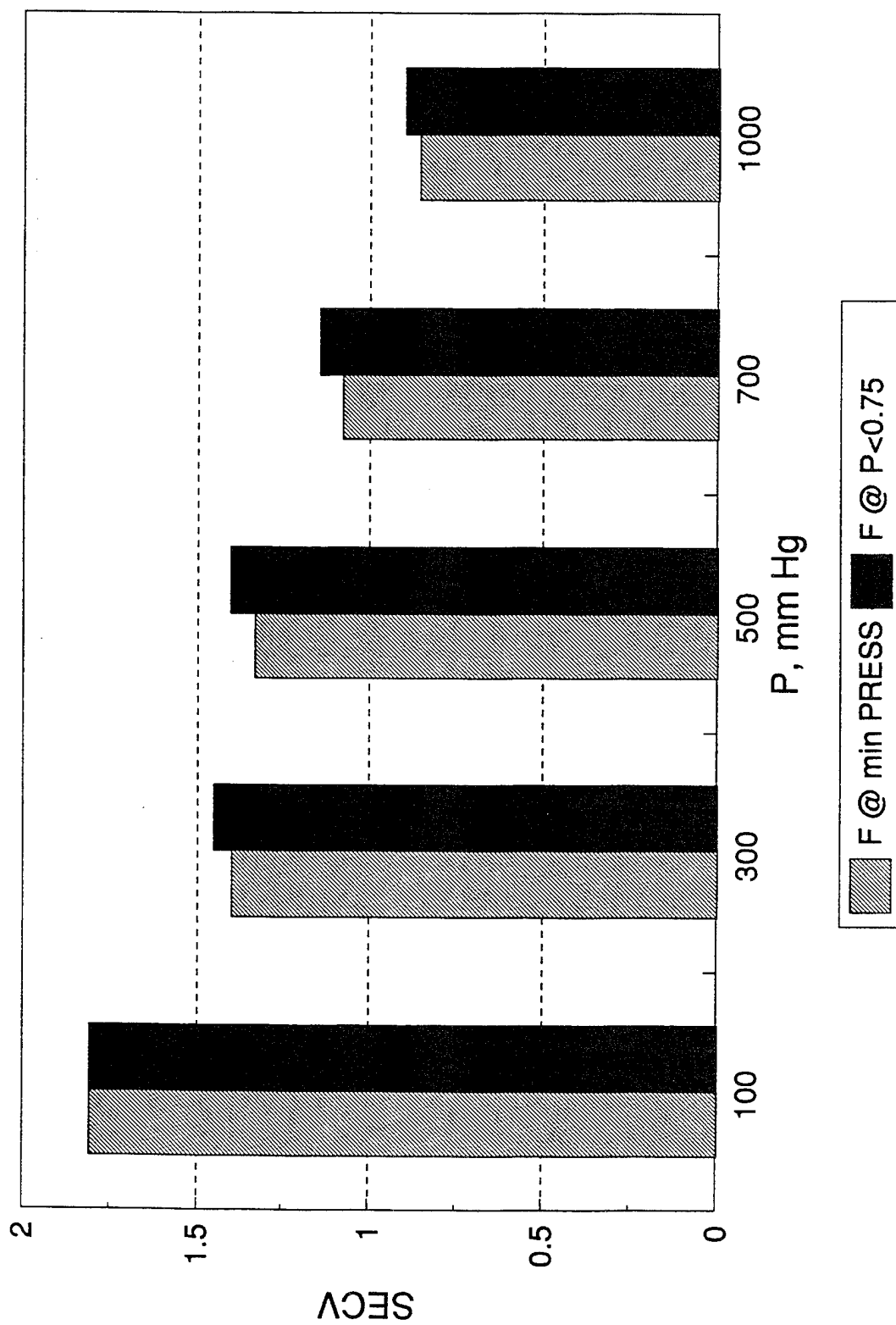


Figure B-17. Effect of cell pressure on the standard error in the analysis for nitrogen (pressure-based calibration data)

