UTILITY PROGRAMS USED FOR EPA CONTRACT
LABORATORY PROGRAM COMPUTATIONS*

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ABSTRACT

Four computer programs were developed to manipulate GC/MS data and expedite both sample turnaround time and data package preparation for presentation of data following the EPA Contract Laboratory Program requirements. One program rapidly determines if the GC/MS daily standard has met QC criteria and therefore allows more samples to be analyzed within the 12-hour time limit. Another extracts total ion current for quantitation of tentatively identified compounds. The limit of detection is obtained on an as needed basis by the third, and the fourth provides a list of the names of target compounds, internal standards, and surrogate standards from the daily standard with their retention times in increasing order of elution. This paper describes the format, data entry approach, and procedures to set up and run these programs.

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INTRODUCTION

The Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) stipulates that sample analysis be conducted under rigorous quality control (QC) requirements, and that the data be reported in a specific data package format. We have developed four computer programs that manipulate data to expedite sample turnaround time and data package preparation. One program rapidly determines if the GC/MS daily (continuing calibration or CC) standard has met QC criteria. Another quantitates tentatively identified compounds (TICs) using the total ion current. The last two calculate the limit of detection (LOD) and correlate each peak in the reconstructed ion chromatogram (RIC) of the daily standard run with the name of the component producing it in increasing order of elution. This paper describes the format, data entry approach, and procedures to set up and run these programs.

EQUIPMENT

A Finnigan 4021C GC/MS with a 9610 GC was used to perform the analyses of the semivolatile priority pollutants. The GC/MS is equipped with a Nova 4X/5 computer and a 70 Mbyte Winchester disc drive and is controlled by Finnigan's Super Incos software version 6.1. An IBM-AT personal computer (PC) with 512 Kbyte of memory was interfaced with an IBM Proprinter. Files were transferred from the GC/MS computer to the PC using Finnigan's Formaster II software with option 691, and from the PC to a DEC VAX 6220 with DECnet DOS version 1.2.

BACKGROUND

The CLP methodology stipulates that, prior to analysis, the GC/MS must meet tuning criteria using decafluorotriphenylphosphine (DFTPP). After these criteria have been met, standards are analyzed to permit evaluation of the responses obtained as area counts of specific compounds. The five-point calibration standards and daily calibration standard consist of the 65 compounds on the semivolatile priority pollutant list, plus six internal standards, and six surrogate standards. Four of the 65 compounds are designated as System Performance Check Compounds (SPCC), and thirteen of the compounds are designated as Continued Calibration Compounds (CCC). The five-point calibration is determined from the responses (in area counts) from the 65 target compounds, the six internal standards, and the six surrogate standards which are used to compute the relative response factors (RF) using the equation

$$RF = \frac{(A_c)(C_{is})}{(A_{is})(C_c)}$$

where A_c = the area counts for a calibration compound,
 C_{is} = concentration of internal standard in the extract,
 A_{is} = the area counts for the internal standard, and
 C_c = concentration of the calibration compound, usually
50 ng/ μ L.

The relative standard deviation (RSD) is then computed from the RF value for each of five concentrations for all compounds. The magnitude of the RSD values

of the 13 CCC compounds determines whether the five-point calibration is acceptable.

Analysis on succeeding days can be conducted if the response values of the same thirteen compounds from the injection of a CC standard meet criteria with respect to the existing five-point curve. This is determined by computing the percent difference between the average response factor for each compound from the five-point and the corresponding response factor calculated from the CC standard. These criteria limit the allowable variation in relative response factors for the thirteen compounds and provide control of the GC/MS system prior to sample analysis.

In addition to these calibration requirements, additional criteria define an allowable range for the internal standard area counts, an allowable range for the percent recovery of the surrogate standards, and a minimum response for the SPCC compounds. Once these criteria are met, samples can be analyzed within 12 hours of the DFTPP injection.

GC/MS manufacturers provide software with many of these capabilities either on the operating system or on personal computers to which the quantitative data must be transmitted. Before acquiring Finnigan's Formaster software, we developed a program on the VAX that would prepare our data to conform to the CLP Form I format. It was necessary to use the VAX text editor to enter the data manually. Later, a 1987 version of Formaster II software was installed on an IBM PC which was connected via RS232 to the Finnigan GC/MS. In comparing the speed of the two approaches, we found that using Formaster software was more time consuming, and we decided to develop a faster approach

which required networking the PC with the VAX. We developed a VAX data entry format that was easy to use and wrote several Fortran programs to read the Finnigan quantitation reports and conduct the calculations.

