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The Impact of Calibration on Data Quality

**Re-evaluating
the calibration
process to
meet more
restrictive
requirements
for litigation
quality data.**

By Richard G. Mealy and
Kim D. Johnson

The calibration process represents the initial controlling mechanism for the generation of quality data, yet there is a general lack of guidance regarding specific evaluation techniques for this process. One of the drawbacks of providing such little guidance is the potential loss of data comparability, one of the chief data quality objectives identified by the EPA. This article examines critical aspects of the calibration process, and identifies those features that, if overlooked, can significantly impact the quality of the data generated. Initially, a comparison of calibration processes, as outlined in the various regulatory programs, is presented. To provide a more focused scope, discussion is limited to the impact on methods for the analysis of volatile organics, pesticide/PCBs and semivolatile organics. The concepts can be extended to other analytical methods.

It is important to note that some of the issues raised here have been addressed in regulatory programs that were not evaluated specifically for this article. The USATHAMA program in particular has incorporated a requirement that calibration data be subject to statistical tests for both Zero Intercept and Lack of Fit, which serve to resolve some of the problems associated with nonlinear data and calibration intercepts.

COMPARISON OF REGULATORY APPROACHES TO CALIBRATION

There exists a great deal of difference in the calibration protocols and requirements of the key regula-

tory programs, including the 500¹ and 600² series of EPA methods, those published in SW-846,³ and the Contract Laboratory Program.⁴ See Table I for a summary of calibration requirements of the various regulatory methodologies.

In general, the 600 series of methods offers the least amount of guidance, and thus is the most open to individual interpretation. More recent revisions to the 500 series of methods for analyses conducted under the Safe Drinking Water Act (SDWA) program introduce several new requirements that provide greater control over the accuracy of the resultant calibration. As Table I indicates, wide variation exists in the number of calibration standards required both within and across the series of regulatory protocols. One particularly important assumption that the 500, 600 and 8000⁵ series all share relates to curve linearity. In each of these methods, if the percent relative standard deviation (%RSD) of response factors associated with calibration standards is within certain criteria (10 to 35 percent), "then linearity through the origin can be assumed." Clearly, there are widely ranging views regarding when the intercept of a calibration curve deviates significantly from the origin. In keeping with the goal to establish data comparability, there is a need to consider the incorporation of a statistical technique to provide an objective means of determining whether a particular set of data essentially has a zero intercept.

In the event that %RSD criteria cannot be achieved, three of the four programs allow the user to simply prepare a calibration "curve" from concentration vs. instrument response. Unfortunately, there are no requirements for the type of curve algorithm (linear regression, polynomial fit, etc.) allowed.

As cleanup criteria continue to evolve, this variability between the different regulator protocols can have significant, adverse impact on the comparability of data generated by laboratories. Due to either regional or site-specific preferences, analytical programs can be based on methodologies from any of these programs. While each of the programs is considered to be designed to produce quality analytical data, the differences between the cali-

bration protocols will result in significantly different data quality.

In order to provide more control over the calibration process, each element of the process must be considered so that the most appropriate combination of elements is employed. The basic "parts" of the calibration are shown below:

- number of calibration levels
- calibration algorithm
- calibration levels
- calibration acceptance criteria
- effect of "curve-smoothing" routines

The remainder of this article focuses on detailed analysis of each of these sections. In particular, those aspects that potentially lead to inaccurate or biased data are discussed. In addition, we identify areas of the methods that are open to interpretation or require further guidance.

NUMBER OF CALIBRATION LEVELS

Essentially, as the number of calibration levels increases, the relative risk is reduced, as a better picture of the analyte's performance is obtained. The analytical run-time is also an important consideration in determining the number of levels to employ. For analyses with a relatively short analysis time, such as the majority of inorganic parameters, additional calibration levels do not represent a burden to production. This is not the case, however, for most organic analyses, with routine run times of 40 to 60 minutes. Laboratories are engaged in a constant struggle between quality and production. While an increased number of calibration levels would improve the quality of the data, this is not always possible. The implications of establishing calibration "curves" with a minimum of data points are brought to light in the next few sections.

CALIBRATION ALGORITHM

While most laboratories default to the standard (least squares) method of linear regression analysis to develop a calibration algorithm, a wide array of nonlinear calibration technique options are available. These options, including polynomial fits, exponential and power curves, segmented fits and even specific manufacturer options, are routinely provided as part of the software bundled with instrument data stations.

The most common approaches to quantitation use an average response fac-

tor (e.g., in GC/MS), single point quantitation (multicomponent analytes such as PCBs), and multiple point calibration "curves." Of these approaches, single point quantitation has the greatest potential for inaccuracy because the response

minimum number of data points required. As the minimum number of points required to form a line is two, then a linear regression (1st order polynomial fit) actually requires a minimum of three data points to be significant. Similarly, with each

Table 1: Comparison of regulatory method requirements for various aspects of the calibration process.

	500	600	8000	CLP
# Standards	<ul style="list-style-type: none"> • 3 to 5 • 5 recommended • 1 point allowable with criteria • 6 pre-set 525 	3 minimum	5 minimum	<ul style="list-style-type: none"> 5: general GC/MS 4: B/VA 3: Pesticides 1: Multicomponents
Low standard	<ul style="list-style-type: none"> • Near, but above EDLs to • 2-10x MDL 	Each analyte near, but above MDL	Each analyte near, but above MDL	Contractually set
Calibration Range	<ul style="list-style-type: none"> Range factor: 20: 3 minimum 50: 4 minimum 100: 5 minimum 	<ul style="list-style-type: none"> • Expected range of samples • Detector range 	<ul style="list-style-type: none"> • Expected range of samples • Detector range 	Contractually set
Initial Calibration: Requirement to use mean RF	<ul style="list-style-type: none"> RSD: • < 10% (502) • < 20% (508,524) • < 30% (525) 	<ul style="list-style-type: none"> RSD: • < 10% (601,602,608) • < 35% (624,625) 	<ul style="list-style-type: none"> RSD < 20% 	<ul style="list-style-type: none"> • Generally, RSD: < 20-35% [GC/MS] • < 10-15% [GC] • No RSD criteria for: <ul style="list-style-type: none"> - 20 B/VA - 10 VQA
Initial Calibration: Alternative to RF	<ul style="list-style-type: none"> • Generate a plot of peak height or area response vs. concentration • No acceptance criteria 	<ul style="list-style-type: none"> • Generate a plot of peak height or area response vs. concentration • No acceptance criteria 	<ul style="list-style-type: none"> • Generate a plot of peak height or area response vs. concentration • No acceptance criteria 	Use mean RF
Continuing Calibration (CCV) Frequency	<ul style="list-style-type: none"> • Daily (502,508) • Every 8 hours (524,525) 	Once daily	<ul style="list-style-type: none"> • Once daily • More frequently for ECD methods (8080) 	Every 12 hours
CCV Acceptance Criteria	<ul style="list-style-type: none"> % of initial standard response: <ul style="list-style-type: none"> ± 30%: 524,525 ± 20%: 502,508 	<ul style="list-style-type: none"> % of initial standard response: <ul style="list-style-type: none"> ± 15%: 608 ± 20%: 625 Analyte specific OC check standard: 601,602,624 	<ul style="list-style-type: none"> Standard response within ± 15% of initial response 	Maximum %D = 25% for most

from the single standard analyzed is deemed to be representative of the linearity of the analyte in question. There are two sources of error in single-point quantitation. First, any error in the preparation or concentration of the standard will directly affect quantitation. In addition, if the level chosen actually represents a significantly nonlinear portion of the relationship between response and concentration, substantial bias will be introduced.

The use of an average response factor is designed to normalize differences in response factors over the calibration range. The drawback to this approach is if only a single response factor deviates significantly from the others, the bias is normalized by distributing an equivalent degree of bias in the opposite direction over the other standards.

Nonlinear data require more advanced statistical treatment. Typically, regressions of a higher order, quadratic equations or polynomial fits of the data are employed. The main precaution associated with these techniques is the mini-

higher order equation, one more data point is required. As with a simple linear regression, the correlation coefficient must not be used as a measure of linearity. The correlation coefficient only provides a measure of how well the data points fit the equation generated. Finally, as the degree of nonlinearity increases, the curve of a 2nd or 3rd order polynomial becomes parabolic (Figures 1, 2). This results, at the upper end of the curve, in two solutions for a given data point. Unless the actual curve is carefully evaluated, the analyst may not even be aware that multiple solutions are possible for a given response. The consequence associated with this type of situation is that significantly inaccurate data could be reported.

Essentially, a linear regression results in the equation for a straight line, whereas polynomial fits above the 1st order will result in the equation for a curve. The most recent versions of 524.1, 524.2 and 525, GC/MS methods for the analysis of volatile and semivolatile organics, specifically allow the use of 2nd or 3rd order

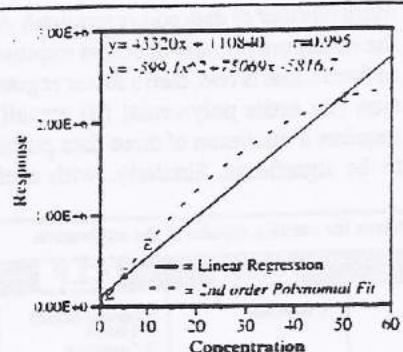


Figure 1: Sample Data Set 1. Comparison of Linear regression vs. 2nd order Polynomial Fit.

regression equations if the response factor criteria cannot be met. Figure 3 shows the curves that are associated with a linear fit as well as polynomial fits of orders 2 through 5 for Sample Data Set #1. Note, in particular, the significant differences in the curve fit to the data in the region between points D and E. If these higher level curves are used for the Sample Data Set, serious inaccuracies would result at the upper range of the curve—the recommended range for sample quantitation.

While, in specific cases, each of these statistical manipulations of calibration data can provide a "better fit" of the calibration equation to the data, they can also have significant impact on the quality of the data generated. Essentially, with the number of statistical programs readily available, an equation can be found that will provide a mathematical solution (i.e., "fit") to any set of data. Consequently, without a complete understanding of the actual effect on the raw data, none of these statistical techniques should be used in the generation of data for regulatory compliance.

CALIBRATION LEVELS

The specific levels that are selected for calibration can have a significant impact on the validity of the calibration equation. Calibration levels should be established based on consideration of: 1. the range of the levels, 2. the reportable detection limit and 3. the linear range of the analyte(s). The majority of the regulatory programs reviewed provide little guidance with respect to the range of calibration levels. A generic statement is provided indicating that the levels selected should be based on the expected range of sample results. In some cases, the "expected" sample concentrations ex-

ceed the working linear range of the detector. In the interest of obtaining accurate results, it is more important to define the linear range of the analyte and/or instrument, and dilute sample concentrations that exceed this range.

