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TITLE

RESULTS OF THE 1984 ANALYTICAL PROFICIENCY TESTING ROUND ROBIN FOR CHLORINATED METHANES

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DESCRIPTIVE SUMMARY WITH CONCLUSIONS

Five laboratories participated in the Analytical Proficiency Testing Round Robin for the chlorinated methanes. Each laboratory analyzed six charcoal tubes (two tubes at each of three different levels). The tubes were prepared by passing compressed nitrogen containing the four compounds through charcoal sorbent tubes for different lengths of time.

The data have been treated statistically in a manner consistent with th soon-to-be distributed Industrial Hygiene Procedure No. 101 -- "Statistical Treatment of APT/Round Robin Data."

The mean percent of actual values reported were 99, 101, 101, and 81 for methyl chloride, methylene chloride, chloroform, and carbon tetra-chloride, respectively, with relative standard deviations of 23, 37, 24, and 28 percent for the same four compounds respectively.

The accuracy goal for this study is that the results reported for each laboratory fall showed between 86% and 114% of the actual value for methyl chloride, between 90% and 110% for methylene chloride, between 87% and 113% for chloroform, and between 86% and 114% for carbon tetrachloride with a goal for precision of ±10% for each chemical. Although some laboratories met the goal for accuracy or precision for at least one of the chemicals, none of the laboratories met the goals for accuracy and precision for all the chemicals. There may have been a variety of reasons for not meeting the goals, which should be addressed on a case-by-case basis.

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INTRODUCTION

One of the components of a good quality assurance program in an analytical laboratory is the analysis of extramural proficiency testing samples, i.e., samples which are prepared externally to the laboratory doing the analyses. For laboratories analyzing industrial hygiene samples within Dow, the Analytical Proficiency Testing Round Robin (APT) is one source of such samples. Approximately once every two years, a different set of samples is sent out to all participating laboratories. The samples cover the spectrum of analytes of interest to Dow industrial hygienists, and the analytes for a given sample set are intended to reflect the compounds which might be expected in a given plant's work environment, at a range of levels from approximately one-tenth to two times the Industrial Hygiene Guide (IHG) or Threshold Limit Value (TLV), assuming an air sample volume of 20 liters.

The APT results discussed in this report are for samples containing the four chlorinated methanes: methyl chloride, methylene chloride, chloroform, and carbon tetrachloride.

Late in December of 1983, a set of six samples and three blanks was sent out to each participating laboratory for analysis of these four compounds. Three pairs of identical samples, each containing a different level of the four compounds (identified as low, medium, and high for simplicity in the tabulations), as specified in the protocol[1] were prepared on 2-gram activated charcoal tubes. The participating laboratories were Louisiana Division Chlorinated Methanes, Louisiana Division Environmental Control, Texas Division Chlorinated Methan s, Dow Europe Stade, and the H&ES Industrial Hygiene Laboratory, with the study director serving as the "reference laboratory."

EXPERIMENTAL

The charcoal tubes were prepared by passing known volumes of a gas containing approximately 120, 300, 200, and 200 mg, respectively, of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 in 7000 g of dry nitrogen, through the charcoal tubes. The tubes were prepared on a twelve-place metal manifold, with each tube having its own pre-calibrated rotameter. Since eighteen tubes of each loading level were prepared in two runs (one with partially used manifold), efforts were made to distribute the tubes such that each laboratory received some tubes from more than one run, and also received tubes loaded at different positions on the manifold, should this be a variable as well. Analysis of the cylinder gas was done to estimate the flow time needed to attain the desired loadings for each analyte. The low, medium, and high loadings had 7, 12, and 20 liters of the "spiked" nitrogen passed over them at a rate of roughly 150 ml/minute.

The gas was analyzed by introducing 500 ul samples directly from the cylinder into a gas sampling valve and then into the gas chromatograph (Hewlett-Packard Model 5730A) with a hydrogen flame ionization detector and a Hewlett-Packard 3380A integrator. The theoretical loading, determined by a direct gas analysis, was not used as the "true" value of the analyte in this study because (1) the gas entering the gas chromatograph may not have b en exactly the same as that

entering the sorbent tubes, (2) the peak shape and location of the CS_2 solvent peak in the chromatogram made the sorbent tube and gas analysis methods slightly different, and (3) the sampling loop may not have a volume of exactly 500 ml. For these reasons, the true value was estimated by the average of the analyses of the sorbent tubes.

