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TITLE

RESULTS OF THE 1988 INDUSTRIAL HYGIENE ANALYTICAL PROFICIENCY TESTING STUDY
FOR VINYL CHLORIDE

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DESCRIPTIVE SUMMARY WITH CONCLUSIONS

Six laboratories participated in the Industrial Hygiene Analytical Proficiency Testing (APT) Study for vinyl chloride. Three other laboratories received samples but did not analyze them. Each laboratory analyzed charcoal tubes which had been loaded with known amounts of the compound. The results were analyzed statistically in accord with Industrial Hygiene (Reference) Procedure #101, "Statistical Guidelines for Evaluating Data from Analytical Proficiency Testing Round Robin Studies of Industrial Hygiene Samples." Using these guidelines, the accuracy goal was 90-110% of the reference value and the precision goal was $\pm 10\%$. The accuracy goal was met by two of the six participating laboratories and all six of the laboratories attained the precision goal.

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INTRODUCTION

One of the elements of a quality assurance program for a laboratory analyzing industrial hygiene samples is the periodic analysis of 'blind' knowns prepared outside of the laboratory performing the analyses. Industrial Hygiene (Reference) Procedure (IHP) 405, "Basic Guidelines for Assuring Quality in Industrial Hygiene Analyses", provides information about all the elements of an adequate quality assurance program for laboratories performing industrial hygiene analyses. Analysis of such extramural unknowns will generally be infrequent, compared to the analysis of knowns prepared in the laboratory and 'blind' knowns submitted by the industrial hygienist or industrial hygiene contact, but serve the purpose of comparing analytical proficiency among a group of geographically scattered and highly diverse laboratories doing the same analyses. The proficiency testing samples provided through the Dow Industrial Hygiene Analytical Proficiency Testing (APT) Program should be only one element of the quality assurance program of a laboratory doing such analyses. Failure to meet the accuracy and precision goals for the APT study should, however, lead to the initiation of a review by the participating laboratory to identify the source(s) of the problem.

Because of the special challenges associated with analyzing a highly volatile compound such as vinyl chloride, this compound was the subject of its own APT study, and not combined with other chlorinated C₂ compounds, as in earlier studies (Refs. 1,2,3).

In this APT study, six unknown samples, one gram charcoal tubes, were sent out to each participating laboratory. The samples were at one of three contaminant levels, representing twenty liter air samples collected in atmospheres with approximately 0.25, 1.0, and 2.0 times the current U.S. Occupational Safety and Health Administration's Permissible Exposure Limit (PEL). The current PEL is 1 ppm for vinyl chloride, as an eight hour time-weighted average.

In addition to the spiked samples, four blank tubes were provided to each participating laboratory to: 1) determine a blank value for the tubes, and 2) determine the desorption efficiency for vinyl chloride with this lot number of charcoal.

The samples were prepared by a contract laboratory, Texas Research Institute (TRI), Austin, Texas. TRI provided analyses of nine samples from the set they had prepared, and the Dow Corporate Industrial Hygiene Laboratory analyzed another nine samples shortly after receipt and obtained values in excellent agreement with those supplied by TRI. In addition, both transportation and storage studies were performed to determine if shipping under uncontrolled conditions or storage for extended periods of time prior to analysis had a significant effect on the analytical results.

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EXPERIMENTAL

The one gram charcoal tubes were prepared by loading the required compounds from the gas phase. Each of the tubes was connected to a central manifold through one of a large number of glass capillary tubes. All of the capillaries were tested in advance to verify that the flow rates through each were identical, within $\pm 5\%$ of their mean value.