A wide calibration range, based on only a few calibration levels, will nearly always result in a correlation coefficient greater than 0.995, which is frequently used as the sole calibration evaluation criterion. In the example of Sample Data Set #2, the linear regression calculated from all five data points yields a correlation coefficient of 0.963. If only the first two and the uppermost data points are used (10, 20 and 200), however, the correlation coefficient is increased to 0.999. This is a consequence of the derivation of

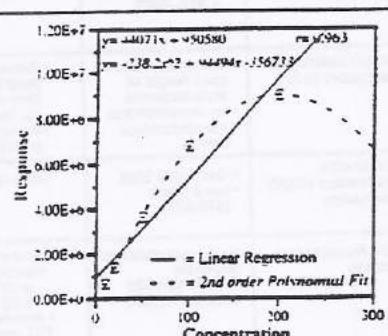


Figure 2: Sample Data Set 2. Comparison of Linear regression vs. 2nd order Polynomial Fit.

the correlation coefficient.

The relative difference between the concentration of the low-level standard and the reportable detection limit is critical to providing confidence in the accuracy of low-level measurements. Bias is more pronounced as the calibration curve approaches the detection limit for a par-

ticular analyte. Consequently, if the low-level standard is significantly greater than the detection limit, then accuracy in the proximity of the detection limit is compromised, because linearity of response has not been evaluated in this region. Ultimately, the detection limit itself may come into question. While the majority of the regulatory methods specify that the low-level standard must be prepared at a concentration "near, but above, the detection limit," methods 524.1 and 524.2 allow the low-level standard concentration to be as much as 10 times higher than the detection limit.¹

Finally, analytes have detector-specific linear ranges. In order to accurately evaluate nonlinear regions of the curve, there must not be a significant difference between the uppermost standard (X) and the (X-1) concentration level. The consequence of not considering this in a calibration is that the user may fail to identify a parabolic curve. This is one of the consequences that can result from establishing calibration levels based solely on the expected concentration range of the samples.

Revisions to the 500 series of methods represent the first attempt (other than the CLP program, where calibration levels are contractually defined) to provide stronger guidance regarding the calibration range. Methods 524.1 and 524.2 require at least three calibration levels to encompass a factor of 20 calibration range (i.e., 1 to 20, 10 to 200). In addition, at least four standards are required to cover a range of a factor of 50, and at least five standards are required for a range factor of 100.

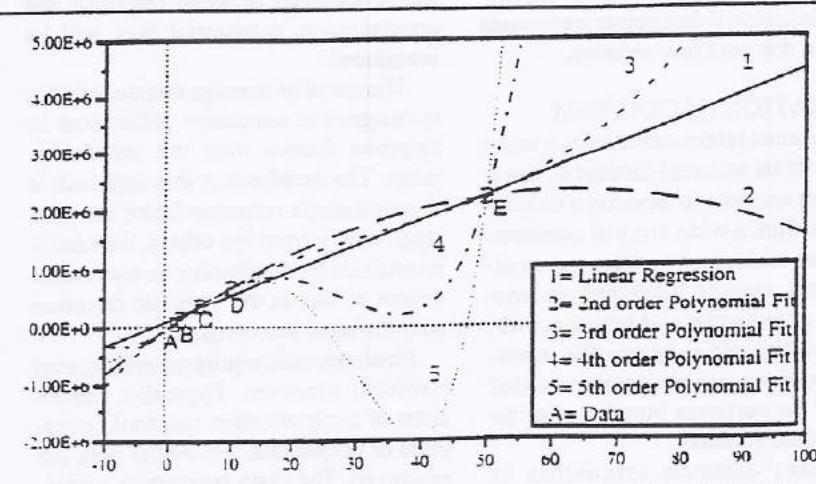


Figure 3: Plot of curves generated using various algorithms. Data from Data Set 1.

CALIBRATION ACCEPTANCE CRITERIA

Once a calibration has been performed, there must be a set of criteria to determine if the curve is acceptable for use in generating analytical results. This is one of the key weaknesses in the published regulatory methodology. With the exception of the CLP program, the referenced regulatory methods have only established acceptance criteria if the mean response factor is to be used for quantitation. The alternative, if %RSD criteria (relative standard deviation of response factors from the calibration curve) cannot be achieved, is to simply generate a plot of concentration vs. response or response factor. This allows the generation of data without control of data quality until the analysis of the first continuing calibration standard, where a

limited measure of control is obtained. In addition to %RSD criteria, the CLP program has established minimum response factor criteria for most analytes. This requirement is associated with confidence in the ability to detect the analyte, how-

ever, rather than in quantitation of the analyte.

offer little assurance of accurate quantitation. The most stringent CCV acceptance criteria are found in Method 502.2, which requires the analysis of a midpoint standard to yield a response within ± 20 percent of that obtained for the same standard in the initial calibration.

In addition, this method requires the analysis of a laboratory fortified blank (LFB) per batch of 20 or fewer samples, fortified at a concentration of 20 $\mu\text{g/L}$.

For a set of data that is essentially linear, the mathematical basis of a linear regression attempts to establish the midpoint of the curve as the point which deviates least from the linear equation. The

extent of the deviation then increases at the extremes. The deviation is absolute rather than relative to concentration, which creates the greatest impact at the lower end of the curve. Due to the mag-

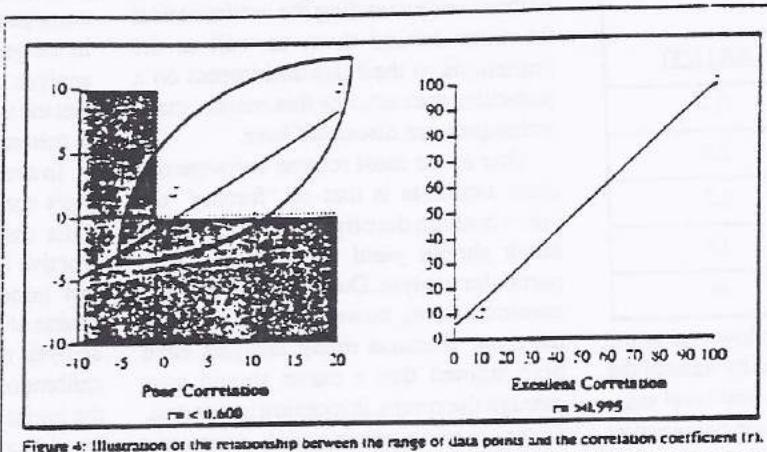


Figure 4: Illustration of the relationship between the range of data points and the correlation coefficient (r).

ever, rather than in quantitation of the analyte.

As indicated in Table 1, even the acceptance criteria associated with continuing calibration verification (CCV)

nitude of response associated with the highest calibration level, the relative effect is minimal. In the case of strongly nonlinear data, such as that in Sample Data Set #2, the point at which the curve becomes nonlinear (in this case, the upper calibration level) is central in the minimization of deviation from the curve. This effect is evident in Table 4, which

concentration has its greatest impact on the continuing calibration verification (CCV) process. The concentration of the CCV is typically equal to the midpoint concentration of the initial multipoint calibration. With linear calibrations (typically the norm), the midpoint level is associated with the least degree of bias from the plot of the calibration equation. Consequently, if the overall accuracy of the analysis is less than 20 percent, there is a significant probability that the acceptance criteria for the CCV and the fortified laboratory blanks can be met.

The correlation coefficient ("r") is the most commonly used statistical measure of calibration acceptability. One long-standing misconception is that this parameter also provides a measure of linearity. The correlation coefficient is a measure of the "goodness of fit" of a series of data points. Basically, the correlation coefficient can be viewed as a mathematical process that determines the tightest ellipse that defines a set of data. The more the ellipse resembles a straight line, the higher the "r" value (to a maximum of 1.00). The more the data appear to be randomly distributed, or the ellipse appears more as a circle, the lower the "r" value (to a minimum of 0). This effect is

illustrated in Figure 4. Consequently, even a particular random set of data can result in a high "r" value if the data range is such that the data can be described by a tight ellipse.

Table 1B: Sample Data Set 2

X	Y	Response Factor
10	650.000	65000
20	1,400.00	70000
50	3,650.00	73000
100	6,800.00	68000
200	9,000.00	45000

RSD = 17.3%

Table 2A: Sample Data Set 1

X	Y	Response Factor
1	65000	65000
2	140000	70000
5	365000	73000
10	680000	68000
50	2250000	45000

RSD = 17.3%

indicates that relatively minimal bias occurs in the upper calibration level, even considering such nonlinear data.

The relationship between bias and

Calibration acceptance criteria should be designed to evaluate the relationship between the intercept of the calibration equation and the reportable detection limit

(RDL). The data in Tables 2A and 2B, for Sample Data Sets #1 and #2 show significant

Table 3: Calculated X values for Sample Data Set 1 using both Linear Regression (LSR) and LSR weighted 1/X.

X	LSR	LSR (1/X)
1	-1.1	0.4
2	0.7	2.0
5	5.9	6.7
10	13	13
50	49	46

cant negative bias at the low end of the calibration. If, as required by most of the regulatory methods, the low-level standard is just slightly greater than the actual RDL, then the RDL would clearly not be valid for these calibration sets. One requirement that should be imposed on calibration data is that the x-intercept (expressed as concentration) should be no greater than 50 percent of the RDL. This will minimize the reporting of low-level false positive results.

One final consideration regarding the evaluation of calibration data is the bias at each calibration level that results from obtaining a concentration from the calibration evaluation using the actual raw calibration data. The software in use today provides graphic representations of the calibration data, but the plots are typically too small and the resolution too poor to be used to accurately evaluate point-specific bias. Each of the generally accepted calibration evaluation mechanisms should be considered no more than a single data assessment tool, rather than an absolute indicator of calibration acceptability. For example, the correlation coefficient, used frequently in the inorganic arena, can provide misleading information if there is a significant range between the uppermost and lower calibration levels.

EFFECT OF CURVE "SMOOTHING" ROUTINES

With the advent of powerful software routines and instrument data stations, the analyst is now provided with a series of tools that can be used to "smooth" the fit of any curve. While these techniques

certainly are not an element of the calibration process, their use is rapidly becoming routine. High-powered calibration algorithms are most often used without understanding the mathematical functions behind them as well as the limitations to their use and impact on a particular data set. For this reason, these techniques are discussed here.

One of the most routine software options available is that of "forcing" the curve through the origin. Theoretically, a blank should yield no response for a particular analyte. Due to signal-to-noise considerations, however, this is rarely the case. Because many analysts have been trained that a curve should pass through the origin, this option is selected. There are two ways in which curves can be forced through the origin. The first is a simple mathematical formula designed to result in a slope and zero-intercept. The other option is a manual one, which

upper range only minimally.

While each of these techniques results in a better fit of the data points to the calibration equation, they remain little more than data manipulation techniques. In the generation of environmental data, analysts must be trained to understand that the use of these techniques can result in misinterpretation of the data.

In a regulatory climate that is increasingly concerned with quality assurance, most data quality assessments remain reactive in that they rely on quality control information generated during the course of analysis, rather than prior to the analysis of environmental samples. The calibration process should be viewed as the initial opportunity to assess the quality of data to be generated. Consequently, there is a need for more structure and guidance in the evaluation process in order to provide analytical methods that ensure data comparability. □

Table 4: Summary of the bias observed in Sample Data Set 1 data using different quantitation techniques.