For practice, the reference laboratory analyzed a dozen tubes loaded in th manner described and did four measurements of recovery using the phase equilibrium recovery method[2]. Of the samples actually prepared for the study, five of each type were set aside to be analyzed by the reference laboratory. One was lost in a laboratory accident. Nine other samples, three each at three different levels of concentration, were analyzed to determine recovery as a function of loading, using the phase equilibrium recovery method.

The reference laboratory performed the final sample analyses using a Hewlett-Packard (H-P) Model 5730A gas chromatograph with an H-P Model 7672A autosampler, the entire system being coupled to a H-P laboratory computer system. Calibration of the gas chromatograph was done using standards of the four compounds in carbon disulfide at two different levels, bracketing the expected responses for the samples to be analyzed. A duplicate of the higher standard was also prepared to verify the accuracy of that standard[3].

RESULTS

Table 1 is a compilation of all the data submitted. Table 2 shows the results submitted as percent of actual. The "actual" mass loading was calculated as the grand mean of all results submitted, after outliers had been eliminated using the Dixon criteria[4]. The results submitted include thirty results from the fiv participating laboratories plus 12-14 results from the reference laboratory. The grand mean, with outliers removed, was used because it is the feeling of the author that the results of a large number of analyses done by proficient analysts gives a better indication of the "true" value than the results of a single analyst. This approach was used in the NIOSH/PAT program for many years, and a grand mean of "reference laboratories" is still used by NIOSH/PAT to determine true values. Table 3 shows the accuracy for each laboratory by determining the mean value and the standard deviation of the percent of actual reported, for each contaminant. Mean values that are significantly different from one hundred percent indicate problems with getting accurate values, while large standard deviations indicate a wide variation in the percent of actual values calculated for each level, for a given contaminant.

Figure 1 shows the overall accuracy of each participating laboratory, for ach contaminant. Each of the four points is an average of the six values of percent of actual found for each contaminant.

Figure 2 shows the precision of the reported values. Each of the numbers was normalized by using the following equation:

$$N \text{ (Normalized)} = \frac{Ri}{\overline{R}} \times 100$$

where Ri = the individual value reported for a compound at a given level,

$\overline{R}$ = the mean of the two values reported for a compound at a given level.

This normalization was done so that all of the precision values could be displayed on the same figure using one set of control limits. Without the normalization, each laboratory would have required a different figure with different control limits shown, because the mean values reported for a given contaminant varied widely from laboratory to laboratory.

Figure 3 shows the mean recovery reported by laboratory and by contaminant, with the relative precision of the calculated average percent recovery shown as the error bar. This is calculated from the formula

$$RP_n = \frac{tS}{\overline{R}_n\sqrt{n}} \times 100$$

Where t = student's t value for the number of measurements made
S = standard deviation of the measurements for a given laboratory,
$\overline{R}_n$ = average percent recovery reported
n = number of measurements made

The accuracy goal for this and subsequent Analytical Proficiency Testing Round Robins will be the larger of the following:

a) 90% to 110% of actual value for compounds whose relative precision of a single determination at the 95% confidence level is 24.5% or less or

b) (100 - X)% to (100 + X)% of the actual value for compounds whose relative precision of a single determination at the 95% confidence level is greater than 24.5%, where

$$X = \frac{RP_s}{\sqrt{n}} \quad \text{and}$$

RP_s = relative precision for a single determination at the 95% confid nce level, as reported in the Industrial Hygiene Methods Manual,

n = the number of measurements reported by the laboratory

The precision goal for this and subsequent studies will be that, for each laboratory, the relative precision of the calculated average per cent of actual values reported (RP_n) be no larger than $\frac{RP_s}{\sqrt{n}}$, where

RP_s and n have the same definitions as in the equation given above.

RP_n is calculated using the following equation:

$$RP_n = \frac{ts}{\bar{R}_n \sqrt{n}} \times 100$$

where S is the standard deviation calculated for a given laboratory's set of measurements
t is the student's t-value for the number of measurements, n, at the 95% confidence level and
$\bar{R}_n$ = average percent of actual reported for the measurements made.