DESCRIPTION OF THE FORMASTER APPROACH

The Finnigan system requires the establishment of six separate libraries, one for each of the six internal standards. Thus, to quantitate all compounds, each library must be successively accessed. Using the Finnigan/Formaster approach, the 65 target compounds, six surrogate standards, and six internal standards are quantitated; the results are edited by the system software; and then the resulting six quantitation reports are combined into one report, converted to an ASCII file, and sent to the PC. There, the Formaster software is used to conduct the calculations and prepare the form from which one can determine if the daily standard criteria have been met and sample analyses can be initiated. This process usually takes 30 to 45 minutes.

EXPEDITING CALIBRATION EVALUATION

Our programs eliminate all these steps, including the editing of the quantitative reports, which is the most time-consuming part of the process. We manually extract the raw data from the quantitative report, enter it on a VAX terminal, and initiate one of the utility programs on the VAX. Each time a CC standard is run, the quantitative data are generated in a report. Area counts from only 22 of the 65 compounds in the standard mixture are needed, and these are manually entered into a menu-type format using the VAX text editor.

The program reads the data, calculates the response factors, compares them to the average response factors from the existing five-point calibration curve, and generates the relative response factors and %RSDs in a fraction of a second.

PROGRAM DESCRIPTION

The algorithm is fairly straightforward, once the input format has been established. This format facilitates keyboard entry of area counts using the VAX text editor while also eliminating the chance of transcription errors. The approach selected entails the choice of several key variables in the input. The key variables are defined as:

- A = total number of calibration standards in the input,
- B = number of internal standards in each calibration
standard mixture, or number of libraries required,
- C = the number of calibration standards to be included
in the computation of % RSD in the initial calibration,
- D = total number of compounds in the library,
- E = total number of surrogate standards, and
- F = Library filename.

By inserting the appropriate values for the variables in the menu-type format as shown in Figure 1, the program can be adapted to calculate the percent RSD and percent difference of the volatile organic and semivolatile

organic compounds contained in the lists from the CLP or the Resource Conversation and Recovery Act (RCRA). Figure 2 shows the specific format setup for the respective organic analyses mentioned.

Compound names are placed at the end of the input file and should correspond to the order in which their area counts are entered (except for the surrogates, which are entered at the end of the compound list). Compounds whose response factors are determined from a four-point calibration (the 20-ng/ μ L standard is not used in the computation of %RSD) should be tagged with "D", SPCCs are tagged with "#", and CCCs are tagged with "*". Surrogates are identified with an "S".

Since most of the information remains the same for a given analysis, only the area counts need to be changed on a daily basis. The area counts are entered in proper order by simply editing the previous file. The program computes %RSD and percent difference and prints the results for each compound after its name in the output. A typical input and output are presented in Figure 3. The method also provides an easy way to include additional compounds that need watching, such as bis(2-ethylhexyl)phthalate for the example in Figure 3.

Before we acquired the Formaster software to generate forms acceptable to the EPA, we used this program to generate the data section of Forms VI and VII. After implementation of the Formaster software, the program was modified to serve as a quick check to determine if the SPCCs and CCCs met criteria.

QUANTITATION OF TENTATIVELY IDENTIFIED COMPOUNDS (TICs)

An important part of the CLP and RCRA analyses is the identification and quantitation of compounds which are not on the target compound list (TCL). Industry-specific compounds may be present that are not part of the TCL but must be included in the site evaluation. Since these compounds can be completely different between sites, their identification and quantitation must be handled differently from the target compounds.

The target compounds are quantitated using a specific ion for each compound. This method cannot be used for the TICs because no standards are available. Both CLP and RCRA require these compounds to be quantitated by comparing their total ion area to the total ion area of the closest internal standard by assuming that the relative response factor is 1.0. Unfortunately, our version of the Formaster II software did not permit referencing the correct internal standard, and the quantitated values did not conform to the equation $C_x A_{I_s} / C_{I_s} A_x = 1$. Therefore, we developed the capability to perform this computation on the VAX.

The approach taken in quantitating TICs is as follows: after a sample run is completed and the quantitation report edited, the results are reviewed with the total ion chromatogram on the computer screen. Peaks not corresponding to any compounds on the TCL are quantitated manually, and the results sent to a separate quantitation report. At the same time, the spectra of the unknown compounds producing the peaks are obtained both with and without background subtraction for identification by the MS library.

The quantitation report is then converted to an ASCII file and sent to the VAX PC. via the PC. The calculations are performed by our TIC program, which outputs two files. One file has the internal standards listed with their total ion area counts and results of the library search for inclusion in the data package. The other output file contains the results of the quantitation of the TICs based on the total ion counts. It is shipped back to the PC and read into the Formaster program to generate Form I TICs. The flow chart that was developed to perform these operations is given in Figure 4.

