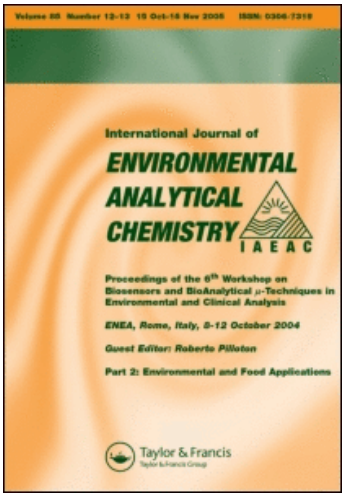

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Automated PCB Analysis, Quantitation and Reporting

E. Dowdall[a]; M. Tardif[a]; C. Chiu[a]
[a] Environment Canada, Chemistry Division, Environmental Technology Centre, Ottawa, Ontario, Canada

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AUTOMATED PCB ANALYSIS, QUANTITATION AND REPORTING

E. DOWDALL, M. TARDIF and C. CHIU

Environment Canada, Chemistry Division, Environmental Technology Centre, 3439 River Road, Ottawa, Ontario, K1A 0H3, Canada

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Sample analysis from a variety of matrices was performed using Gas Chromatography-Mass Spectrometry (GC-MS). Average relative response factors were calculated for each polychlorinated biphenyl homologue (tri- to deca-chlorobiphenyl) using in-house calibration standard solutions. Sample quantitation using RRFs provided homologue specific results. A series of software macros were used to automate the interpretation of spectral data and the selection of possible PCB congener peaks.

KEY WORDS: PCB's, relative response factors, quantitation, GC-MS analysis.

INTRODUCTION

Polychlorinated biphenyl (PCB) quantitation using Gas Chromatography-Electron Capture Detector (GC-ECD) relies upon pattern recognition by matching samples with one or more Aroclor standards[1-3]. Relative response factors (RRFs) and relative retention times of several PCB peaks must be determined for each Aroclor solution. Computer modelling has simplified the process of pattern recognition for Aroclor mixtures[4,5]. This type of analysis provides total PCB results using pattern recognition and does not consider the effects of weathering or other forms of sample degradation. Unlike the ECD analysis, the GC-MS quantitation provides homologue specific identification and is applicable to samples containing any PCB congener(s) or Aroclor(s).

One responsibility of our laboratory is the GC-MS analysis of PCBs in support of Canadian Environmental Protection Act (CEPA) regulations. Samples originate from a variety of matrices including transformer and motor oils, fly ash, waste sludge, stack emissions, air samples, fire and spill samples. Tri- to deca-chlorobiphenyls (CBs) consisting of 194 possible congeners, defined as PCBs under CEPA regulations, are the target compounds of interest.

Timely and accurate sample analysis and reporting is essential. The use of the GC-MS, homologue specific average RRFs, and computer aided data interpretation and handling provides more confidence in the results. The recovery of each homologue is calculated thereby allowing the experimental efficiencies to be monitored. Computer assisted data manipulation reduces sample reporting times while minimizing the chance of human error.

EXPERIMENTAL

GC-MS parameters

A 30 meter DB-5 column, 0.25 mm id and 0.25 µm film thickness, with a 10 meter pre-column for cool on-column injection was used. The GC oven temperature program was set to 90°C for 2 minutes followed by temperature ramps of 15°C/min to 185°C, 3°C/min to 240°C, 10°C/min to 285°C and a hold for 5 minutes. The mass spectrometer was operated using positive electron impact and selected ion monitoring mode with a dwell time of 100 msec/ion.

As shown in Table 1, a window defining standard was analysed to determine the elution time window for each homologue. Four acquisition windows containing the characteristic ion masses for each homologue were defined as in Table 2. Because of the overlapping elution patterns, each homologue typically appears in two acquisition windows. The number of ions monitored in each acquisition window was kept to a minimum to enhance sensitivity by reducing cycle time and increasing the number of scans.

Calibration

MS linearity was established using a five-point calibration curve. The concentration of the individual congeners ranged from 0.01 ng/µL to 5.0 ng/µL. Each calibration standard

Table 1 Elution windows, selected ion masses monitored and PCB congeners used for GC-MS analysis.