Any laboratory submitting data points which were determined to be outliers by the Dixon criteria (Laboratories A and E) should review its analytical methods to ascertain possible sources of error. Possible sources of error includ the following:

1. Incorrect preparation of standards. Action: check calculations used to determine how to prepare standards; prepare two independent standards at the same or similar concentrations; loss of methyl chloride in preparing or handling standard would lead to a larger response factor and high results.

2. Erroneous calculations. Action: recheck all calculations.

3. Loss of compounds during desorption. Action: cool carbon disulfide to dry ice temperature before adding charcoal from tubes.

4. Loss of methyl chloride during storage, prior to analysis. Action: in the future, refrigerate prior to analysis.

5. Adsorption of compounds (especially CCl_4) on charcoal after desorption. Action: if the desorbed sample is not analyzed shortly after preparation, remove the sample from the charcoal since CCl_4, in particular, appears to irreversibly adsorb on the charcoal after standing for an extended period.

The study director will be in contact with each of the Dow Chemical U.S.A. industrial hygiene managers where laboratory problems were experienced to discuss corrective actions.

Because of the mixed performance on this APT, it is likely that it will be repeated earlier than its next scheduled date of December 1985, in order to assist laboratories in improving their analytical proficiency for these four compounds.

REFERENCES

1. Poettcker, G., Program for conducting Industrial Hygiene Analytical Proficiency Round Robins, HEH2.12-39-1, 1983-84, August 1983.

2. Melcher, R. G., Industrial Hygiene (Reference) Procedure 106, "Desorption Efficiency and Recovery," Dow Chemical U.S.A., Midland, Michigan.

3. Coyne, L. B., Industrial Hygiene (Reference) Procedure 102, "Standard Preparation," Dow Chemical U.S.A., Midland, Michigan.

4. Dixon, W. J., Processing Data for Outliers, Biometrics, 9:89, 1953.

Table 1. ANALYTICAL PROFICIENCY TESTING: RESULTS (MG/TUBE)

Lab	Level	Actual CH_3Cl	Found CH_3Cl	Actual CH_2Cl_2	Found CH_2Cl_2	Actual $CHCl_3$	Found $CHCl_3$	Actual CCl_4	Found CCl_4
A	HIGH	0.30	0.18	1.25	1.33	0.78	1.00	0.74	0.82
A	HIGH	0.30	0.22	1.25	1.40	0.78	1.20	0.74	1.03
A	MED	0.18	0.12	0.76	0.94	0.47	0.69*	0.45	0.62
A	MED	0.18	0.12	0.76	0.77	0.47	0.69*	0.45	0.62
A	LOW	0.11	0.07	0.40	0.42	0.26	0.44*	0.24	0.41
A	LOW	0.11	0.07	0.40	0.31	0.26	0.38*	0.24	0.48*
B	HIGH	0.30	0.21	1.25	1.09	0.78	0.53	0.74	0.60
B	HIGH	0.30	0.25	1.25	1.02	0.78	0.50	0.74	0.57
B	MED	0.18	0.16	0.76	0.66	0.47	0.33	0.45	0.38
B	MED	0.18	0.16	0.76	0.69	0.47	0.34	0.45	0.40
B	LOW	0.11	0.08	0.40	0.38	0.26	0.18	0.24	0.20
B	LOW	0.11	0.09	0.40	0.38	0.26	0.18	0.24	0.21
C	HIGH	0.30	0.29	1.25	1.06	0.78	0.74	0.74	0.56
C	HIGH	0.30	0.38	1.25	1.29	0.78	0.85	0.74	0.86
C	MED	0.18	0.26	0.76	0.77	0.47	0.49	0.45	0.50
C	MED	0.18	0.18	0.76	0.70	0.47	0.46	0.45	0.46
C	LOW	0.11	0.15	0.40	0.42	0.26	0.27	0.24	0.27
C	LOW	0.11	0.13	0.40	0.42	0.26	0.28	0.24	0.27
D	HIGH	0.30	0.36	1.25	1.29	0.78	0.90	0.74	0.92
D	HIGH	0.30	0.33	1.25	1.25	0.78	0.84	0.74	0.84
D	MED	0.18	0.21	0.76	0.74	0.47	0.51	0.45	0.55
D	MED	0.18	0.23	0.76	0.75	0.47	0.51	0.45	0.53
D	LOW	0.11	0.13	0.40	0.43	0.26	0.29	0.24	0.29
D	LOW	0.11	0.12	0.40	0.41	0.26	0.29	0.24	0.30
E	HIGH	0.30	0.29	1.25	1.46	0.78	0.34	0.74	0.73
E	HIGH	0.30	0.28	1.25	1.30	0.78	0.74	0.74	0.73
E	MED	0.18	0.20	0.76	1.37*	0.47	0.50	0.45	0.45
E	MED	0.18	0.16	0.76	0.94	0.47	0.50	0.45	0.48
E	LOW	0.11	0.14	0.40	0.87*	0.26	0.29	0.24	0.28
E	LOW	0.11	0.12	0.40	1.17*	0.26	0.28	0.24	0.25
F	HIGH	0.30	0.33	1.25	1.20	0.78	0.77	0.74	0.82
F	HIGH	0.30	0.36	1.25	1.21	0.78	0.76	0.74	0.72
F	HIGH	0.30	0.32	1.25	1.21	0.78	0.80	0.74	0.68
F	HIGH	0.30	0.35	1.25	1.30	0.78	0.86	0.74	0.55
F	HIGH	0.30	0.35	1.25	1.34	0.78	0.87	0.74	0.75
F	MED	0.18	0.22	0.76	--	0.47	0.46	0.45	0.44
F	MED	0.18	0.19	0.76	0.69	0.47	0.42	0.45	0.38
F	MED	0.18	0.20	0.76	0.75	0.47	0.47	0.45	0.29
F	MED	0.18	0.08*	0.76	0.72	0.47	0.47	0.45	0.23
F	LOW	0.11	0.11	0.40	0.43	0.26	0.27	0.24	0.15
F	LOW	0.11	0.11	0.40	0.42	0.26	0.26	0.24	0.17
F	LOW	0.11	0.14	0.40	--	0.26	0.26	0.24	0.24
F	LOW	0.11	0.11	0.40	0.43	0.26	0.27	0.24	0.13
F	LOW	0.11	0.13	0.40	0.45	0.26	0.27	0.24	0.23