To this manifold, pressurized with dry nitrogen, a known quantity of vinyl chloride gas was added and the mixture was forced through the capillaries and into each of the tubes until the flow through the capillaries had essentially ceased. The target loading levels for the tubes were 15, 40, and 120 micrograms per tube, respectively, for the three loading levels. After loading had been completed, the samples were flame sealed and nine of these tubes, three at each level, were opened and analyzed by TRI to confirm the mass loadings. The samples were shipped to Midland from Austin, Texas, on May 25, 1988, having been prepared a day or two earlier, and were shipped from Midland to the participating laboratories, using the most rapid means of transportation, on May 27. Reports of analytical results were requested no later than July 5. A summary of the timeliness of analysis and reporting of results follows:

<u>Laboratory Code</u>	<u>Date Analyzed</u>	<u>Date Results Received</u>	<u>Days Between Sample Receipt and Analysis</u>
A	REFERENCE LABORATORY		
B	6-13-88	6-16-88	12
C	6-16-88	7-1-88	3
D	6-24-88	7-1-88	11
E	6-21-88	7-5-88	11
F	7-19-88	7-26-88	20
G	6-3-88	6-3-88	7

All but one of the participating laboratories met the reporting deadline.

RESULTS

The guidelines given in Industrial Hygiene (Reference) Procedure #101, "Statistical Guidelines for Evaluating Data from Analytical Proficiency Testing (APT) Round Robin Studies of Industrial Hygiene Samples" led to the the following goals for the analysis of vinyl chloride:

Accuracy: 90-110% of the reference value

Precision: $\pm 10\%$

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These values are based on the reported relative precision for a single measurement for the analytical method found in HEH-IHM-83-25A. The attainment of goals for the various laboratories that participated in the study is evaluated using the data provided by Texas Research Institute as the reference values.

As it turned out, the attainment of goals was identical for all of the participating laboratories regardless of whether the TRI values, the Corporate Industrial Hygiene Laboratory values, or the grand mean of all data submitted were used as reference values for this study. The attainment of goals is summarized in the following table:

<u>Lab I.D.</u>	<u>Precision</u>	<u>Accuracy</u>	
A	+	#	
B	+	-	
C	+	+	
D	+	-	+ = attained goal
E	+	-	
F	+	-	- = did not attain goal
G	+	+	

= Reference Value; results defined as 100%

Table 1 lists all values submitted by the participating laboratories, corrected for desorption efficiency (FOUND1), as well as the reference values (ACT1) for each level. Table 2 lists all the values submitted as a percent of the reference value for that loading level. Table 3 gives the mean percent of the reference value reported for each of the laboratories, along with the standard deviation of that value.

Figure 1 is a display of each laboratory's precision and shows the individual data points submitted by each participating laboratory, as a percent of the reference value, after normalizing the mean percent for each individual laboratory to 100 to keep (nearly) all the data points on the figure. Some points may be obscured because they are too close together (see Table 1 for the individual values reported), and any values in excess of 200% will not be shown.

Figure 2 shows the mean percent of the reference value for all results reported, for each participating laboratory, with the error bars indicating the relative precision of the calculated average percent of the reference values, RP_n , which is calculated as follows:

$$RP_n = \frac{t \times S}{R_n \times \sqrt{n}} \times 100$$

Where R_n = mean percent of the reference value, for the results of an individual laboratory

S = standard deviation of the individual R_n values

t = student's t value for the number of measurements made

n = number of measurements made

For $n = 6$, $RP_n = S/R_n \times 100$, which is the relative standard deviation.

Figure 3 shows the trends in attainment of accuracy and precision goals for the participating laboratories during the last four APT studies which included vinyl chloride. The study reported on September 21, 1982, was the repeat of a study reported four months earlier, and included only those laboratories that did poorly in the earlier study. It is not unexpected that the attainment of goals for this study would be higher than for other studies. The long term trend indicates that laboratories analyzing for vinyl chloride are getting results that are more consistent (for example, all of the values are 20% low), and thus the percent of laboratories meeting the precision goal has increased over the past six years. Unfortunately, the attainment of the accuracy goal has remained consistently low, with no significant improvement over the past six years. This is probably a reflection of infrequent or inadequate calibration of the gas chromatograph, difficulties in preparing accurate standard solutions, and/or the lack of regular analysis of spiked samples to be analyzed along with the unknowns. It is most likely not a reflection of sample degradation, for two reasons. First, the participating laboratories submitted results both above and below the reference values (from TRI). The grand mean of all data submitted was 103.5% of the reference value.