X	LSR	PF2	RF	Single Point Quantitation		
				Low(1)	Mid(10)	High(50)
1	(206%)	6%	1%	0%	(4%)	44%
2	(66%)	(2%)	9%	8%	3%	56%
5	17%	(1%)	14%	12%	7%	62%
10	31%	0%	6%	5%	0%	51%
50	(1%)	0%	(30%)	(31%)	(34%)	0%

RF = Average Response Factor

LSR = Linear Regression (Least Squares)

PF2 = Polynomial Fit (2nd order)

is based on the repetitive inclusion of (0,0) data points until the curve is eventually forced through the origin.

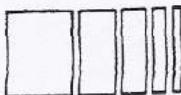
Curve "weighting" techniques are often used to obtain a better fit of the data points at either extreme of the calibration range. Typically, the low end of the curve is susceptible to poor fit of the calibration equation. The most common weighting routine employed to improve the fit is a 1/X manipulation of the data. Basically, each data point is weighted by a factor of the inverse of the associated concentration. The result of this weighting, for the entire set of data, is a 91-point curve vs. the original five-point curve. The results of this weighting are summarized in Table 3. The table indicates that a significantly better fit is achieved at the low end of the curve while affecting the midpoint and

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REFERENCES

- U.S. EPA. 1988. Methods for the Determination of Organic Compounds in Drinking Water. EPA/600/4-88/039. December.
- U.S. EPA. 1985. Methods for the Organic Chemical Analysis of Municipal and Industrial Wastewater. 40 CFR Part 136. Appendix A. July.
- U.S. EPA. 1990. Test Methods for Evaluating Solid Waste. Volume II: Laboratory Manual. Physical/Chemical Methods. SW-846. 3rd ed. Revision 1. November.
- U.S. EPA. 1990. Contract Laboratory Program. SOW 390. Statement of Work for Organic Analyses. Multi-Media. Multi-Concentration. March.
- USATHAMA. 1990. United States Army Toxic and Hazardous Materials Agency. Quality Assurance Program. USATHAMA PAM 11-41, rev. 0. January.



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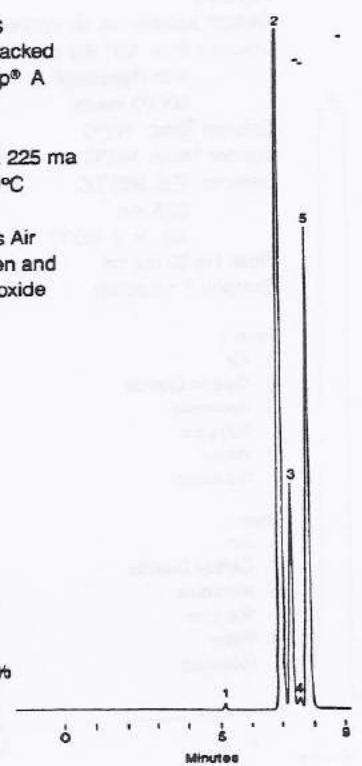
HayeSep® A This polymer separates permanent gases (hydrogen, nitrogen, oxygen, argon, carbon monoxide, and nitric oxide) at ambient temperatures. It also exhibits good separation characteristics for the C2's, hydrogen sulphide and water at higher temperatures.

HayeSep® Polymer	Operating Temp.	Maximum Surface Area m²/gram	Tapped Bulk Density gram/cc	Polymer Composition*	Polarity (1=lowest 9=highest)
A	165°C	526	0.356	DVB (high purity) EGDM (high purity)	7
B	190°C	608	0.330	DVB/PEI	8
C	250°C	442	0.322	DVB/ACN	6
D	290°C	795	0.3311	DVB (high purity)	1
N	165°C	405	0.355	DVB/EGDM	9
P	250°C	165	0.420	DVB/Styrene	3
Q	275°C	582	0.351	DVB	2
R	250°C	344	0.324	DVB/NV2P	5
S	250°C	583	0.334	DVB/4VP	4
T	165°C	250	0.381	EGDM	10

*DVB Divinylbenzene
EGDM Ethyleneglycoldimethacrylate
PEI Polyethyleneimine

ACN Acrylonitrile
NV2P N-vinyl-2-pyrrolidinone
4VP 4-vinyl-pyridine

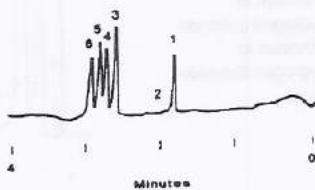
Figure 1
PERMANENT GASES
Column: 36' x 1/8" packed
with HayeSep® A
80/100 mesh
Column Temp: 25°
Detector: P.E. 900 T.C. 225 ma
Att. x 2 180°C
Flow: He 23 cc/min
Sample: 25 microliters Air
plus Hydrogen and
Carbon Monoxide



1. Hydrogen 5%
2. Nitrogen 48.5%
3. Oxygen 13%
4. Argon 0.5%
5. Carbon Monoxide 33%

Figure 2
PERMANENT GAS
STANDARD 500 ppm
Column: 25' x 1mm packed
with HayeSep® A
170/200 mesh
Column Temp: 23°C
Flow: He 15 cc/min
Sample: 20 microliters

1. Neon
2. Hydrogen
3. Nitrogen
4. Oxygen
5. Argon
6. Carbon Monoxide



HayeSep® B Designed to separate the C1 and C2 amines as well as trace levels of ammonia and water; this polymer eliminates the need for caustic washing of material prior to packing.

Figure 3

AMINES #1

Column: 5' x 1/8"
SS packed with
HayeSep® B
80/100 mesh
Column Temp: 140° up to
190°C at
16°C/min
Injector Temp: 150°C
Detector: P.E. 900 T.C.
175 ma
Att. x 8 180°C
Flow: He 30 cc/min
Sample: 0.2 microliters
with on-
column
injection

1. Air
2. Water
3. Methylamine
4. Dimethylamine
5. Trimethylamine
6. Ethylene diamine

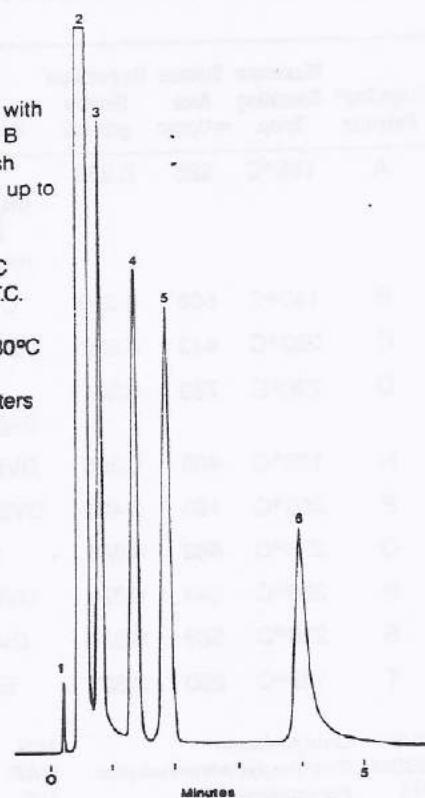
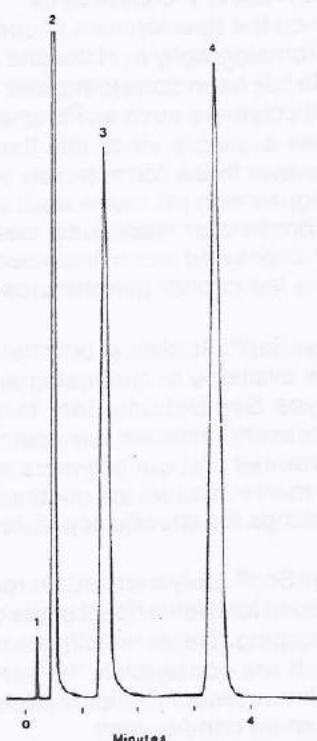


Figure 4

AMINES #2

Column: 5' x 1/8" packed
with HayeSep® B
80/100 mesh
Column Temp: 140°C up to
190°C at 16°C/min
Injector Temp: 150°C
Detector: P.E. 900 T.C.
175 ma
Att. x 8 180°C
Flow: He 30 cc/min
Sample: On-column injection

1. Air
2. Water
3. Ethylamine
4. Diethylamine



HayeSep® C This polymer is designed for polar hydrocarbons such as hydrogen cyanide, ammonia, hydrogen sulphide and water. HayeSep C® has similar separation characteristics to Chromosorb® 104.

Figure 5

AMMONIA IN
HYDROGEN SULPHIDE

Column: 5' x 1/8" packed
with HayeSep® C
80/100 mesh
Column Temp: 70°C
Injector Temp: 200°C
Detector: P.E. 900 T.C.
225 ma
Att. x 2 180°C
Flow: He 30 cc/min
Sample: 100 microliters

1. Air
2. Carbon Dioxide
3. Ammonia
Trace 1: approx 15%
Trace 2: approx 1.5%
4. Hydrogen Sulphide
5. Unknown in
Hydrogen Sulphide
6. Unknown in
Hydrogen Sulphide
7. Water

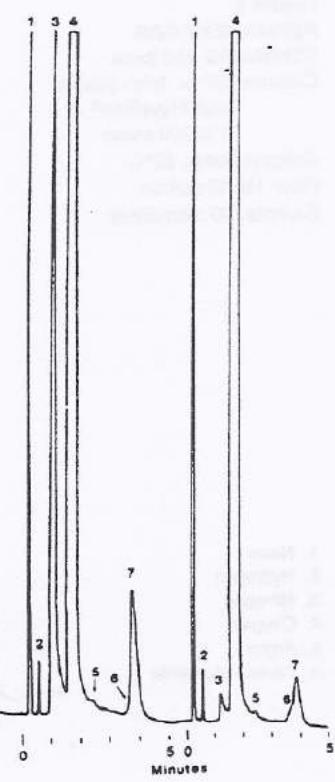


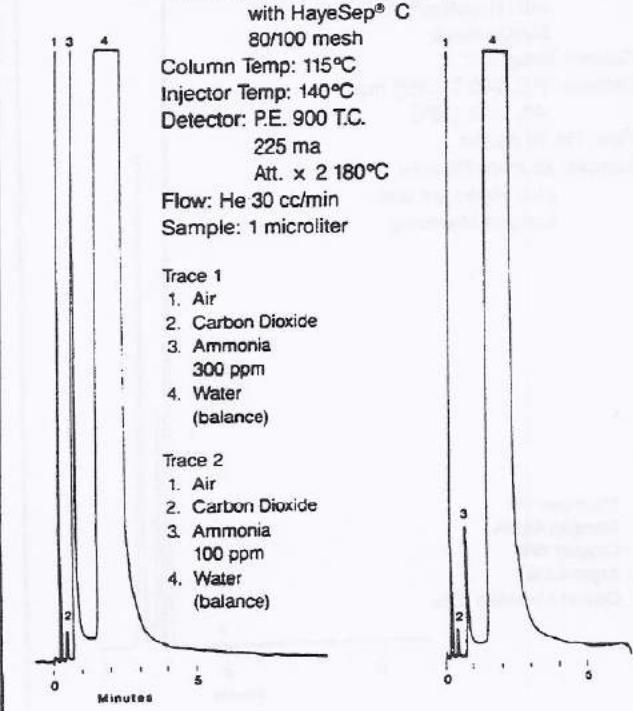
Figure 6

TRACE AMMONIA IN WATER

Column: 5' x 1/8" SS packed
with HayeSep® C
80/100 mesh
Column Temp: 115°C
Injector Temp: 140°C
Detector: P.E. 900 T.C.
225 ma
Att. x 2 180°C
Flow: He 30 cc/min
Sample: 1 microliter

- Trace 1
1. Air
 2. Carbon Dioxide
 3. Ammonia
300 ppm
 4. Water
(balance)

- Trace 2
1. Air
 2. Carbon Dioxide
 3. Ammonia
100 ppm
 4. Water
(balance)



HayeSep® N, P, Q, R, S, and T These polymers are interchangeable with the Porapak® series for separations of low molecular weight materials containing halogens, sulphurs, water, alcohols, glycols, free fatty acids, esters, ketones and aldehydes.

