

## Automated Data Reduction for Mass Spectrometric Determination of Chlorinated Dibenzo-*p*-Dioxin and Dibenzofuran Isomers

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The determination of chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDD/CDFs) frequently requires the measurement of a large number of compounds in each sample analyzed. In the past, the calculations associated with such determinations were accomplished after a significant amount of manual data entry by the analyst. While there are some manufacturer-developed data output packages which could be used to calculate results, they lack the flexibility to customize calculation procedures or output formats to the analyst's individual needs. The most important features for such a program include: automation of program set-up, instrument control, data reduction, and Good Laboratory Practices (GLP) documentation. This presentation describes the structure and features of such a software package, the Dow Quantitation Package (DQP), which can be used to substantially automate data reduction for CDD/CDF measurements on a Finnigan MAT 95 HRGC-HRMS controlled by the ICIS II operating system.

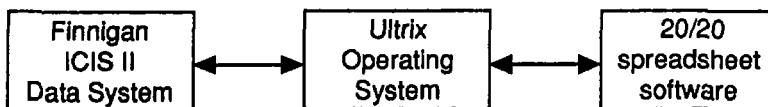
GC-MS measurement of CDD/CDF concentrations is typically accomplished in multiple ion detection mode (MID) as described in the U.S. Environmental Protection Agency (USEPA) Method 1613. Calculation of the analytical results requires consideration of many parameters which can affect the final analyte concentration (*e.g.*, sample size, final extract volume, internal standard fortification level, analyte recovery, peak area and baseline noise assessment for each analyte). The manual calculation of such results can be time consuming and subject to operator errors. Use of the DQP permits automatic input of most required data with little operator intervention while at the same time allowing:

1. automatic data reduction, QA/QC evaluation, and report generation during the data acquisition process;
2. automatic batch data reduction of any portion of a data set after acquisition is complete;
3. semi-automatic data reduction after acquisition allowing the analyst to modify peak and baseline identification parameters for any analyte.

In all of the cases described above, there is no need for the analyst to manually input raw data, perform calculations, or make QA/QC assessments. The raw data are measured by the Finnigan QUAN program and subsequently transferred via a series of Ultrix c-shell

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programs to a 20/20® (registered trademark of Computer Associates) spreadsheet package which performs the calculations and prints the final reports. The relationship between the programs is as follows.



Analyst initiation of the DQP begins with entry of specific parameter definitions as illustrated in Figure 1. These parameters become system default values for all samples but may be altered whenever necessary.

Next, the "Run Sequence Table" (see Figure 2) is defined by entering the order of calibration standards, blanks, washes, and samples that will be examined during data acquisition. At this point in the process, the only entries required are values in the *ID* column of this table. Each sample parameter listed in this worksheet is automatically transferred from the "Sample

Sample Calculation Information	
AVERAGE_ALL_CAL_STD_(y/n)_:	Y
INJECTION_STANDARD_(y/n)_:	Y
PEAK_AREA_(a)_OR_HEIGHT_(h)_:	a
SAMPLE_UNIT_VOL(v)/WT(w)_:	w
SIGNIFICANT_DIGIT_(ANALYTE)_:	3
SIGNIFICANT_DIGIT_(LOD)_:	2
SAMPLE_AMOUNT_(dscm/grams)_:	900
INT_STD_ADDED_TO_SAMPLE(ng)_:	0.2
INJ_STD_ADDED_TO_SAMPLE(ng)_:	2
SAMPLE_DILUTION_FACTOR_(>=1)_:	0.5

Figure 1: Sample calculation information.

Calculation Information" table (Figure 1), but any cell may be modified as necessary. The analysis sequence must agree with the order defined in the Finnigan ICIS II "Analysis View" (Figure 4) which controls the MAT 95 instrument during data acquisition.