SAMPLE STABILITY

Two sets of vinyl chloride APT samples were sent to Freeport, Texas, and Stade, Federal Republic of Germany, respectively, and returned to Midland for analysis. Both sets were sent out on May 27 and were received on June 14 and June 13, respectively, at which time they were put in a freezer until analysis on June 30. The analytical results from the transported samples were compared statistically with the results provided by TRI initially. For the low and high loading level samples, there was no statistical difference between the results, at the 95% confidence level, using a two-sided t -test. For the medium loading level samples, there was a difference at this confidence level, with the mean value of the transported samples being 12.5% lower than that of the original samples. This suggests that little or no degradation of the samples occurred during the time and under the conditions of shipping from Midland and returning again from one of these two destinations.

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In order to evaluate the long-term stability of the vinyl chloride samples, five samples at each of the loading levels were stored in a refrigerator at approximately 2°C for six months after preparation and analyzed on December 6, 1988. The analytical results were compared against the combined mean values of TRI and the Dow Industrial Hygiene Laboratory. A two-sided t-test was performed and the results of the stored samples were determined to be statistically different from the reference values, at the 95% confidence level. The fractional losses from the three loading levels of samples were remarkably similar, with percent losses of 16.4, 18.3, and 16.1 for the low, medium, and high loading level samples, respectively. This suggests that flame-sealed samples maintained at refrigerator temperatures experience an average 2.6 percent loss of vinyl chloride per month over as long as six months. This information should be of value in the preparation of spiked samples which are stored for future use and in the storage of unknowns prior to analysis. A similar set of samples will be analyzed one year after preparation.

DISCUSSION

Twice in 1982 and again in 1985, global APT studies for the Vinyl Chloride Technology Center (now included in the Chlorinated Ethane Products/Thermal Oxidizer Technology Center) were carried out, as well as three times prior to 1982. The second study in 1982 was a repetition of a study done earlier that year for which the results were highly unsatisfactory for several participating laboratories. All of those studies included vinyl chloride as one of the compounds loaded on the sorbent tubes. Figure 3 shows the performance of the participating laboratories for the four most recent studies, including this one, both with regard to accuracy and precision. Study B is the repeat study done only a few months after Study A and had a small number of participants (4). Clearly, the participants benefitted from having analyzed similar samples only a few months earlier--and perhaps from perceiving some urgency in improving their analytical performance from the study done a few months previously. Another way of looking for improvement or degradation of performance over the past six years is to look at the trend in the grand mean and standard deviation of all laboratories' mean percent of the reference values reported. Excluding the repeat study in 1982, which is anomalous, for reasons just mentioned, the grand mean and standard deviation have gone from $158 \pm 183\%$ to $72 \pm 31\%$ to 104 ± 21 percent in the three studies mentioned. This indicates that, as a group, the labs' data are more highly clustered (higher precision) as a whole, and that the grand mean is getting closer to the 100% value, which one would desire, not only overall, but for each individual laboratory.

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REFERENCES

1. Results of Industrial Hygiene Quality Assurance Round Robin Series 1D: Vinyl Group; HEH2.12-39-3(2); G. Poettcker; May 15, 1982.
2. Repeat of Industrial Hygiene Quality Assurance Round Robin Series 1D: Vinyl Group; HEH2.12-39-3(3); G. Poettcker; September 21, 1982.
3. Results of the 1984 Analytical Proficiency Testing Round Robin for the Vinyl Chloride Series; HEH2.12-39-3(10); R. M. A. Hahne; May 28, 1985

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Table 1. VALUES SUBMITTED BY PARTICIPATING LABORATORIES ($\mu\text{g}/\text{tube}$),
VINYL CHLORIDE ANALYTICAL PROFICIENCY TESTING (APT)