Figure 7

AMMONIA

Column: 8' x 1/8" SS packed with HayeSep® P
60/80 mesh
Column Temp: 80°C
Injector Temp: 150°C
Manifold Temp: 180°C
Detector: T.C. 175 ma 200°C
Flow: He 30 cc/min
Sample: 0.1 microliters of NH₄OH with on-column injection

1. Air
2. Ammonia 35%
3. Water 65%

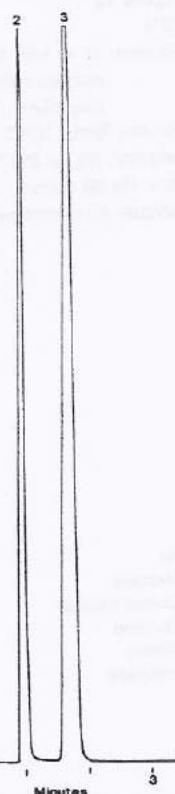


Figure 8

SOLVENTS

Column: 8' x 1/8" SS packed with HayeSep® P
60/80 mesh
Column Temp: 80°C up to 180°C at 16°C/min
Injector Temp: 150°C
Manifold Temp: 180°C
Detector: 175 ma 200°C
Flow: He 30 cc/min
Sample: 0.2 microliters with on-column injection

1. Air
2. Water
3. Methanol
4. Ethanol
5. Acetone
6. Chloroform

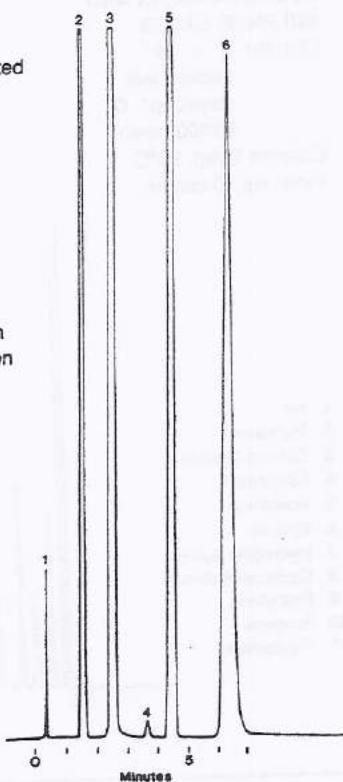


Figure 9

TRACE WATER ANALYSIS

Column: 9' x 1/8" Ni packed with HayeSep® R
80/100 mesh
Column Temp: 118°C
Flow: He 30 cc/min
Detector: Varian T.C.
with Bendix On-Line Process Analyzer
Sample: 10 microliters
Ethyl Chloride

1. Air
2. Water 12 ppm
3. Hydrogen Chloride
4. Ethyl Chloride

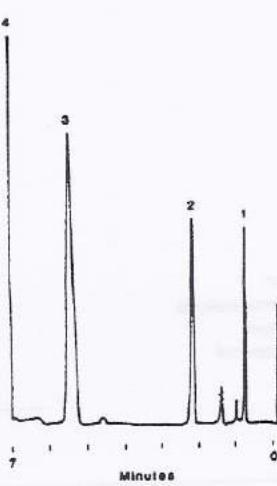


Figure 10

MAPP GAS

Column: 10' x 1/8" SS packed with HayeSep® R
Column Temp: 80°
Flow: He 30 cc/min
Sample: 15 microliters

1. Air
2. Methane
3. Carbon Dioxide
4. Ethane
5. Propylene
6. Propane
7. Propadiene
8. Methyl Acetylene

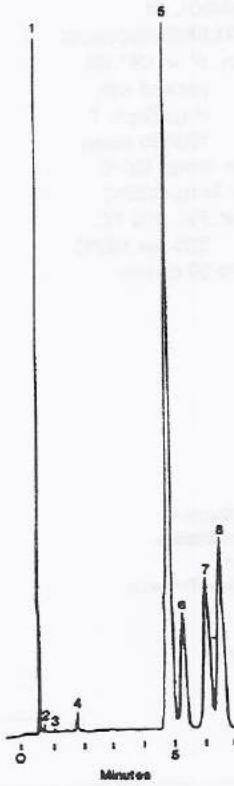


Figure 11
HYDROCARBONS AND SULPHUR GASES

Column: 8' x 1/8"
packed with
HayeSep® Q
80/100 mesh
Column Temp: 90°C
Flow: He 30 cc/min

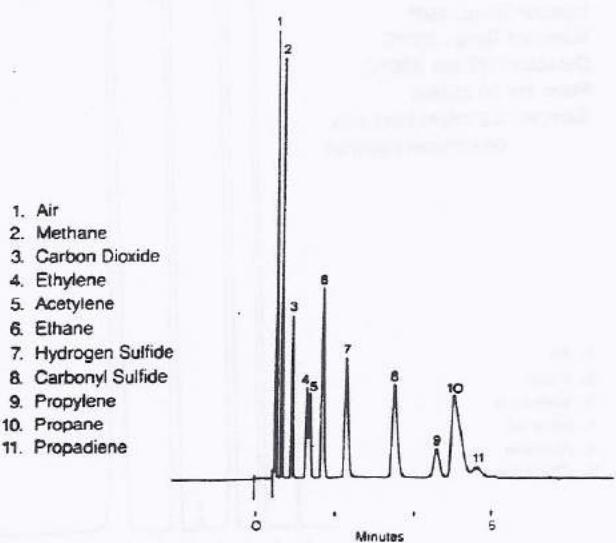


Figure 12

C₂'s
Column: 5' x 1/8" SS packed with HayeSep® T
Column Temp: 32°C
Detector: Att. x 216 180°C
Flow: He 30 cc/min
Sample: 50 microliters

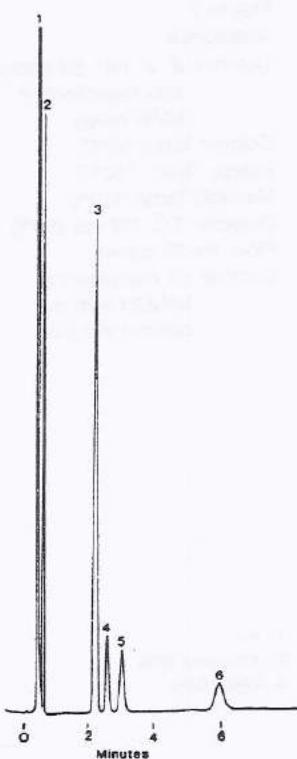


Figure 13
METHANOL IN PROPYLENE/PROPANE

Column: 5' x 1/8" SS packed with HayeSep® T 100/120 mesh
Column Temp: 120°C
Injector Temp: 132°C
Detector: P.E. 900 T.C.
225 ma 150°C
Flow: He 30 cc/min

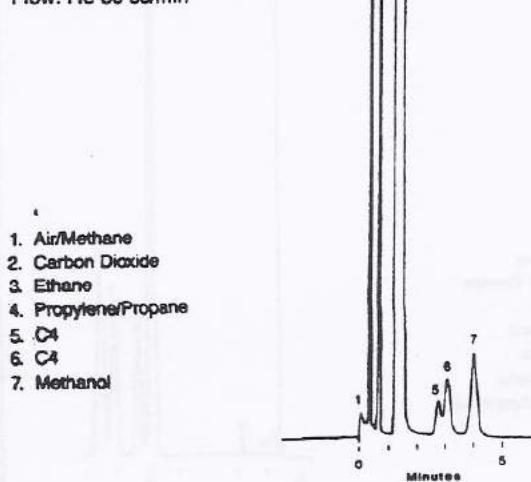
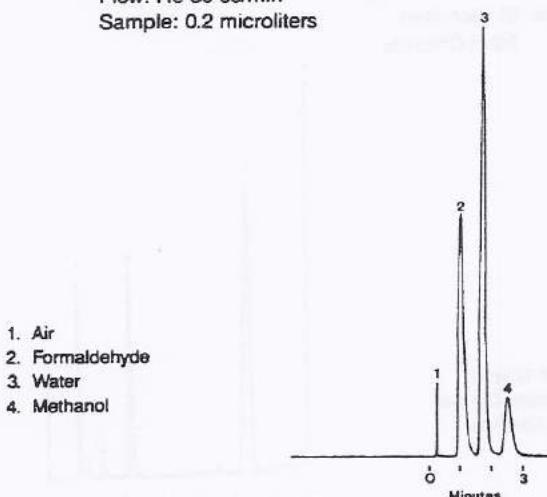


Figure 14
FORMALDEHYDE

Column: 5' x 1/8" SS packed with HayeSep® T 100/120 mesh
Column Temp: 132°C
Injector Temp: 165°
Detector: P.E. 900 T.C.
175 MA
Att. x 32 180°C
Flow: He 30 cc/min
Sample: 0.2 microliters



INTRODUCING A UNIQUE NEW PRODUCT

HayeSep® D This new polymer made from high purity divinylbenzene is unavailable anywhere else. It has a high surface area and higher operating temperatures than competitive polymers. Available in four different porosities with surface areas from 790 to over 800 m²/gram, this range allows flexibility, since in water/ethane separations porosity determines the order of elution.

These D formulations exhibit superior separation characteristics for light gases. Significant separation abilities include the separation of CO and CO₂ from room air at ambient temperatures and the separation of acetylene prior to other C2's. HayeSep® D is particularly useful in the separation and analysis of water and hydrogen sulphide.

Comparisons of D Formulations

	Average Diameter (microns)	Bulk Density gram/cc	Porosity %	Surface Area m ² /gram
Dip	.0317	.3283	69.1	774
D	.0308	.3311	70.35	803
D _B	.0332	.3334	64.2	781

Figure 15

SCOTT MIX 237

Column: 20' × 1/8" Ni packed
with HayeSep® D
100/120 mesh

Column Temp: 25°C

Injector Temp: 100°C

Detector: P.E. 900 T.C.