*Outliers

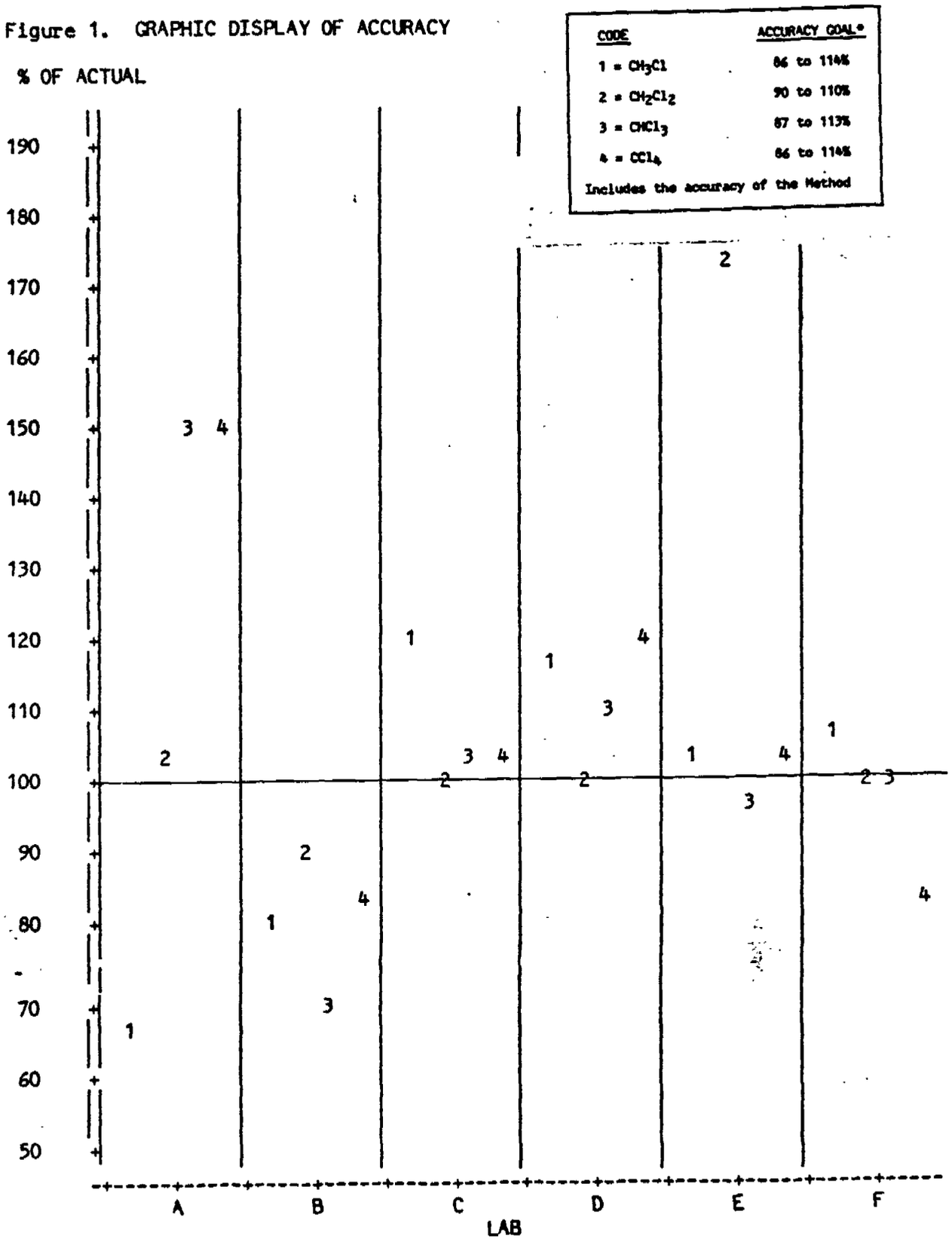
Table 2. ANALYTICAL PROFICIENCY TESTING: RESULTS (PERCENTAGE OF ACTUAL)

