Test Monitoring Center
6555 Penn Avenue
Pittsburgh, PA 15206-4489
(412) 365-1000

MEMORANDUM: 02-046

DATE: May 9, 2002

TO: D02.B07 EOVTSP and CONTACTS Mailing List
D02.B07 EOV GC Mailing List
D02.B07 EOV GC Participants

FROM: Tom Schofield

SUBJECT: D6417 Post-Workshop Round-Robin Matrix Summary

A D6417 workshop was held on January 29, 2002, with a follow-up round-robin matrix run on three TMC reference oils. This memo and attachment summarize the results of that matrix.

Eight labs participated in the round-robin matrix. A ninth lab was unable to contribute data due to problems with their instrument. Seven of the eight labs contributing matrix data also had a representative attending the workshop; Lab H contributed matrix data but was not represented at the workshop. Seven of the labs contributing matrix data routinely calibrate with the TMC, Lab AG contributed data but does not calibrate with the TMC at this time.

Each lab ran the three current TMC reference oils (oils 52, 55 and 58) in a blind round-robin format. Each lab ran all three oils in duplicate and at three different integration frequencies (1, 5 and 10 Hz) for a total of 18 runs, and each chromatograph curves was integrated for % volatized results at two different temperatures, 371°C and 385°C.

The data, as reported to the TMC, is available on the TMC's website as a spreadsheet with the blind oil samples identified and the contributing lab ID's coded:

ftp://ftp.astmtmc.cmu.edu/refdata/bench/d6417/data/D6417_2002_WS_Matrix1.xls

Attachment 1 is a summary of the TMC analysis of the D6417 round-robin matrix. Please direct any inquiries to my attention.

TMS/tms

Attachments

c: ftp://www.astmtmc.cmu.edu/docs/bench/d6417/mem02-046.pdf

Distribution: Email

D6417 20020129 Post-Workshop Round-Robin Matrix Summary

TMS 20020508

A. Comparison of Integration Frequencies:

Table 1 shows a comparison of the different integration frequencies used in the round robin.

Table 1

	Percent Volatized at 371°C				Percent Volatized at 385°C			
Integration Frequency Hz	n	Overall Mean	*Pooled s_r	Pooled s_R	n	Overall Mean	*Pooled s_r	Pooled s_R
1	48	7.93	0.16	0.39	36	13.60	0.37	1.61
5	48	8.04	0.18	0.38	36	13.78	0.38	1.51
10	48	7.98	0.15	0.49	36	13.68	0.38	1.58

*Pooled s_r is intermediate precision.

Note: Due to software limitations, some labs used 1.25 Hz rather than 1 Hz; the TMC combined all of the 1.25 and 1 Hz results as 1 Hz in our analysis.

The results in Table 1 show the 385°C results perform more severe than the 371°C as would be expected, but also that the precision of the 385°C results is substantially worse than the 371°C results at all integration frequencies. Because of the substantially poorer precision it cannot be recommended to run the test by percent volatized at 385°C.

Comparison of the overall mean and precision estimates for the three integration frequencies under Percent Volatized at 371°C in Table 1 shows no practical difference between the three frequencies except for the s_R value at 10 Hz, which is somewhat worse than at 1 and 5 Hz.

B. Comparison of Individual Oil Results By Integration Frequencies:

Table 2 shows a comparison of the individual oil results at each frequency for the Percent Volatized at 371°C. Comparisons at 385°C are not made due to the poor precision at that temperature as demonstrated in Table 1.

Table 2
Percent Volatized at 371°C

	Current Targets			Matrix 1 Hz			Matrix 5 Hz			Matrix 10 Hz		
Oil	n	Mean	s_R	n	Mean	s_R	n	Mean	s_R	n	Mean	s_R
52	18	6.97	0.31	16	6.85	0.36	16	6.93	0.33	16	6.86	0.44
55	18	11.68	0.51	16	11.40	0.50	16	11.57	0.52	16	11.49	0.58
58	18	5.61	0.30	16	5.55	0.28	16	5.62	0.23	16	5.58	0.42

Table 2 shows that there is little difference in the precision estimates at 1 and 5 Hz integration frequencies on all three oils, while the precision at 10 Hz is somewhat poorer for all oils. The precision estimates of the 1 and 5 Hz matrix results are comparable to the current target precision estimates for the reference oils. Mean performance across all integration frequencies and oils shows little overall difference from the current targets.