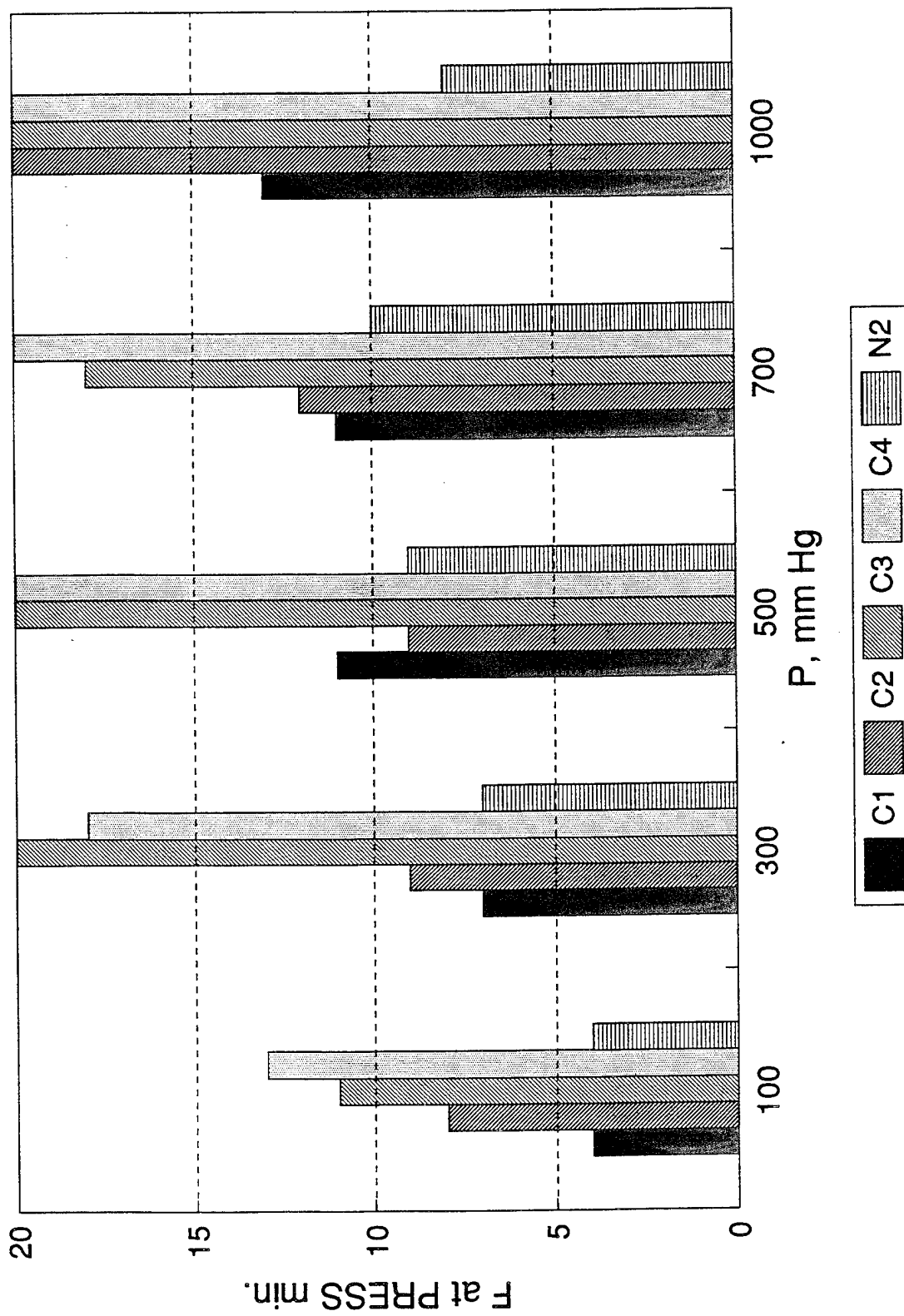


Figure B-18. Analysis of natural gas by FT-IR [(F at PRESS min. vs. pressure (P-based))]