Lab	Level	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
A	HIGH	60	106	128	111
A	HIGH	73	112	154	139
A	MED	67	124	147	138
A	MED	67	101	147	138
A	LOW	64	105	169	171
A	LOW	64	77	146	200
B	HIGH	70	87	67	81
B	HIGH	84	82	64	77
B	MED	89	87	70	84
B	MED	87	90	72	89
B	LOW	74	94	69	83
B	LOW	85	95	70	85
C	HIGH	98	85	94	75
C	HIGH	127	103	109	116
C	MED	142	101	104	111
C	MED	100	91	97	102
C	LOW	138	105	105	113
C	LOW	115	106	107	111
D	HIGH	121	103	115	124
D	HIGH	109	100	108	114
D	MED	114	97	109	122
D	MED	126	99	109	118
D	LOW	115	107	112	121
D	LOW	105	102	112	125
E	HIGH	96	117	44	98
E	HIGH	94	104	95	98
E	MED	111	180	106	100
E	MED	87	124	107	106
E	LOW	128	217	112	118
E	LOW	110	292	107	105
F	HIGH	111	96	99	110
F	HIGH	119	97	97	97
F	HIGH	107	97	102	91
F	HIGH	116	104	110	74
F	HIGH	118	107	112	102
F	MED	121	--	98	97
F	MED	108	91	90	84
F	MED	111	99	100	64
F	MED	46	94	101	51
F	LOW	103	108	105	61
F	LOW	104	104	100	73
F	LOW	125	--	100	101
F	LOW	102	108	102	53
F	LOW	118	112	104	96

Table 3. ANALYTICAL PROFICIENCY TESTING: RESULTS (PERCENTAGE OF ACTUAL)

Laboratory	CH_3Cl		CH_2Cl_2		$CHCl_3$		CCl_4	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std
A	66	4	104	16	149	13	150	31
B	82	8	89	5	69	3	83	4
C	120	19	99	9	103	6	105	15
D	115	8	101	4	111	3	121	4
E	104	15	172	73	95	26	104	8
F	108	19	101	7	101	5	82	20