<u>Lab Code</u>	<u>Loading Level</u>	<u>Reference Value</u>	<u>Laboratory Data</u>
A	L	16.77	16.8
A	L	16.77	17.3
A	L	16.77	16.2
A	M	43.37	43.5
A	M	43.37	43.2
A	M	43.37	43.4
A	H	145.3	144.0
A	H	145.3	146.0
A	H	145.3	146.0
B	L	16.77	24.0
B	L	16.77	23.0
B	M	43.37	56.0
B	M	43.37	57.0
B	H	145.3	200.0
B	H	145.3	185.0
C	L	16.77	18.3
C	L	16.77	18.7
C	M	43.37	44.7
C	M	43.37	45.3
C	H	145.3	163.6
C	H	145.3	161.1
D	L	16.77	13.0
D	L	16.77	15.0
D	M	43.37	35.0
D	M	43.37	34.0
D	H	145.3	111.0
D	H	145.3	107.0
E	L	16.77	20.0
E	L	16.77	20.0
E	M	43.37	48.0
E	M	43.37	49.0
E	H	145.3	185.0
E	H	145.3	172.0

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Table 1. (Continued)

<u>Lab Code</u>	<u>Loading Level</u>	<u>Reference Value</u>	<u>Laboratory Data</u>
F	L	16.77	14.2
F	L	16.77	12.6
F	M	43.37	39.2
F	M	43.37	35.3
F	H	145.3	109.4
F	H	145.3	117.0
G	L	16.77	17.5
G	L	16.77	16.7
G	L	16.77	17.9
G	M	43.37	41.5
G	M	43.37	44.0
G	M	43.37	43.7
G	H	145.3	138.0
G	H	145.3	139.0
G	H	145.3	147.0

Table 2. PARTICIPATING LABORATORIES' DATA EXPRESSED AS PERCENT OF
REFERENCE VALUE: VINYL CHLORIDE A.P.T.

<u>Lab Code</u>	<u>Loading Level</u>	<u>Percent of Reference Value</u>
A	L	100.2
A	L	103.2
A	L	96.6
A	M	100.3
A	M	99.6
A	M	100.1
A	H	99.1
A	H	100.5
A	H	100.5
B	L	143.1
B	L	137.2
B	M	129.1
B	M	131.4
B	H	137.6
B	H	127.3
C	L	109.1
C	L	111.5
C	M	103.1
C	M	104.5
C	H	112.6
C	H	110.8
D	L	77.5
D	L	89.5
D	M	80.7
D	M	78.4
D	H	76.4
D	H	73.6
E	L	119.3
E	L	119.3
E	M	110.7
E	M	113.0
E	H	127.3
E	H	118.3

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Table 2. (Continued)

<u>Lab Code</u>	<u>Loading Level</u>	<u>Percent of Reference Value</u>
F	L	84.7
F	L	75.1
F	M	90.4
F	M	81.4
F	H	75.3
F	H	80.5
G	L	104.4
G	L	99.6
G	L	106.8
G	M	95.7
G	M	101.5
G	M	100.8
G	H	95.0
G	H	95.6
G	H	101.1