LISTING OF TARGET COMPOUNDS AND ELUTION ORDER

The third program is used to provide a listing of the target compounds in their order of elution. CLP protocol requires that every peak on at least one of the CC reconstructed ion chromatograms (RIC) in the data package be identified and labeled. While some GC/MS operating systems have this capability, ours does not. It can be accomplished either by manually writing the peak identifications on an RIC supplied in the data package or by generating a list of compounds with their order of elution. We chose the latter.

We developed a Fortran program to extract the information from the CC quantitation report that had been transmitted to the VAX computer. The program sorts the target compounds, internal standards, and surrogate standards according to their respective order of elution (in ascending order of the scan number) and prints out compound names, target ions, scan number, and elution time. The following portion of the program is an excerpt of the sort routine

after compound names, respective primary ion information, scan number, and elution time have been read into the program.

```
      CALL ORDER(CPD,TIME,NSCAN,ION,NCPD)

      DO 16 I=1,NCPD

      WRITE(6,500)(CPD(I,J),J=1,15),ION(I),NSCAN(I),(TIME(I,J),
          J=1,2)
500  FORMAT(1H0,3X,15A4,2X,I5,5X,I6,5X,2A4)
16  CONTINUE

      STOP

      END

      SUBROUTINE ORDER(TITLE1,TITLE2,NS,IN,NN)

      DIMENSION TITLE1(100,15),TITLE2(100,2),TEMP1(100,15),TEMP2
          (100,2)

      DIMENSION NS(100),IN(100)

      N1=NN-1

      DO 1 I=1,N1

          I1=I+1

          DO 2 J=I1,NN

              IF(NS(I).LE.NS(J))GO TO 2

              ITEMP=NS(I)

              NS(I)=NS(J)

              NS(J)=ITEMP

              JTEMP=IN(I)

              IN(I)=IN(J)

              IN(J)=JTEMP
```

```
DO 3 L=1,15
    TEMP1(I,L)=TITLE1(I,L)
    TITLE1(I,L)=TITLE1(J,L)
    TITLE1(J,L)=TEMP1(I,L)
3  CONTINUE
DO 4 L=1,2
    TEMP2(I,L)=TITLE2(I,L)
    TITLE2(I,L)=TITLE2(J,L)
    TITLE2(J,L)=TEMP2(I,L)
4  CONTINUE
2  CONTINUE
1  CONTINUE
RETURN
END
```

The programming logic is very simple. However, in this program and the following one, we encountered difficulties in extracting the necessary information from the Finnigan quantitation reports because they have mixed-mode character data. Hidden characters and randomly generated upper- and lower-case characters play havoc with the input file. These obstacles are not readily recognizable because the hard copies do not show any variations, despite the fact that they are stored differently in the computer. Our program circumvents the problem by setting a test for all upper and lower case characters such as "No Name", "NO NAME", "N", and "O" as one of the possible headings. The flow chart for reading in the data from the Finnigan quantitation report is presented in Figure 5.

REPORTING LIMITS OF DETECTION (LOD)

The CLP specifies that every data package must include the limit of detection for the instrument. Presently, there is no software that prepares an LOD for insertion in the data package. To compute an LOD, it is necessary to determine the number of counts needed to satisfy the CLP requirements for qualitative verification for each compound and to base each calculation on these determinations.

We chose to make the assumption that at least 1000 area counts are needed for the primary ion of any compound to satisfy our specific instrument requirements for qualitative verification. We also decided to calculate the LOD using the area counts of target compounds from the 20-ng/ μ L calibration standard, which is the lowest concentration standard used. For the nine compounds that require only a four-point calibration curve, the area counts are taken from the 50 ng/ μ L standard analysis. The LOD is then calculated using the equation

$$\frac{(C_{std})}{(A_t)} \times 1000 = LOD$$

where C_{std} = the concentration of the compound in the standard solution, and A_t = the area counts obtained.