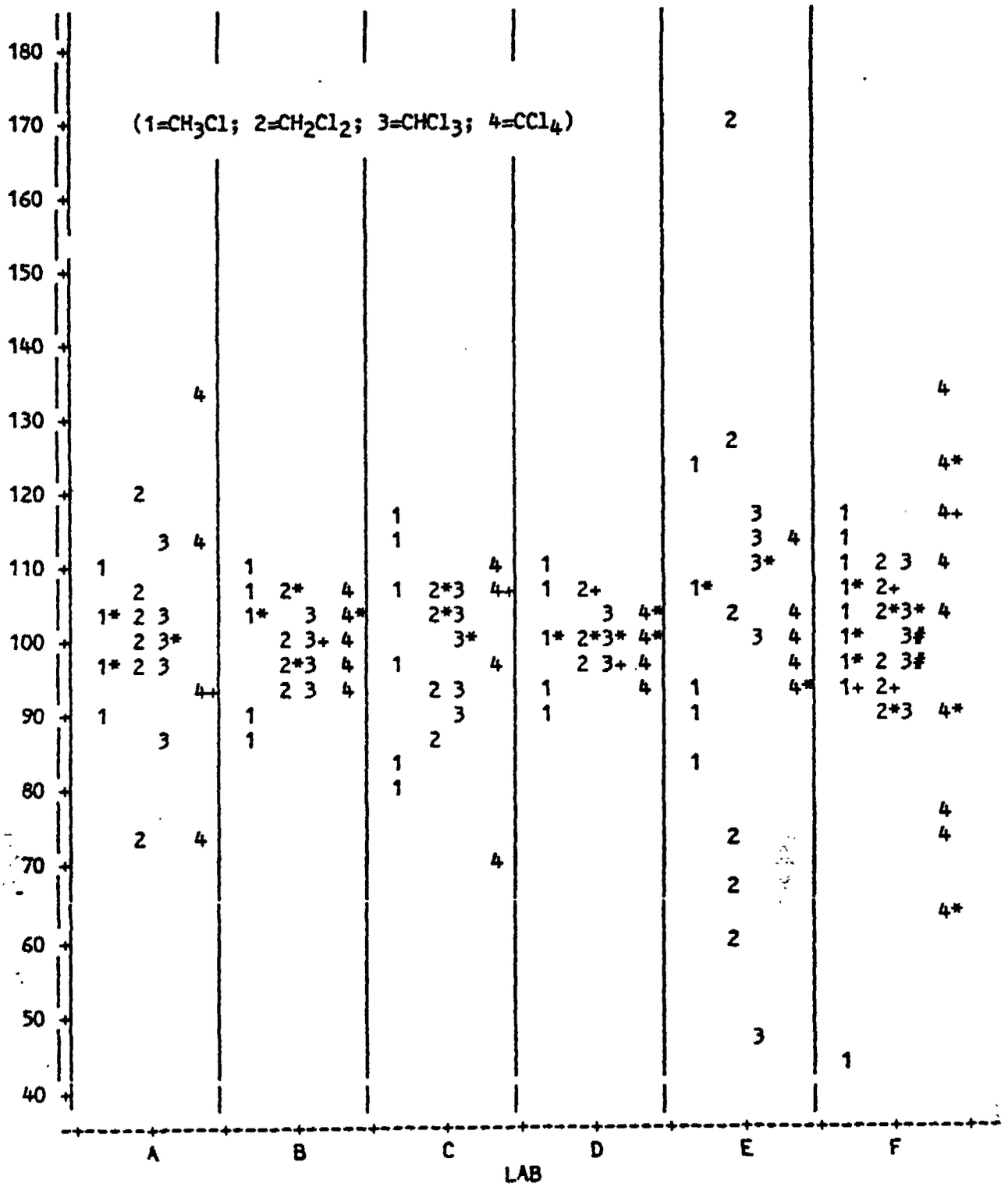
Figure 1. GRAPHIC DISPLAY OF ACCURACY



CODE	ACCURACY GOAL*
1 = CH_3Cl	86 to 114%
2 = CH_2Cl_2	90 to 110%
3 = $CHCl_3$	87 to 113%
4 = CCl_4	86 to 114%