The "Analyte and Calibration Standard Information" table (Figure 3) specifies and defines the analytes to be quantified during a specific project. Selection of any analyte from a predetermined list simply requires entry of a yes or no (y or n) instruction. In addition, the analyst defines the concentrations of internal (isotopically labeled) and native standards used for GC-MS calibration. The program can use up to three different concentrations of calibration solutions in order to calculate average response factors, however only one standard is shown in this example. Although not shown here, a table of GC retention times and peak measurement parameters, for each analyte, is required by the Finnigan ICIS II QUAN program. Prior to actual analysis, the analyte retention times are verified to ensure that quantitation windows are correctly defined.

Run Sequence Table							
	ID	AM	INT	INJ	K	CAL	QC
RUN 1	w						-
RUN 2	c					1	-
RUN 3	w						-
RUN 4	c					1	-
RUN 5	b						-
RUN 6	s	900	0.2	2	0.5		-
RUN 7	w						-
RUN 8	s	875	0.2	2	0.5		-
RUN 9	w						-
RUN 10	s	900	0.2	2	0.4		-
RUN 11	w						-
RUN 12	c					1	-
RUN 13	w						-
RUN 14	c					1	-
RUN 15							-

#Run sequence: c - cal. std., s - sample,  
b - blank and w - wash.  
#QC: d - delete from data reduction.

Figure 2: Analysis run-sequence parameter table

Automatic data reduction is controlled through the c-shell programs "atcdi \$" and "atcd \$" under DS PROC in the Finnigan ICIS II "Analysis View" which defines the sample analysis sequence, instrumental operation, and data acquisition (see Figure 4). In this automatic mode, analytical results are printed as the data are generated. The data reduction procedure can be repeated in a semi-automatic mode if modifications in chromatographic integrations are required. This is accomplished through a menu item in a 20/20 worksheet after batch sample analysis has been completed. In the semi-automatic mode, all ion chromatograms are displayed sequentially by the Finnigan ICIS II QUAN program for inspection and measurement. The operator may reassess questionable analyte peaks. Any new peak data are automatically transferred to the appropriate output files by the DQP.

Figures 5 and 6 are examples of final reports for CDDs and CDFs, respectively. They are formatted according to the operator-defined analytes shown in the "Analyte and Calibration Standard Information" table (Figure 3). The DQP produces results containing the appropriate number of significant figures as specified in the "Sample Calculation Information" table (Figure 1). An important aspect of this feature is the ability of the program to perform the appropriate numerical rounding of results to conform with laboratory Standard Operating Procedures (SOPs) governing significant figures. Additionally, the

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DQP will automatically change the number of significant figures reported as a function of the observed signal to noise ratio. Typically, analytical results above the Limit of Quantitation are reported with more significant figures than results that are near the Limit of Detection (LoD).