The LOD calculated by this method is an estimate of the lowest concentration of a target compound in a sample that will provide 1000 counts

and, therefore, sufficient spectral information to ensure its identification when matrices and/or coeluting compounds affect the spectral data. The key to this program is to read in two files, isolate the internal and surrogate standards, and exclude them from the calculations. The nine compounds that require only a four-point calibration curve (detection at less than 50 ng is difficult), use data from the 50-ng/ μ L standard. Salient features specific for the presentation of the detection limit are given below:

```
DIMENSION INDEX(2,100),TEST(9)
DATA CI,CS,C1/'CI','CS','CI'/
DATA TEST/'C520','C530','C545','C555','C560','C595','C610,
C'C635','C735'/
DO 100 K=1,2
N=9+K
.
.
INDEX(K,I)=0
IF(TP.EQ.CI.OR.TP.EQ.CS)INDEX(K,I)=1
.
.
DO 40 L=1,9
IF(CNAME(K,I).EQ.TEST(L))INDEX(K,I)=2
.
.
AREA(1,L)=AREA(1,I)
INDEX(1,L)=INDEX(1,I)
```



```
.  
.   
IF(INDEX(1,I)EQ.0)GO TO 58  
DL=50.0*1000.0/AREA(1,I)  
W=DL*2.0  
S=DL*66.7  
  
.   
.   
58 DL=20.0*1000.0/AREA(1,I)  
W=DL*2.0  
S=DL*66.7  
  
.   
.   
END
```

The term K=1,2 instructs the program to read from two files (20 ng and 50 ng). For most compounds, Index(K,I) will be zero; but for an internal or surrogate standard, Index(K,I) will be one; and for the nine compounds that use the 50-ng/ μ L standard, it will be two. The output from the program presents the LODs in three ways: as the minimum quantifiable amount in ng of the specified compound, in μ g/L (assuming a one-liter water sample was analyzed), and in μ g/kg (assuming a 30-g [dry] soil sample was analyzed.) The programming logic for accessing these two files is similar to that used to read the quantitation report as described above. The resulting list is inserted in the data package just prior to the corresponding RIC. Since the GC/MS software prints scan numbers for the major peaks on the RIC, identification of the

compounds producing the peaks is easily obtained. An example of the list is given in Figure 6.

CONCLUSION

These programs collectively have cut the data package preparation time by almost 20%, a significant savings in this labor-intensive task. Finnigan recently began marketing a new software package called QA Report to address some of these needs. It is used along with the INCOS autoquantitation and Formaster software and provides quantitation and library identification of TICs, and labeling of chromatograms with internal standards and surrogate standards. However, QA report does not provide the LOD for a specific analysis, and it still requires minor editing of the quantitation report.

Eliminating the need to edit the quantitation report saves a considerable amount of time. Because our data entry format requires input of area counts for only 22 compounds (which includes the internal standards), the validity of continued calibration is rapidly determined. The same approach has been routinely used to determine the validity of the five point calibration, with approximately the same time savings. The biggest advantage this program offers is that it is not limited by the type of GC/MS instrumentation used. Both the program and data entry can be done on the VAX or on the PC. Anyone who does not have the latest and newest software can benefit from this time saving step since it permits one or two additional sample analyses to be completed within the 12-hour tuning interval.

Our approach for the handling of TICs may seem cumbersome, but it does eliminate manual calculation and transcription of data and depends on only a few key strokes. Since the EPA prefers a TIC report without the internal and surrogate standards, we designed the report to exclude them. There are additional advantages to the handling of TICs manually compared to the computer-generated approach. First, finding a TIC peak by visual examination of the total ion chromatogram can be accomplished at very low concentrations. Second, a trained mass spectroscopist can usually select a more appropriate background for subtraction and, therefore, improve the likelihood of correct identification. Third, it is our experience that most of the non-TCL compounds observed (~85%) have not been correctly identified by the MS library search, probably because the data base does not contain many environmentally pertinent compounds. As a result, evaluation from a trained mass spectroscopist is essential to increase the number of compounds identified and to improve the chance of their correct identification.

The program devised to relate compound identification to the peaks in order of ascending elution time and the computerized preparation of the LOD eliminates manual calculation for each data package prepared. Our approach to identification of the peaks eliminates clutter of the chromatograms from the printing, which can become a problem when many components are present, elute close together, and/or have a wide disparity in their concentrations.

(A)	(B)	(C)	
(C _{S1})	(C _{S2})	(C _{S3})	(C _{S4}) (C _{S5}) (C _{SD})
			C _{S1} , C _{S2} , ... = concentration of standards
(F)			C _{DS} = conc of daily std
(D)	(E)		
(A _{IS})	(C _{IS})		A _{IS} = area of internal std C _{IS} = its conc
A ₁	A ₂	A ₃	...A _n
			A _n = areas of compounds
C _{SS1}	C _{SS2}		C _{SSn} = conc of surrogate std

Figure 1. General menu format for data entry of experimentally obtained areas and concentrations.