225 ma 140°C

Flow: He 30 cc/min

Sample: Valco valve
50 microliters vapor
(ambient)

1. Nitrogen (balance)
2. Oxygen 7% Att. x8
3. Carbon Monoxide 7% Att. x8
4. Methane 4.5% Att. x4
5. Carbon Dioxide 15% Att. x4

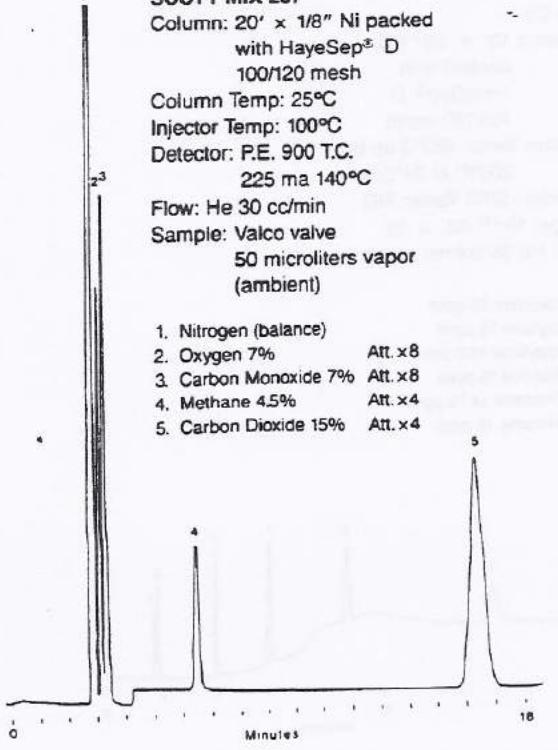


Figure 16

GAS MIXTURE

Column: 10' × 1/8" SS packed
with HayeSep® D
100/120 mesh

Column Temp: 80°C

Injector Temp: 140°C

Detector: P.E. 900 T.C.

225 ma

Att. x 4

Flow: He 30 cc/min

Sample: Valco valve
100 microliters

1. Nitrogen (balance)
2. Carbon Dioxide 2%
3. Nitrous Oxide 3%
4. Water 0.5%
5. Hydrogen Sulphide 3%

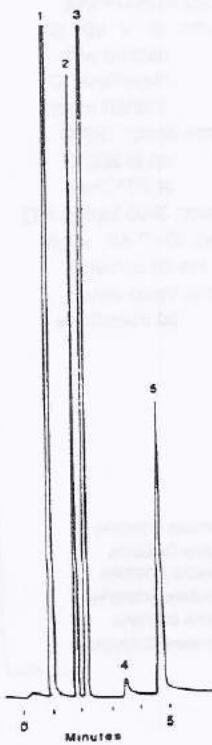


Figure 17

SCOTT MIX 216 (Programmed)

Column: 20' x 1/8" Ni packed
with HayeSep® D
100/120 mesh

Column Temp: 40°C/2 min
programmed
up to 110°C
at 24°C/min

Injector Temp: 100°C

Detector: P.E. 900 T.C.
225 ma 140°C

Flow: He 30 cc/min

Sample: Valco valve
100 microliters
(ambient)

1. Nitrogen (balance)
2. Carbon Monoxide 1% Att. x2
3. Methane 1% Att. x2
4. Carbon Dioxide 1% Att. x2
5. Acetylene 1% Att. x2
6. Ethylene 1% Att. x2
7. Ethane 1% Att. x2

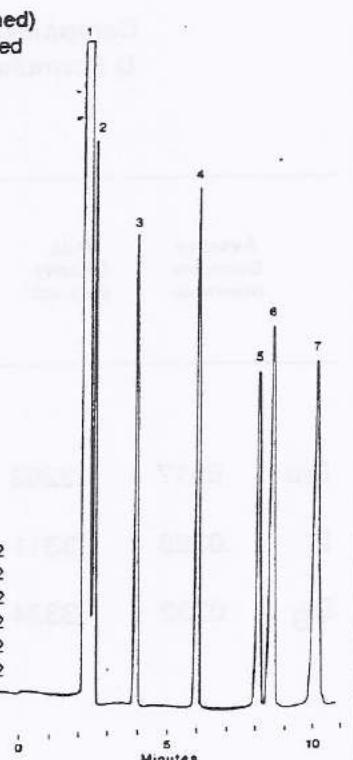


Figure 18

C1 - C2's

Column: 10' x 1/8" SS packed
with HayeSep® D
100/120 mesh

Column Temp: 80°C Isothermal

Detector: 3700 Varian FID

Range: 10⁻¹¹ Att. x 16

Flow: He 35 cc/min

1. Methane 1%
2. Acetylene 1%
3. Ethylene 1%
4. Ethane 1%

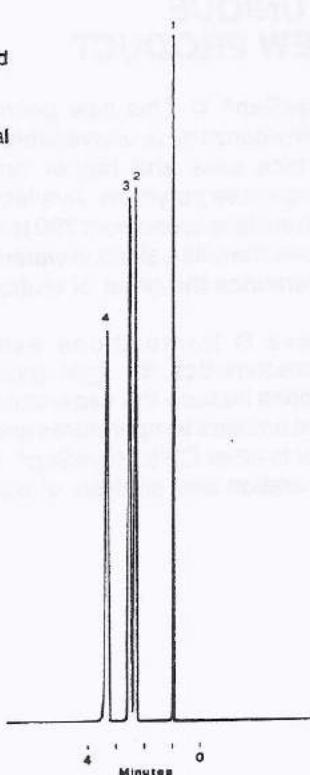


Figure 19

C1 - C5 PARAFFINS

Column: 10' x 1/8" SS
packed with
HayeSep® D
100/120 mesh

Column Temp: 120°C
up to 200°C
at 20°C/min

Detector: 3700 Varian FID

Range: 10⁻¹¹ Att. x 16

Flow: He 35 cc/min

Sample: Valco valve
50 microliters

1. Methane 0.1894%
2. Ethane 0.0965%
3. Propane 0.0989%
4. Isobutane 0.1019%
5. Butane 0.1019%
6. n-Pentane 0.2002%

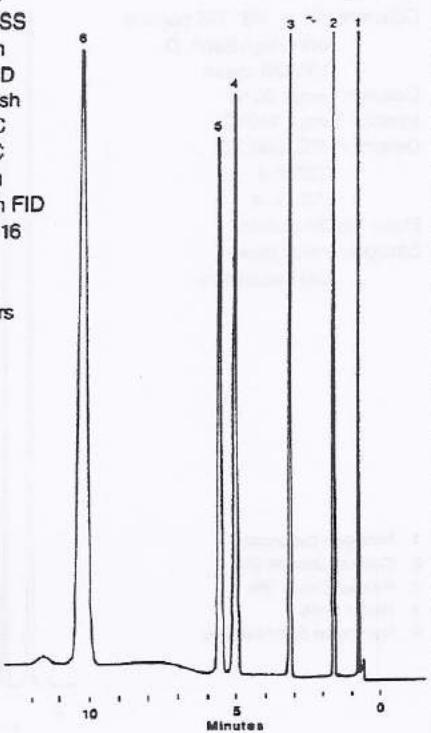


Figure 20

TRACE UNSATURATES

C2 - C6

Column: 10' x 1/8" SS
packed with
HayeSep® D
100/120 mesh

Column Temp: 120°C up to
200°C at 24°C/min

Detector: 3700 Varian FID

Range: 10⁻¹¹ Att. x 16

Flow: He 35 cc/min

1. Acetylene 16 ppm
2. Ethylene 15 ppm
3. Propylene 14.3 ppm
4. 1-Butene 15 ppm
5. 1-Pentene 14.75 ppm
6. 1-Hexene 16 ppm

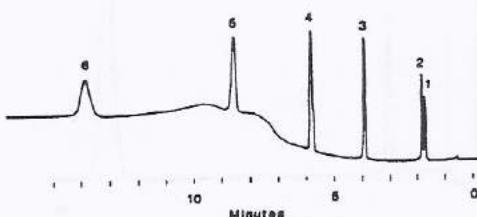


Figure 21
TRACE ACETALDEHYDE

IN AIR 2500 ppm
Column: 3' x 1/8" SS
packed with
HayeSep® D
100/120 mesh
Column Temp: 100°C
Injector Temp: 140°C
Detector: P.E. 900 T.C.
225 ma 140°C
Flow: He 30 cc/min
Sample: Valco valve
100 microliters

1. Air
2. Water
3. Acetaldehyde
2500 ppm (vol.)

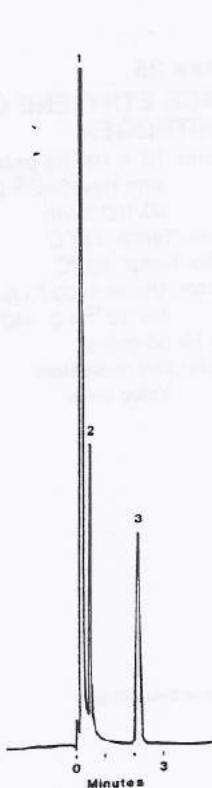


Figure 22
TEQUILA HEADSPACE

Column: 3' x 1/8" SS packed
with HayeSep® D
80/120 mesh
Column Temp: 100°
Injector Temp: 140°C
Detector: P.E. 900 T.C.
225 ma 140°C
Flow: He 30 cc/min
Sample: Valco valve
100 microliters

1. Air Att. x1
2. Carbon Dioxide Att. x1
3. Water Att. x1
4. Methanol Att. x1
5. Acetaldehyde Att. x1
6. Ethanol Att. x8

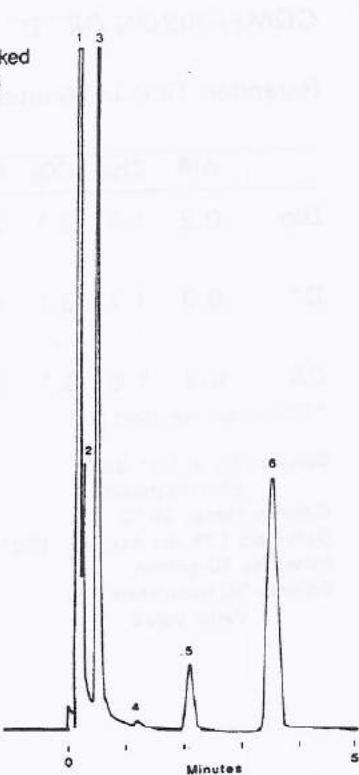


Figure 23
TRACE ALCOHOLS

IN WATER
Column: 10' x 1/8" packed
with HayeSep® D
80/100 mesh
Column Temp: 75°C up to
150°C at 16°C/min
Flow: He 33 cc/min
Injector Temp: 125°C
Detector: P.E. 900 T.C.
225 ma
Att. x 1 140°C
Sample: 3 microliters