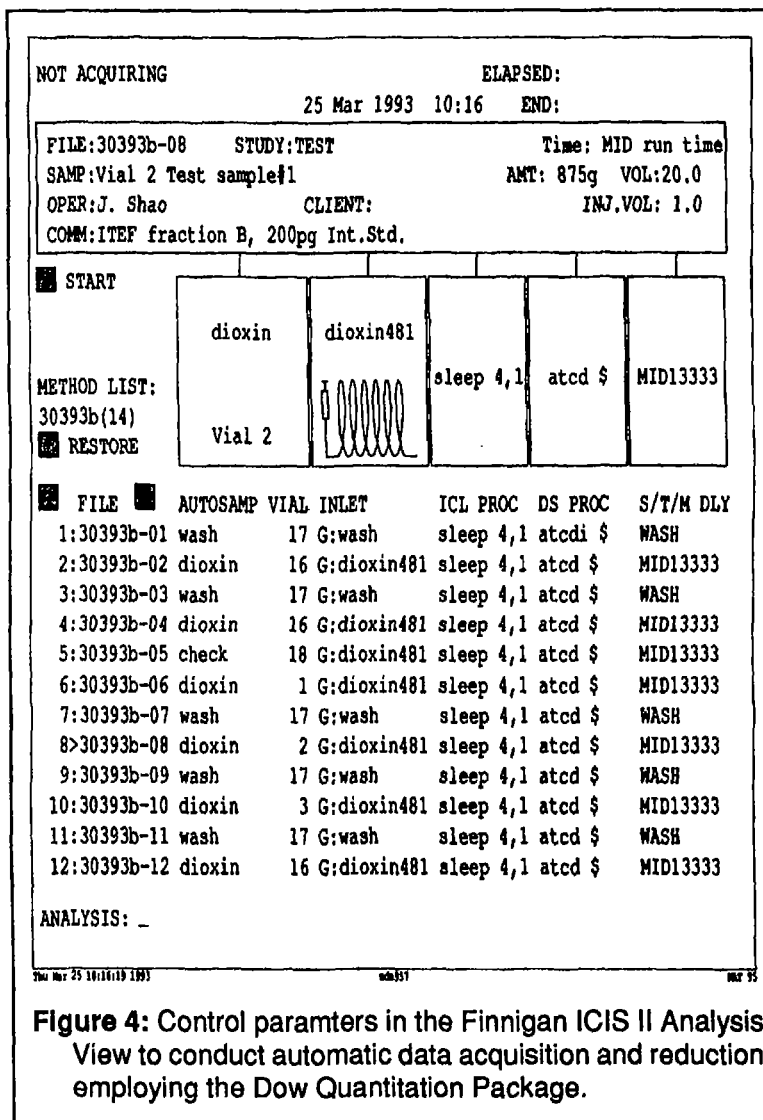
Within EPA methods for the measurement of CDD/CDFs, such as Method 1613, there exist defined QA/QC criteria for data acceptability. Basically, an analyte chlorine isotope ratio must be within certain defined limits based upon the theoretical value for a given number of chlorine atoms. The DQP permits the use of five additional QA/QC criteria within the data evaluation process. These criteria have been internally developed to take into account normal instrumental variations which may affect the observed chlorine isotope

----- Analyte and Calibration Standard Information -----				
Analyte	I			
	Run y/n	Int (pg)	Nat (pg)	Inj (pg)
2, 3, 7, 8-TCDD	y	5	2	5
1, 2, 3, 7, 8-PCDD	y	5	2	5
1, 2, 3, 4, 7, 8-HxCDD	y	5	2	5
1, 2, 3, 7, 8, 9-HxCDD	y	5	2	5
1, 2, 3, 4, 6, 7, 8-HpCDD	y	5	2	5
OCDD	y	5	2	5
2, 3, 7, 8-TCDF	y	5	2	5
1, 2, 3, 7, 8-PCDF	y	5	2	5
2, 3, 4, 7, 8-PCDF	y	5	2	5
1, 2, 3, 4, 7, 8-HxCDF	y	5	2	5
2, 3, 4, 6, 7, 8-HxCDF	y	5	2	5
1, 2, 3, 7, 8, 9-HxCDF	y	5	2	5
1, 2, 3, 4, 6, 7, 8-HpCDF	y	5	2	5
1, 2, 3, 4, 7, 8, 9-HpCDF	y	5	2	5
OCDF	y	5	2	5
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Injection_std.	y			

Figure 3: Analyte and calibration standard information

ratio. These additional criteria, which are actually more stringent than the EPA guidelines, can be used to more accurately evaluate the suitability of results that are near the LoD. Such evaluations are automatically processed in the DQP to assess chlorine isotope ratio and peak detection criteria for any analyte peak according to a set of selection rules defined by the laboratory SOP.

In addition to the automatic output of final results for analyte concentrations, the DQP is interfaced to the Finnigan ICIS II CHRO program to permit output of the Ion chromatograms and also to generate corresponding files in an HPGL format which allows subsequent import into word processing programs (e.g., via X-Windows) for computerized



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documentation. All aspects of this software package have been optimized so as to minimize operator intervention while simultaneously assuring the accuracy of data transmission and report generation.