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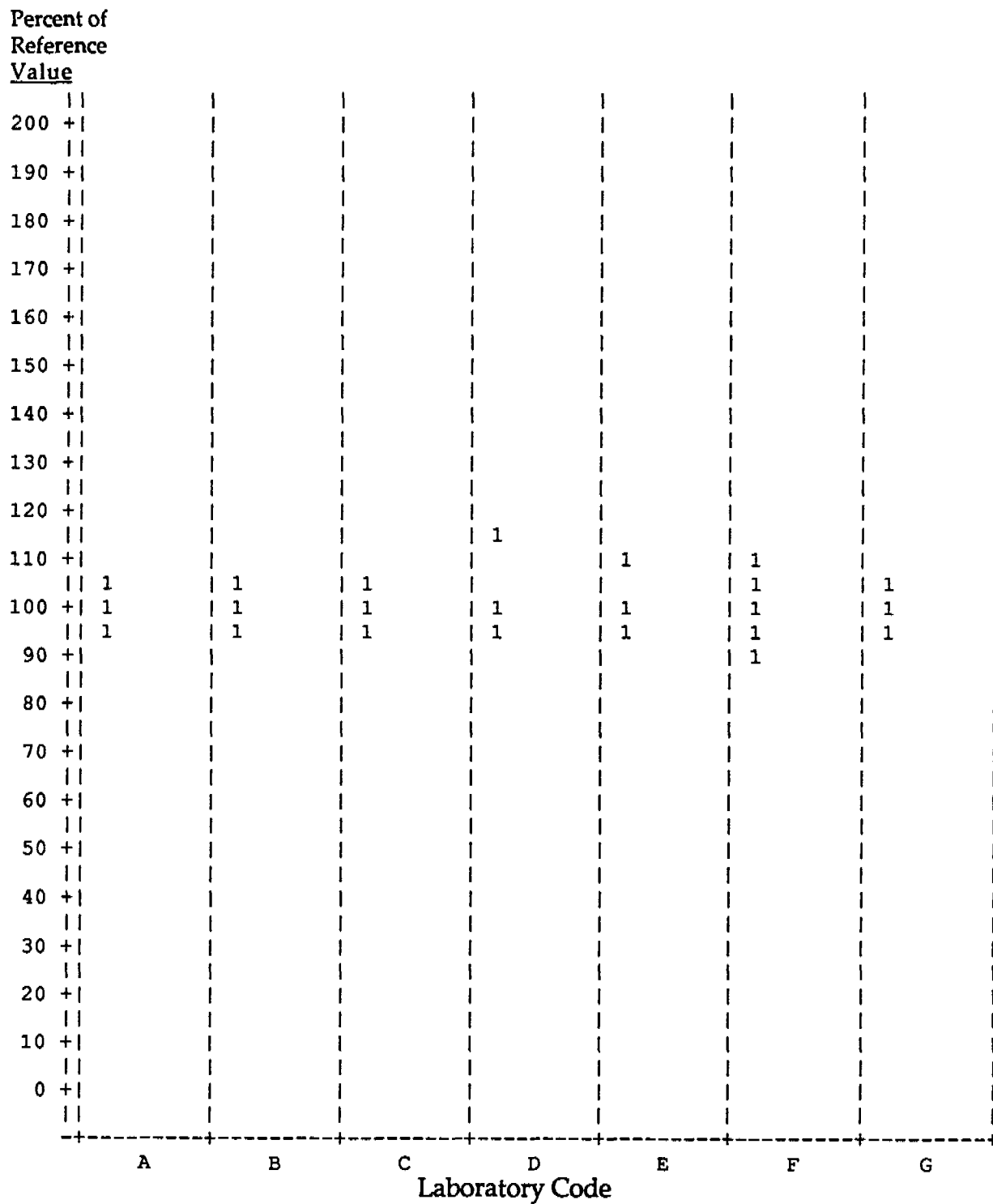
Table 3. MEAN AND STANDARD DEVIATION OF LABORATORIES' DATA
EXPRESSED AS PERCENT OF REFERENCE VALUES: VINYL CHLORIDE
A.P.T.

<u>LAB</u>	<u>MEAN</u>	<u>STD. DEV.</u>
A	100	2
B	134	6
C	109	4
D	79	5
E	118	6
F	81	6
G	100	4

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Figure 1. GRAPHIC DISPLAY OF TABLE 2