1. Methanol
500 ppm
2. Ethanol
200 ppm

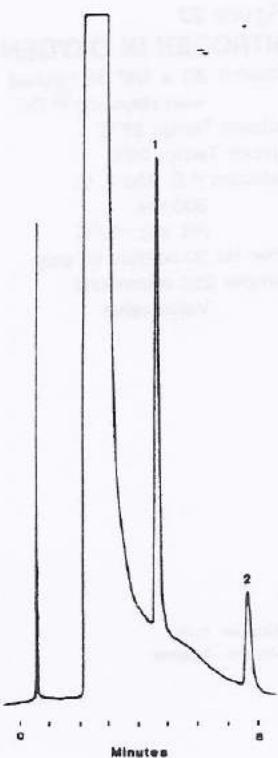
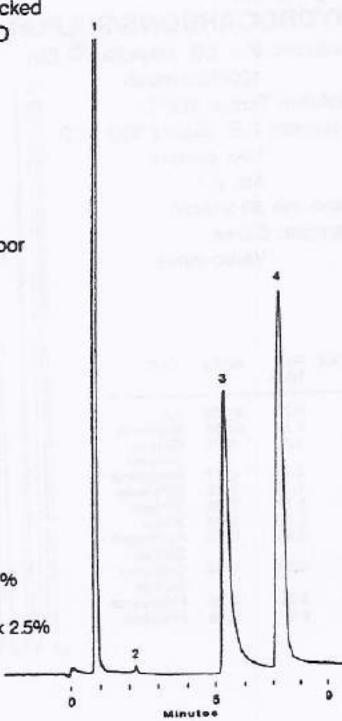


Figure 24
HYDROGEN SULPHIDE

Column: 10' x 1/8" Ni packed
with HayeSep® D
100/120 mesh
Column Temp: 60°C
Injector Temp: 100°C
Detector: P.E. 900 T.C.
225 ma 140°C
Flow: He 30 cc/min
Sample: Valco valve
50 microliters vapor
(ambient)

1. Air (balance)
2. Carbon Dioxide approx 0.1%
3. Water approx 2.5%
4. Hydrogen Sulphide approx 2.5%



COMPARISON OF "D" FORMULATIONS

Retention Time in Minutes

	AIR	CH ₄	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	H ₂ O
Dip	0.9	1.7	3.1	5.4	5.8	8.3	9.0
D*	0.9	1.7	3.1	5.8	6.1	8.4	8.6
DB	0.9	1.6	3.1	6.1	6.6	8.7	8.1

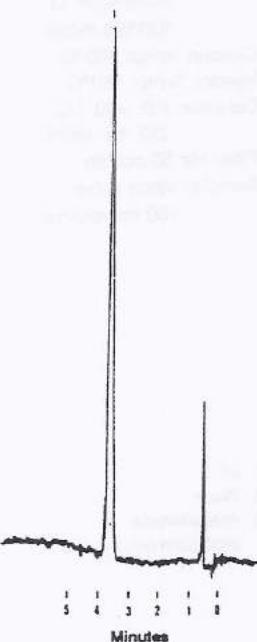
*This is our standard D.

Column: 10' x 1/8" SS
80/100 mesh
Column Temp: 45°C
Detector: 175 ma Att. x 2 150°
Flow: He 30 cc/min
Sample: 50 microliters
Valco valve

Figure 25
TRACE ETHYLENE OXIDE
IN NITROGEN

Column: 10' x 1/8" SS packed
with HayeSep® D
80/100 mesh
Column Temp: 130°C
Injector Temp: 100°C
Detector: Varian 1400 F.I.D.
Att. 10⁻¹² x 2 140°C
Flow: He 30 cc/min
Sample: 250 microliters
Valco valve

1. Ethylene Oxide 23 ppm



Courtesy of John Book Co.

Figure 26
HYDROCARBONS/SULFUR GASES

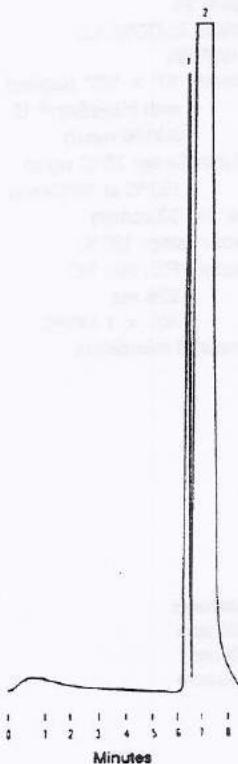
Column: 9' x 1/8" HayeSep® Dip
100/120 mesh
Column Temp: 100°C
Detector: P.E. Sigma 300 TCD
Low current
Att. x 1
Flow: He 30 cc/min
Sample: 0.5 cc
Valco valve

PEAK	RET. TIME	AREA	CPD %
1.	0.71	31.59	Air
2.	0.86	46.88	Methane
3.	1.23	5.48	Carbon Dioxide
4.	1.71	2.17	Acetylene
5.	1.79	2.72	Ethylene
6.	2.19	3.09	Ethane
7.	2.52	0.45	Water
8.	2.83	0.19	Hydrogen Sulfide
9.	4.30	0.44	Carbonyl Sulfide
10.	5.82	3.38	Propylene
11.	6.57	3.59	Propane

Figure 27
NITROGEN IN OXYGEN

Column: 30' x 1/8" SS packed
with HayeSep® DB
Column Temp: 25°C
Injector Temp: 25°C
Detector: P.E. 900 T. C.
300 ma
Att. x 2 140°C
Flow: He 30 cc/min, 90 psig
Sample: 250 microliters
Valco valve

1. Nitrogen 0.4%
2. Oxygen - balance



Courtesy of John Book Co.

Figure 28
SCOTT MIX 234

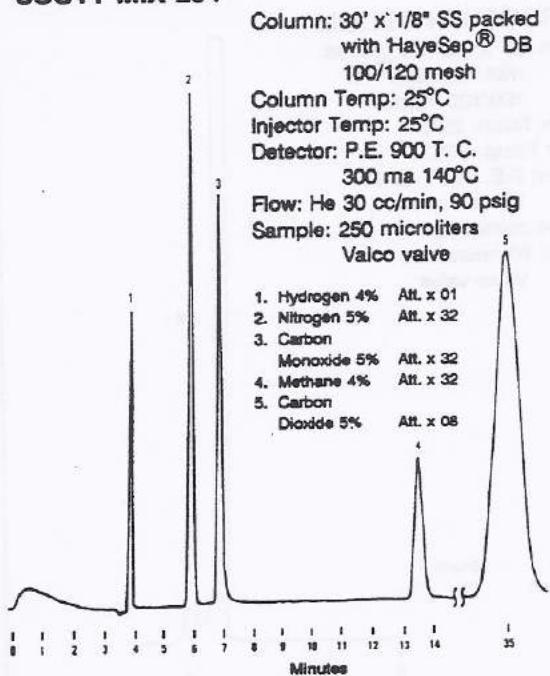


Figure 29



Figure 30
NITROGEN IN ARGON

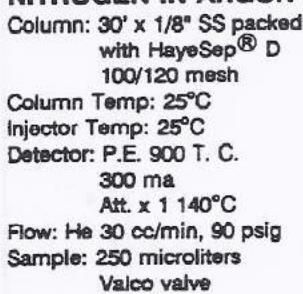


Figure 31
ETHYLENE AND SCOTT MIX 216

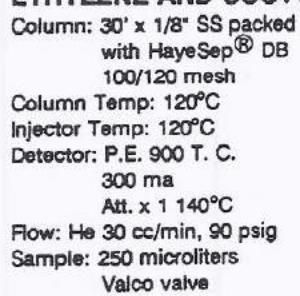


Figure 32
NITRIC OXIDE IN NITROGEN

Column: 30' x 1/8" SS packed
with HayeSep® DB
100/120 mesh

Column Temp: 22°C
Injector Temp: 22°C
Detector: P.E. 900 T. C. D.
225 ma 140°C

Flow: 30 cc/min
Sample: 100 microliters

1. Nitrogen Balance
2. Argon
3. Nitric Oxide 0.58%

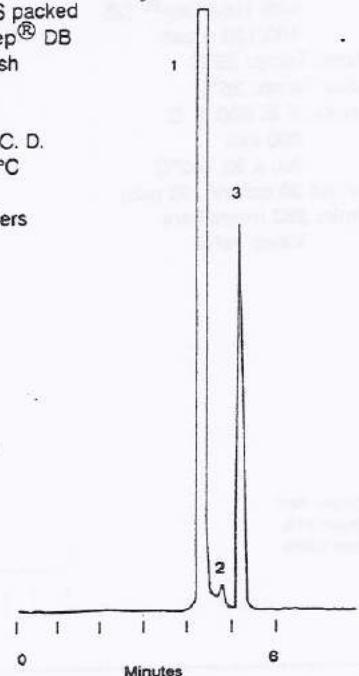


Figure 33
HYDROGEN IN HELIUM

Column: 25' x 1/8" SS packed
with HayeSep® D
100/120 mesh

Column Temp: 25°C
Injector Temp: 25°C
Detector: P.E. 900 T. C. D.
150 ma at 140°C

Flow: 24 cc/min N₂
Sample: 50 microliters
Valco valve

1. Helium Balance
2. Hydrogen 1%

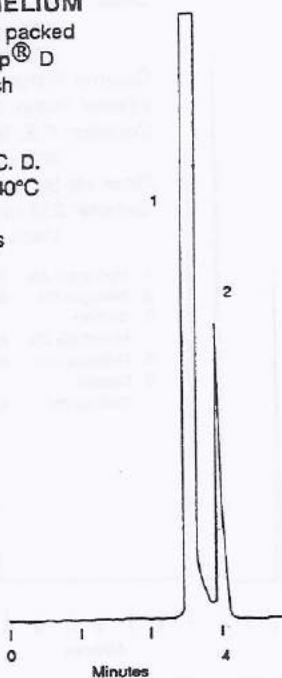


Figure 34
IMPURITIES IN HYDROGEN

Column: 25' x 1/8" SS packed
with HayeSep® DB
100/120 mesh

Column Temp: 25°C
Injector Temp: 25°C
Detector: P.E. 900 T. C. D.
225 ma

Flow: He 25 cc/min
Sample: 250 microliters
Valco valve

1. Hydrogen Balance
2. Nitrogen 80 ppm
3. Oxygen 20 ppm

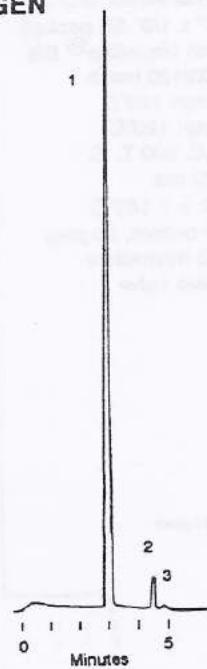


Figure 35
AIR IN ARGON

Column: 30' x 1/8" SS packed
with HayeSep® DB
100/120 mesh

Column Temp: 22°C
Injector Temp: 22°C
Detector: P.E. 900 T. C. D.
225 ma 140°C

Flow: He 30 cc/min
Sample: 100 microliters
Valco valve

1. Nitrogen 6000 ppm
2. Oxygen 1800 ppm
3. Argon 25%
4. Helium Balance

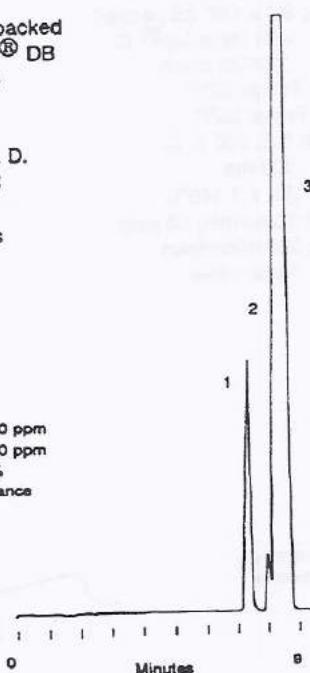


Figure 36
HYDROGEN/AIR 50/50
 Column: 25' x 1/8" SS packed
 with HayeSep® D
 100/120 mesh
 Column Temp: 25°C
 Injector Temp: 25°C
 Detector: P.E. 900 T. C. D.
 225 ma 140°C
 Atten x 8
 Flow: He 24 cc/min
 Sample: 50 microliters
 Valco valve