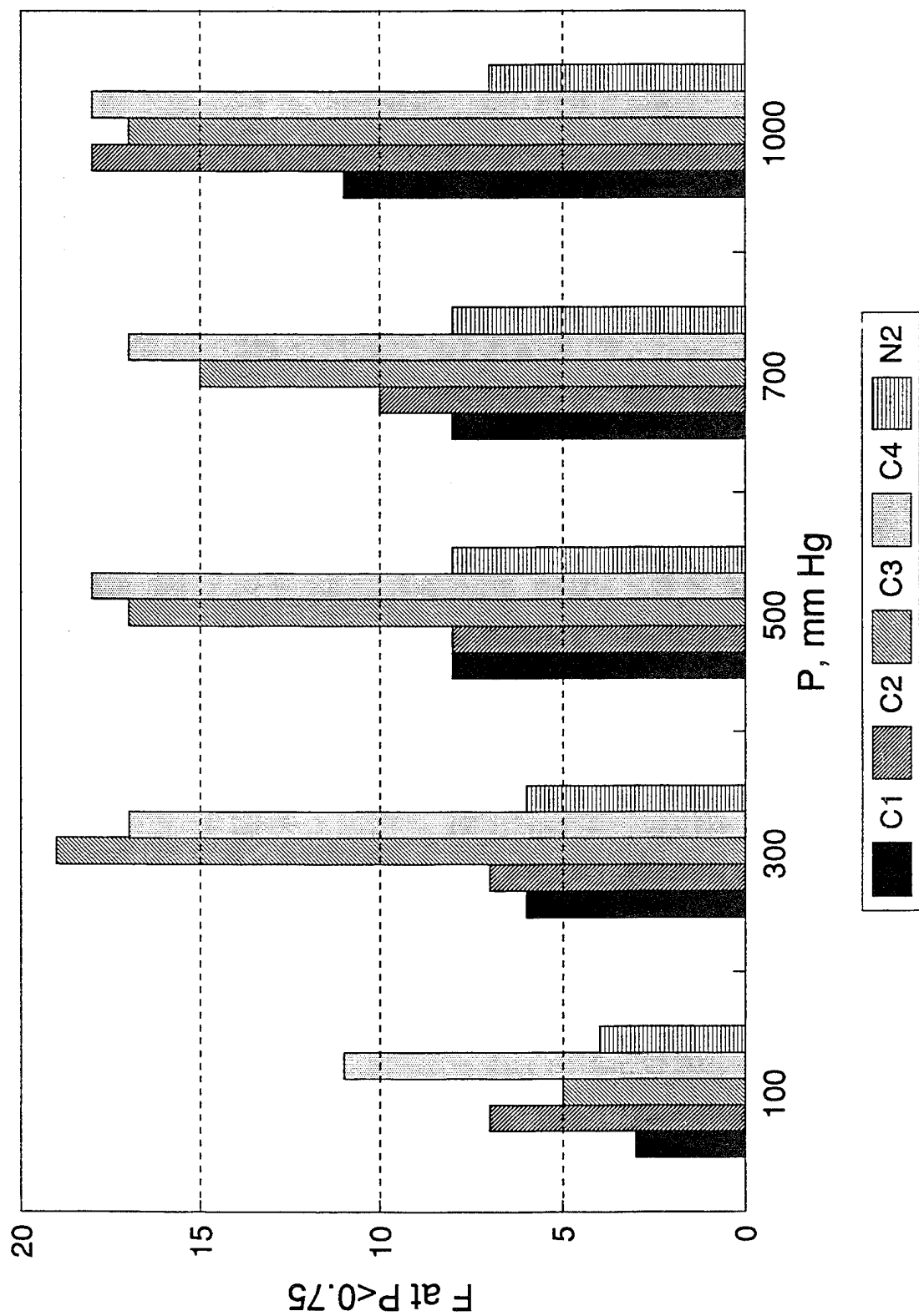


Figure B-19. Analysis of natural gas by FT-IR [(F at $P \leq 0.75$ vs. cell pressure (P-based)]

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