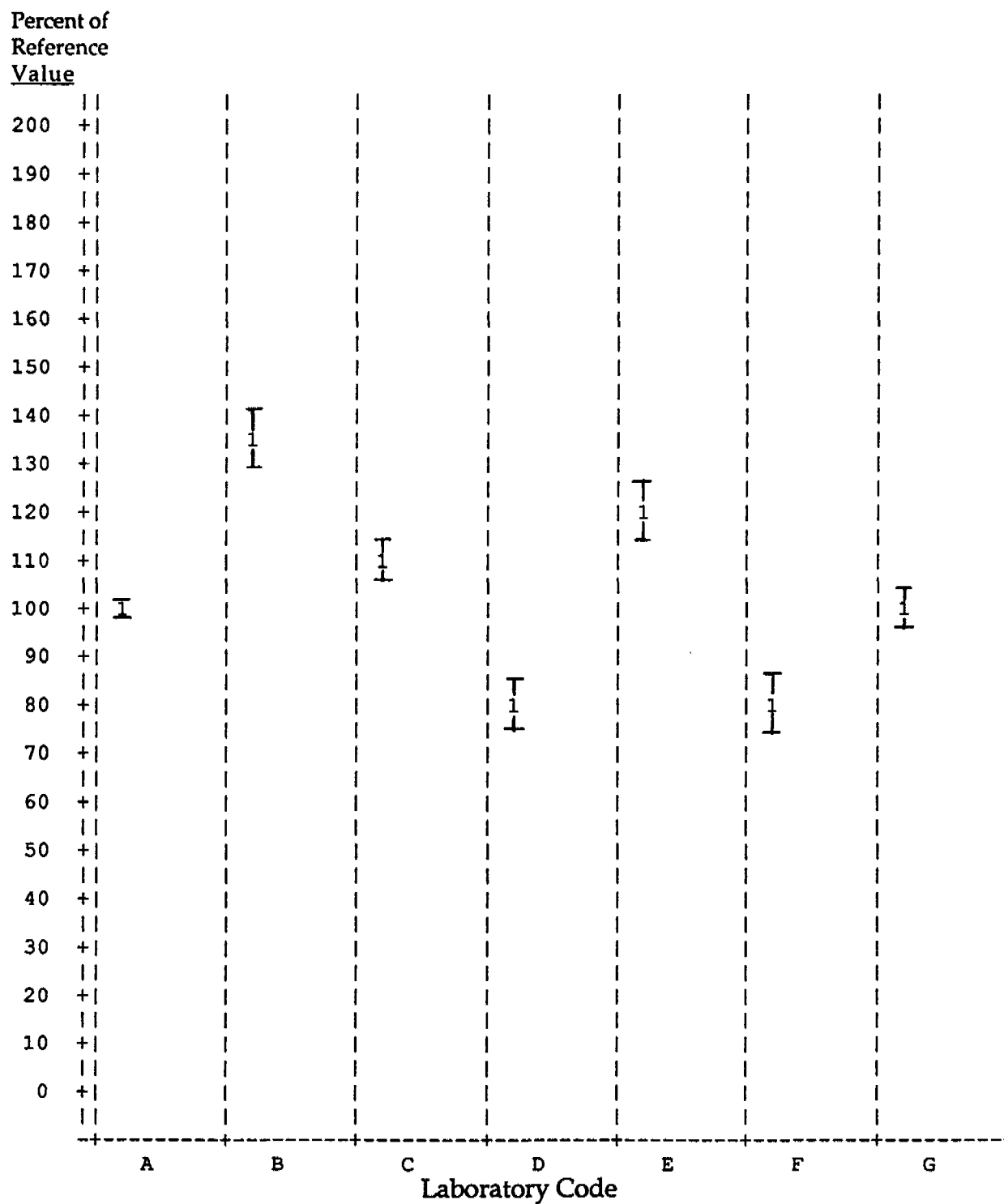


Note: Each laboratory submitted six results, but closely spaced values may be obscured.