1. Hydrogen
2. Nitrogen
3. Oxygen
4. Argon

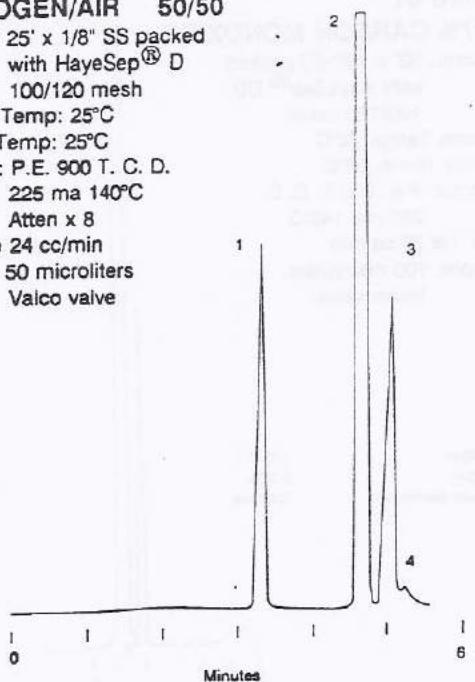


Figure 37
99.6% OXYGEN
 Column: 30' x 1/8" SS packed
 with HayeSep® DB
 100/120 mesh
 Column Temp: 22°C
 Injector Temp: 22°C
 Detector: P.E. 900 T. C. D.
 225 ma 140°C
 Flow: He 20 cc/min
 Sample: 100 microliters
 Valco valve

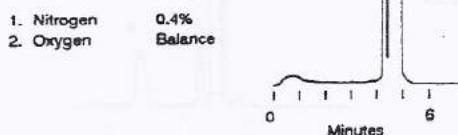


Figure 38
99.995% ARGON
 Column: 30' x 1/8" SS packed
 with HayeSep® DB
 100/120 mesh
 Column Temp: 22°C
 Injector Temp: 22°C
 Detector: P.E. 900 T. C. D.
 225 ma 140°C
 Flow: He 30 cc/min
 Sample: 100 microliters
 Valco valve

1. Nitrogen 50 ppm
2. Argon Balance

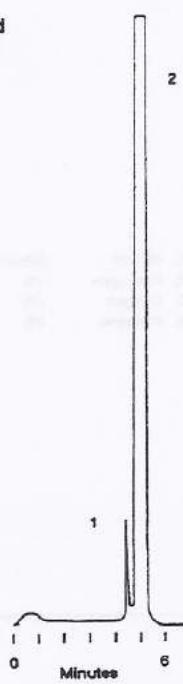


Figure 39
IMPURITIES IN NITROGEN TRIFLUORIDE
 Column: 25' x 1/8" SS packed
 with HayeSep® DB
 100/120 mesh
 Column Temp: 25°C
 Injector Temp: 25°C
 Detector: P.E. 900 T. C. D.
 275 ma 140°C
 Flow: He 30 cc/min
 Sample: 250 microliters
 Valco valve
 Chart Speed: 1 cm/min

1. Nitrogen 50 ppm
2. Oxygen 250 ppm
3. Carbon Tetrafluoride 400 ppm
4. Nitrogen Trifluoride Balance

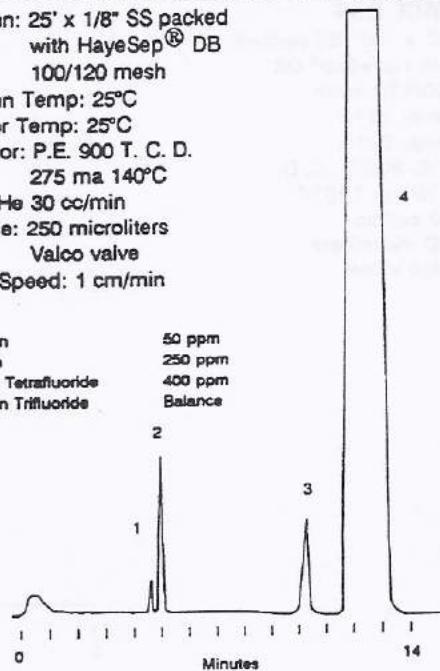


Figure 40
FAST ANALYSIS

Column: 48" x 1/16" x .04" ID SS
packed with HayeSep® DB
100/120 mesh
Column Temp: 70°C
Injector Temp: 70°C
Detector: P.E. 900 T. C. D.
225 ma 140°C
Flow: He 16 cc/min
Sample: 10 microliters
Valco valve

1. Nitrogen 2.7%
2. Methane Balance
3. Carbon Dioxide 3.0%
4. Ethane 3.5%



Figure 41
99.7% CARBON MONOXIDE

Column: 30' x 1/8" SS packed
with HayeSep® DB
100/120 mesh
Column Temp: 22°C
Injector Temp: 22°C
Detector: P.E. 900 T. C. D.
225 ma 140°C
Flow: He 30 cc/min
Sample: 100 microliters
Valco valve

1. Nitrogen 0.28%
2. Oxygen 0.02%
4. Carbon Monoxide Balance

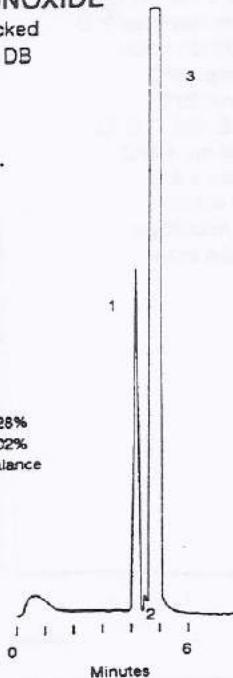
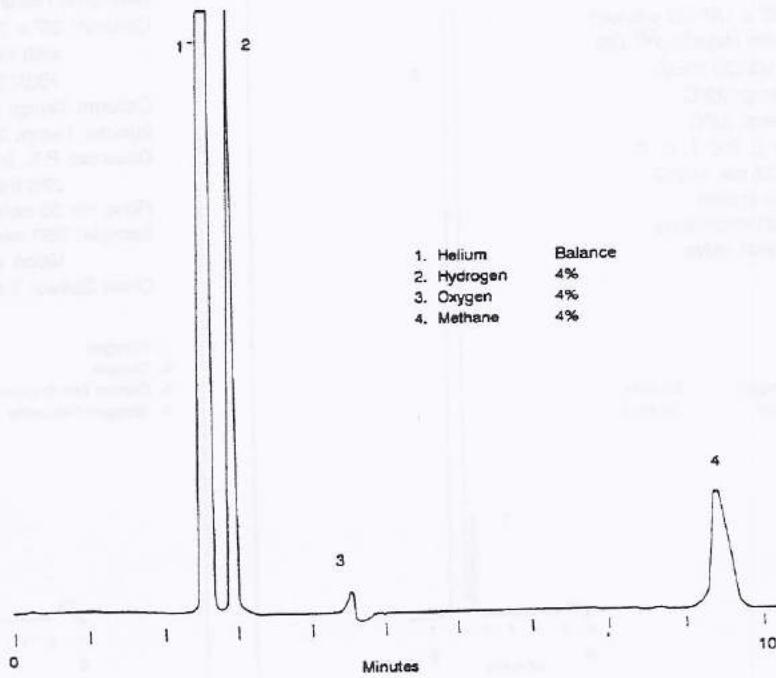


Figure 42
SCOTT MIX 234

Column: 30' x 1/8" SS packed
with HayeSep® DB
100/120 mesh
Column Temp: 22°C
Injector Temp: 22°C
Detector: P.E. 900 T. C. D.
225 ma 140°C
Flow: N₂ 30 cc/min
Sample: 100 microliters
Valco valve

1. Helium Balance
2. Hydrogen 4%
3. Oxygen 4%
4. Methane 4%



POROUS POLYMER MICROPACKED COLUMNS

Hayes Separations, Inc. has been making porous polymers for ten years. We have occasionally made micropacked columns for various customers as well as supplied packings for this purpose. A few examples of these are listed on the following pages. Of interest is the elution time of acetylene relative to ethylene and ethane. Figure 43 shows acetylene between ethylene and ethane; Figure 47 shows acetylene behind ethylene and ethane; Figure 46 shows acetylene in front of ethylene and ethane; Figure 48 shows rapid elution of impurities in methane. References for the production of porous polymers are listed below.

- 1) Hollis, O.L., Analytical Chemistry 38:309-316 (1966).
- 2) Hollis, O.L. and Hayes, W.V., J. Gas Chrom. 4:235-239 (1966).
- 3) Hollis, O.L. and Hayes, W.V., Gas Chrom., A.B. Littlewood, editor, The Institute of Petroleum, Rome, 1966, p. 57-74.
- 4) U.S. Patent - 3,357,158 December 12, 1967.
- 5) U.S. Patent - 3,458,976 August 5, 1969.
- 6) 1966 IR 100 Award (R&D magazine).