C. Comparison of Laboratory Performance:

Table 3 compares overall (least squares) mean performance between the individual laboratories in the matrix for percent volatized at 371°C. The n size for each lab in Table 3 is 18.

Table 3
Percent Volatized at 371°C

Lab	Overall Mean
A	7.44
B	8.76
D	7.98
G	7.69
H	8.27
L	7.80
S	7.89
AG	8.03

Table 3 indicates the labs are performing at different levels in the post-workshop matrix, as they are in the TMC's calibration monitoring. In fact, in the TMC's analysis, lab performance differences were found to be highly significant by F test (in the TMC's analysis, lab differences are second in significance only to oil differences; oil differences are expected, but lab differences should be minimized).

D. Comparison of Laboratories' Normal Integration Frequencies:

Table 4 shows a comparison of the participating laboratories "normal" integration frequencies for commercial testing and TMC calibrations using the D6417 method (values as reported by the individual labs to the TMC's inquiry of the matter).

Table 4

Lab	"Normal" Integration Frequency Hz
A	5
B	50
D	10
G	10
H	10
L	3.3
S	0.5
AG	5

As Table 4 demonstrates, the participating labs are using quite a large range of integration frequencies in their normal operations.

E. Comparison of Round-Robin Matrix Precision to D6417 Precision Statement:

Table 5 compares the round-robin matrix precision to the precision as stated in method D6417.

Table 5

	Percent Volatized at 371°C Round-Robin Results				Expected Precision As Calculated From D6417	
Integration Frequency Hz	n	Overall Mean	r	R	r	R
1	48	7.93	0.45	1.10	0.38	1.70
5	48	8.04	0.51	1.07	0.38	1.71
10	48	7.98	0.42	1.39	0.38	1.71

The results in table 5 suggest that the overall repeatability (intermediate precision) of the round-robin matrix is worse than expected by using the matrix overall mean values in the repeatability precision equation provided by method D6417-99 (Section 12.1.1). However, the round-robin reproducibility is better than would be expected by using the overall mean values in the reproducibility equation given in D6417-99 (Section 12.1.2).

F. Conclusions:

1. Results for percent off at 385°C are very imprecise compared to 371°C results (Table 1). A change in method to using percent off at 385°C is not recommended based on the round-robin matrix discussed in this summary.

2. Comparison of 1, 5 and 10 Hz integration rates for percent off at 371°C results (Table 1) shows 1, 5 and 10 Hz rates give comparable overall mean results. Also, overall precisions for 1 and 5 Hz are comparable while 10 Hz results are slightly less precise.

3. Comparison of percent volatized at 371°C results by integration frequency and by oil (Table 2) do not show practical performance differences between the different frequencies or from the already established target performances of the three TMC reference oils. The same is true for precision, except the 10 Hz results are somewhat less precise for all three oils. For this reason, changing targets based on these round-robin matrix results would not be expected to substantially change overall calibration performance (precision and severity).

4. Lab performance differences have been noted as a significant adverse factor in TMC calibration data, and continues to contribute significantly (and adversely) to the precision estimates in the post-workshop matrix (Table 3). Rather than adjust current reference oil targets, which would have little effect on performance, continued focus should be aimed at finding ways to mitigate actual lab-to-lab performance differences. As noted in Table 4, substantial operational differences still exist between participating laboratories using the D6417 method. The method allows for a number of other differences (column manufacture, column film thickness, column length, sample dilution concentrations, etc.) to be selected in combination at the discretion of the analyst. And, through discussions at the workshop and in the operational parameters reported for this matrix, we have found a number of differences in these parameters among the participating laboratories.