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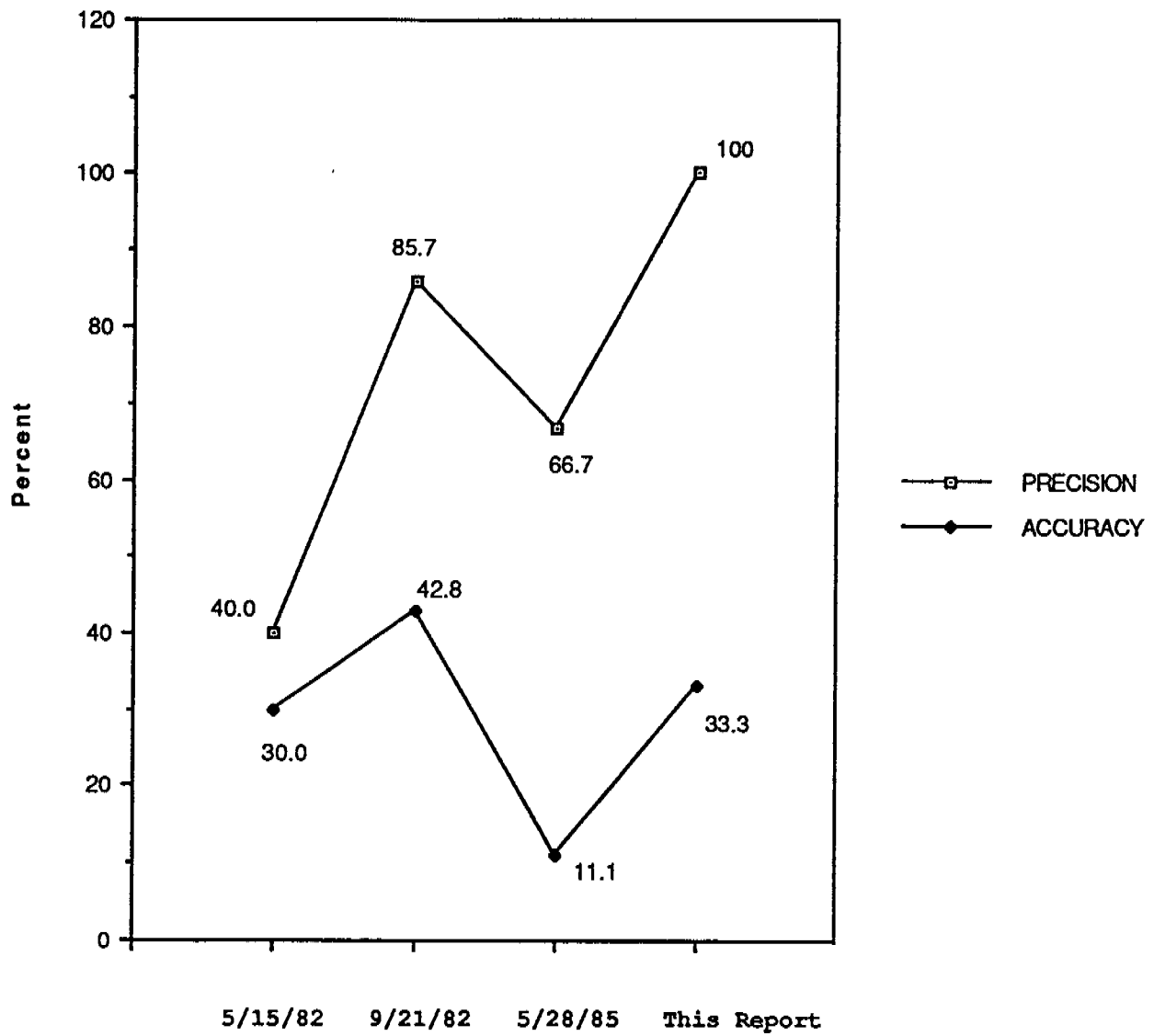
Figure 2. GRAPHIC DISPLAY OF TABLE 3



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Figure 3. PERCENT OF LABORATORIES ATTAINING GOALS



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IDENTIFICATION OF PARTICIPANTS IN
VINYL CHLORIDE A.P.T. STUDY

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<u>Lab Code</u>	<u>Location</u>	<u>Analyst</u>
A	Texas Research Institute, Austin, Texas	
B	Plaquemine, Louisiana, Environmental Lab	L. Almo
C	Freeport, Texas, OC Unit I	H. Klinegardner
D	Freeport, Texas, Analytical Services	L. Jones
E	Stade, FRG, Ecology Department	U. Theodorczyk
F	Sarnia, Ontario, Canada, C.P. Lab, Building 311	J. Ruby
G	Midland, Michigan, I.H. Analytical Lab	C. Jenkins

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