Figure 43
SCOTT MIX 216 + MAPP GAS

Column: 10' x 1/16" x .04"
packed with HayeSep® S
100/120 mesh
Column Temp: 60°C 3min up to
90°C at 8°C/min
Detector: P.E. 990 T. C. D. 225 ma
Flow: He 14 cc/min
Chart Speed: 1 cm/min
Sample: 50 microliters

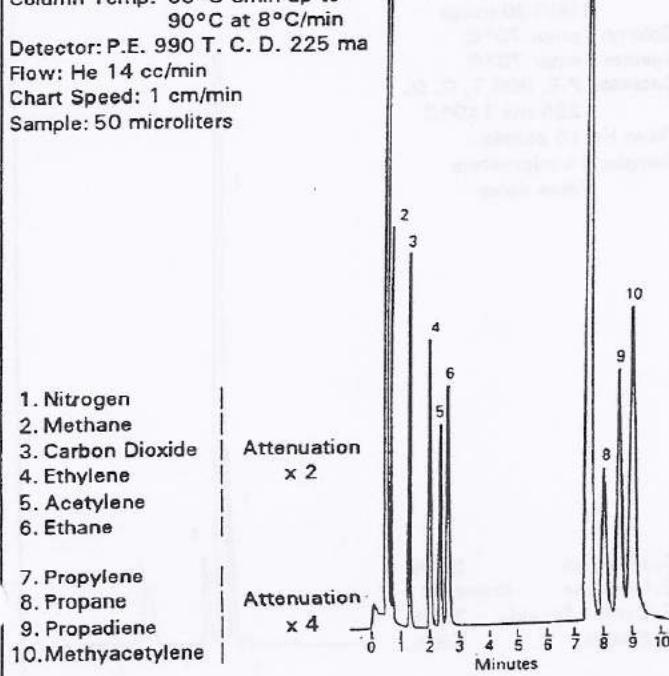


Figure 44
SCOTT MIX 234

Column: 20' x 1/16" x .04" SS
packed with HayeSep® D
100/120 mesh
Column Temp: 25°C
Detector: P.E. 900 T. C. D. 225 ma
140°C
Att. x 4
Flow: 13.3 cc/min He
Chart Speed: 1 cm/min
Sample Size: 25 microliters

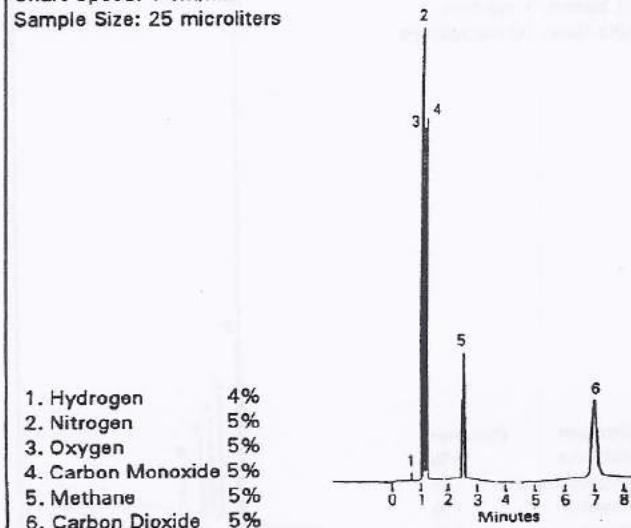


Figure 45

MIX 216 PROGRAMMED

Column: 20' x 1/16" x .04" SS
packed with HayeSep® D
100/120 mesh

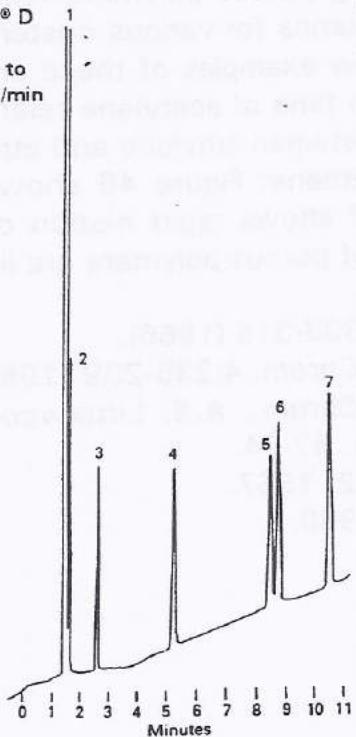
Column Temp: 25°C 2min up to
110°C at 8°C/min

Detector: P.E. 900 T. C. D. at
225 ma 140°C
Att. x 4

Flow: 13.33 cc/min He

Chart Speed: 1 cm/min

Sample Size: 25 microliters



1. Nitrogen 1%
2. Carbon Monoxide 1%
3. Methane 1%
4. Carbon Dioxide 1%
5. Acetylene 1%
6. Ethylene 1%
7. Ethane 1%

Figure 46

SCOTT MIX 216

Column: 20' x 1/16" x .04" SS
packed with HayeSep® D
100/120 mesh

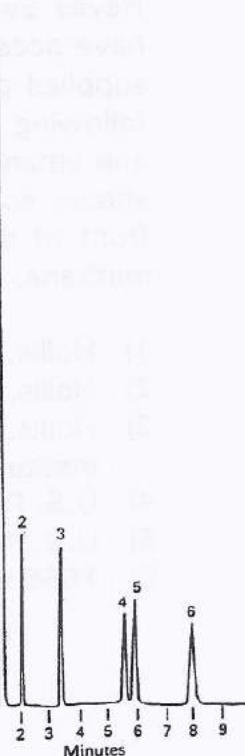
Column Temp: 70°C Isothermal

Detector: P.E. 900 T. C. D. at 225 ma
140°C
Att. x 4

Flow: 13.3 cc/min He

Chart Speed: 1 cm/min

Sample Size: 10 microliters



1. Nitrogen (balance)
2. Methane 1%
3. Carbon Dioxide 1%
4. Acetylene 1%
5. Ethylene 1%
6. Ethane 1%

Figure 47

SCOTT MIX 216

Column: 15' x 1/16" x .03"
packed with HayeSep® A
120/140 mesh

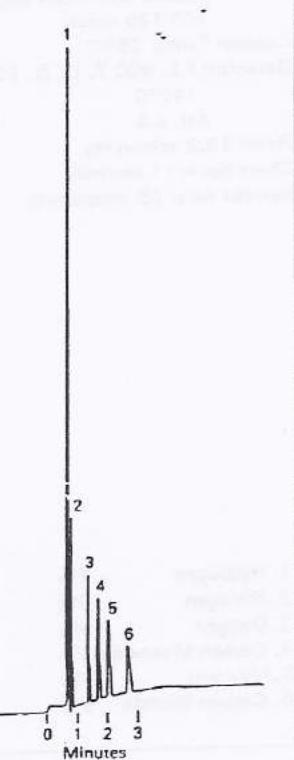
Column Temp: 45°C

Detector: VICI micro T. C. D. 120°C
Att. x 8

Flow: He 8 cc/min

Chart Speed: 1 cm/min

Sample Size: 10 microliters



1. Nitrogen (balance)
2. Methane 1%
3. Carbon Dioxide 1%
4. Ethylene 1%
5. Ethane 1%
6. Acetylene 1%

Figure 48

FAST ANALYSIS

Column: 48' x 1/16" x .04" ID SS
packed with HayeSep® DB
100/120 mesh

Column Temp: 70°C

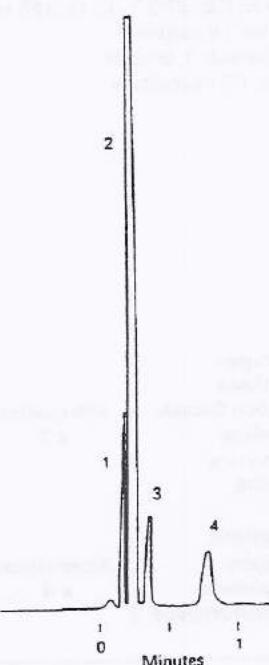
Injector Temp: 70°C

Detector: P.E. 900 T. C. D.
225 ma 140°C

Flow: He 16 cc/min

Sample: 10 microliters

Valco valve



1. Nitrogen 2.7%
2. Methane (balance)
3. Carbon Dioxide 3.0%
4. Ethane 3.5%

HAYESEP RT'S RELATIVE TO C₂H₆

6' X 1/8" ss Columns

HayeSep 80/100 mesh

60°C - 30 cc/min. Helium

Courtesy: Brian Thompson, Varian

Compound	A	B	C	D	DB	DIP
CF ₄	.13	.10	.08	.10	.10	.10
CH ₄	.09	.12	.11	.11	.11	.12
CO ₂	.54	.32	.47	.31	.30	.30
N ₂ O	.62	.44	.59	.42	.42	.43
F116	.63	.49	.45	.51	.52	.53
C ₂ H ₂	1.29	.65	1.03	.64	.62	.64
SF ₆	.81	.65	.64	.68	.68	.68
C ₂ H ₄	.81	.71	.75	.70	.70	.70
NH ₃	1.58	.71	1.21	.90	.65	.98
F13	1.10	.90	.84	.87	.88	.90
C ₂ H ₆	1.00	1.00	1.00	1.00	1.00	1.00
H ₂ O	7.06	1.14	5.31	1.08	.95	1.10
H ₂ S	2.06	1.45	2.20	1.36	1.35	1.39
COS	3.02	2.59	3.10	2.56	2.58	2.59
F22	7.63	3.11	6.34	3.30	3.31	3.35
C ₃ H ₆	4.70	3.75	4.41	4.01	4.11	4.10
C ₃ H ₈	4.94	4.43	4.70	4.73	4.84	4.84
SO ₂	10.23	3.84	5.31	3.67	3.82	3.68
PD	6.19	4.63	5.80	4.79	4.87	4.90
MA	8.09	4.70	7.03	4.92	4.96	5.00
CP	5.90	5.02	5.89	5.18	5.32	5.26
F12	7.83	5.71	6.79	6.38	6.47	6.46
IC ₄	17.92	14.73	16.21	16.74	17.18	17.32
1 , 3 BD	24.94	16.00	22.93	18.62	19.10	19.48
F114	27.35	18.35	21.46	21.48	22.11	22.88
NC ₄	23.60	19.33	21.21	22.26	22.66	23.01

RELATIVE RETENTION TIMES

Ethane = 1.00

Columns 6' x 1/8" SS 65°C

He 30 cc/min

Compound	N	Q	R	S	T
Hydrogen	0.19	.143	0.17	.19	.21
Air	0.23	.186	0.2	.21	.25
Nitric oxide	0.25	.217	0.21	.23	.33
Methane	0.30	.256	0.28	0.3	.35
Carbon dioxide	0.71	0.45	0.50	0.52	0.85
Nitrous oxide	0.80	0.57	0.59	0.59	—
Ethylene	0.83	0.74	0.78	0.78	0.9
Acetylene	1.41	0.74	1.0	0.87	2.11
Ethane	1.0	1.0	1.0	1.0	1.0
Water	10.1	1.45	6.8	4.12	19.1
Hydrogen sulphide	2.1	1.40	1.73	1.87	2.88
Hydrogen cyanide	19.3	2.31	15.6	8.26	28.8
Carbonyl sulphide	2.82	2.33	2.46	2.63	3.4
Sulphur dioxide	12.0	3.05	9.78	17.8	19.0
Propylene	4.66	3.20	3.45	3.65	4.91
Propane	4.66	3.67	3.88	4.1	4.63
Propadiene	6.50	4.12	4.39	4.7	7.55
Methylacetylene	9.5	4.12	4.84	5.14	11.3
Methyl chloride	7.43	3.93	4.67	4.92	9.2
Vinyl chloride	14.9	6.04	9.04	9.7	17.3
Ethylene oxide	17.7	6.06	8.78	9.7	23.3
Ethyl chloride	35.0	12.25	19.3	20.7	43.2
Carbon disulphide	—	32.4	—	—	40.7