VOLATILES

	20	6	3	5	200	50
		50	100	150		
Library 1						
14 1						
Area _{IS1} 50						
A ₁ to A ₁₄						
50						
Library 2						
12 0						
Area _{IS2} 50						
A ₁ to A ₁₂						
Library 3						
21 1						
Area _{IS3} 50						
A ₁ to A ₂₁						
50 50						

SEMIVOLATILES

	20	6	6	5	120	160	50
		50	80				
Library 1							
14 2							
Area _{IS1} 40							
A ₁ to A ₁₄							
100 100							
Library 2							
14 1							
Area _{IS2} 40							
A ₁ to A ₁₄							
50							
Library 3							
21 1							
Area _{IS3} 40							
A ₁ to A ₂₁							
50							
Library 4							
9 1							
Area _{IS4} 40							
A ₁ to A ₉							
100							
Library 5							
6 1							
Area _{IS5} 40							
A ₁ to A ₆							
50							
Library 6							
7 0							
Area _{IS6} 40							
A ₁ to A ₇							

RCRA

20	6	6	5		
	50	80	120	160	50
Library 1			Library 2		Library 3
19	2		19	1	26 2
Area _{IS1}	40		Area _{IS2}	40	Area _{IS3} 40
A ₁ to A ₁₉			A ₁ to A ₁₉		A ₁ to A ₂₆
100 100			50		50 100
Library 4			Library 5		Library 6
15	0		9	1	10 0
Area _{IS4}	40		Area _{IS5}	40	Area _{IS6} 40
A ₁ to A ₁₅			A ₁ to A ₉		A ₁ to A ₁₀
			50		

Figure 2. Specific menu for the CLP volatile and CLP and RCRA semivolatile compounds.

SONG CONTINUED CALIBRATION STD

qbcc5D1

3 0

47590 40

101860 95094 44446

qbcc5D2

4 0

149895 40

34593 47244 31831 38721

qbcc5D3

6 0

66812 40

16788 28672 92924 9198 4469 13455

qbcc5D4

2 0

78269 40

10314 95092

qbcc5D5

2 1

79231 40

qbcc5D6

2 0

24446 40

6464 43886

COMPOUNDS		AVRF	RF50	%D
PHENOL	*	1.9815	1.7123	13.59
1,4-DICHLOROBENZENE	*	1.6624	1.5986	3.84
N-NITROSO-DI-N-PROPYLAMINE	#	0.9898	0.7471	24.52
2-NITROPHENOL	*	0.2212	0.1846	16.53
2,4-DICHLOROPHENOL	*	0.2713	0.2521	7.07
HEXACHLOROBUTADIENE	*	0.1600	0.1699	-6.15
4-CHLORO-3-METHYLPHENOL	*	0.2716	0.2067	23.90
HEXACHLOROCYCLOPENTADIENE	#	0.2151	0.2010	6.56
2,4,6-TRICHLOROPHENOL	*	0.3462	0.3433	0.84
ACENAPHTHENE	*	1.1243	1.1127	1.04
2,4-DINITROPHENOL	D#	0.1572	0.1101	29.95
4-NITROPHENOL	D#	0.0690	0.0535	22.41
N-NITROSO-DIPHENYLAMINE	*	0.2132	0.1611	24.43
PENTACHLOROPHENOL	D*	0.1183	0.1054	10.89
FLUORANTHENE	*	1.0859	0.9720	10.50
BIS(2-ETHYLHEXYL)PHTHALATE		0.9600	0.8772	8.63
DI-N-OCTYLPHTHALATE	*	1.9626	1.5205	22.52
BENZO(A)PYRENE	*	1.3266	1.4362	-8.26
SURROGATE	S	1.3275	1.2194	8.15

Figure 3. Reproduction of input and resulting output used to determine if continuing calibration meets requirements.

TO FULLY UNDERSTAND THE LOGIC OF THE FLOW CHART, PLEASE REFER TO THE FINNIGAN QUANTITATION REPORT FORMAT. THE FOLLOWING IS A BRIEF EXPLANATION OF THE BEGINNING OF THE FLOW CHART.

Fig. 5. Flow chart for reading the data from Finnigan quantitation report.

Fig. 5A. Flow chart for reading the data from Finnigan quantitation report.

Fig. 6. Reproduction of the limit of detection list computed for each target compound.

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Figure Captions

- Figure 1. General menu format for data entry of experimentally obtained areas and concentrations.
- Figure 2. Specific menu for the CLP volatile and CLP and RCRA semivolatile compounds.
- Figure 3. Reproduction of input and resulting output used to determine if continuing calibration meets requirements.
- Figure 4. Flow chart for the quantitation of tentatively identified compounds.
- Figure 5 and 5A. Flow chart for reading in the data from Finnigan quantitation report.
- Figure 6. Reproduction of the limit of detection list computed for each target compound.

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