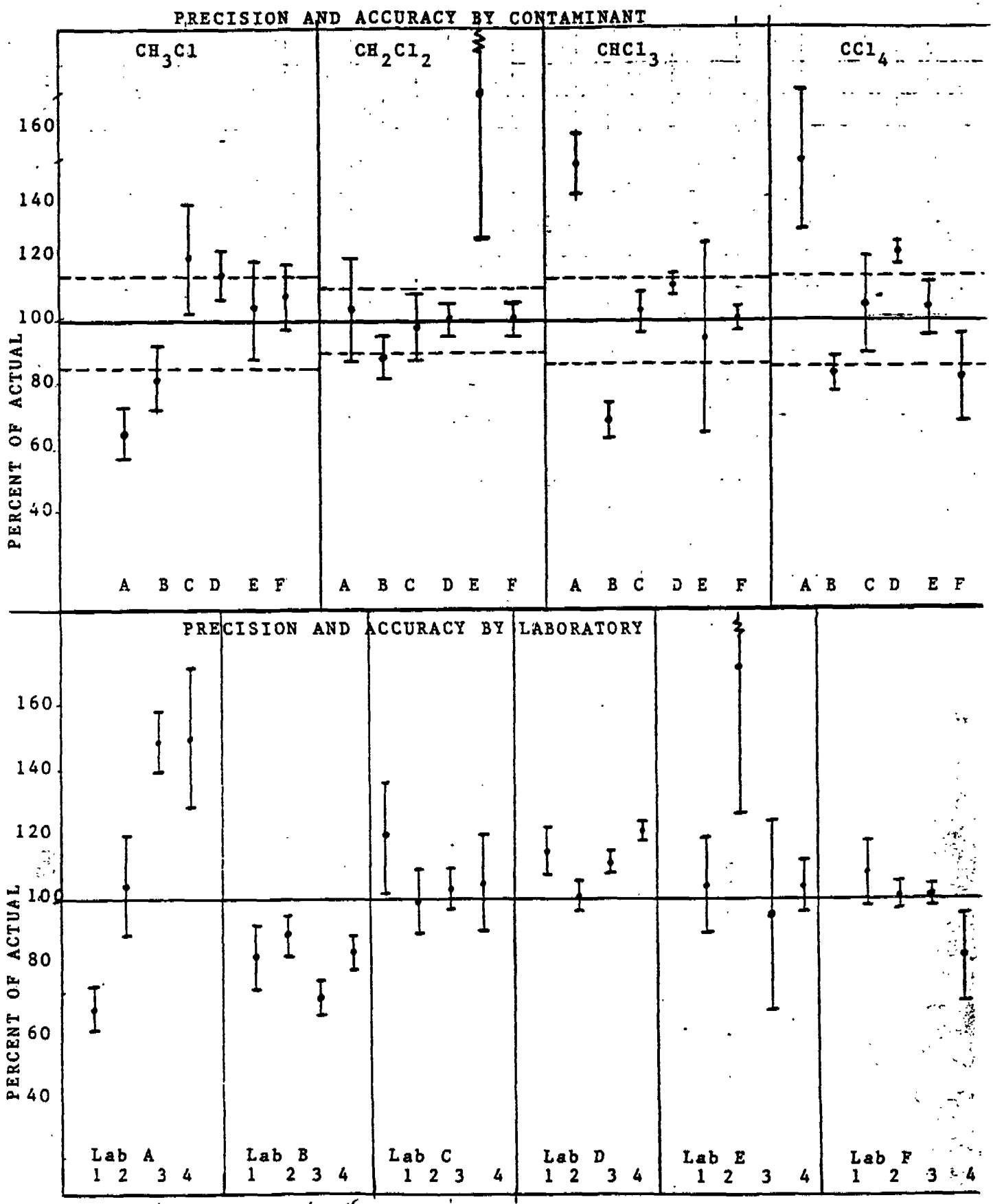
Includes the accuracy of the Method

Figure 2. GRAPHIC DISPLAY OF PRECISION



* two points
\+ three points
\# six points

FIGURE 3



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REV 8/E1

August 6, 1984

MIDLAND, MICHIGAN 48640

J. Lay
Plaquemine, Louisiana

cc: C. E. Halphen, Industrial Hygiene Manager, Louisiana Division

CHLORINATED METHANES APT: HEH2.12-39-3(11)

The results of the chlorinated methanes analytical proficiency testing (APT) are enclosed.

The Plaquemine Environmental Control laboratory is identified as letter D in the report.

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ewh

enclosure