Homologue (no. of chlorines)	*Retention time windows (min)*	*PCB congeners in calibration stds (IUPAC #)*	*Ions monitored (m/z)*	*PCB C-13 labelled surrogate congeners (IUPAC #)*	*Ion monitored (m/z)*
3	11 to 16	18, 28, 33	258, 256, 188	28	270
4	13 to 20	52, 44, 70	292, 290, 222	52	304
5	15 to 25	101, 118, 105	326, 324, 256	118, 101(R.S.)	338
6	18 to 29	153, 138, 128	360, 358, 290	153	372
7	22 to 30	187, 180, 170	394, 396, 324	180	406
8	26 to 32	195, 194	430, 428, 358	202	442
9	31 to 34	206	464, 462, 394	NA	NA
10	33 to 39	209	498, 500, 428	209	510

R.S. = Recovery standard
N.A. = Not applicable

Table 2 Acquisition windows for individual PCB homologues.

Homologue (no. of chlorines)	*No. ions monitored*	*Retention time windows (min)*
3, 4,	8	6 to 14
3, 4, 5, 6,	13	14 to21
5, 6, 7, 8,	14	21 to 31
8, 9, 10	9	31 to 39

contained three congeners for each of tri, tetra, penta, hexa, and hepta CB homologues, two octa CB congeners and one nona and deca CB congener. These congeners were chosen because they represent some of the major compounds found in Aroclor mixtures. Each calibration standard also contains one carbon-13 labelled tri, tetra, penta, hexa, hepta, octa and deca CB as surrogate standards and carbon-13 labelled PCB-101 (0.4 ng/μL) as the recovery standard.

Sample preparation

Before extraction each sample was spiked with a surrogate standard solution consisting of 200 ng each of the same isotopically-labelled ($^{13}C_{12}$) congeners as found in the calibration solutions. To monitor surrogate recoveries a known quantity of isotopically labelled PCB-101 was added as the recovery standard prior to sample analysis.

Identification criteria

To be identified as a PCB congener, a chromatographic peak must exhibit the following criteria:

- the peak must fall within a preset homologue specific retention time window established using a window defining mixture.
- the abundance ratio of the first qualifier ion peak to quantitation ion peak must not deviate from theoretical values by more than 20%.
- the retention time difference must not vary by more than three seconds between the quantitation ion peak and the qualifier ion peaks.
- the peak shape must be symmetrical and have a signal to noise ratio greater than three.
- an M + 2Cl peak must not be present and an M-2Cl peak must be observed.

Relative response factors (RRFs)

A set of five calibration standard solutions was analysed to determine the average RRFs. The average RRFs for the native/surrogate standards were calculated for each homologue using equation 1. The RRFs for the surrogate/recovery standards were calculated using equation 2.

Sample quantitation

Homologue concentrations were calculated using equation 3. Data interpretation identified the total area response for each homologue. All concentrations were automatically corrected for surrogate losses. Surrogate recoveries were calculated using equation 4.

Relative response factors:

$$RRF_{n/s} = \frac{\sum_{i=1}^{m} \left(\frac{\text{native area}_i}{\text{native conc}_i} \right) / m}{\text{surr. area/surr. conc}} \qquad (1)$$

$$RRF_{s/rs} = \frac{(\text{surr. area})}{(\text{surr. conc})} \times \frac{(\text{r.s. conc})}{(\text{r.s. area})} \quad (2)$$

Homologue concentrations:

$$C = \frac{\sum \text{native area}}{\text{surr. area}} \times \frac{\text{amount surr. added}}{RRF_{n/s} \times \text{sample size}} \quad (3)$$

Surrogate recoveries:

$$\%R = \frac{\text{surr. area}}{\text{r.s. area}} \times \frac{\text{amount recovery standard added} \times 100}{RRF_{s/rs}} \quad (4)$$

where:
area = quantitation ion peak area;
surr. = surrogate standard;
r.s. = recovery standard;
$RRF_{n/s}$ = average relative response factor, native standard to surrogate standard;
$RRF_{s/rs}$ = relative response factor, surrogate standard to recovery standard;
m = number of congeners.

Computer aided data interpretation

The identification criteria, as listed above, must be satisfied before the quantitation process begins. Manual data interpretation was time consuming because of the need to search for qualifier peaks and calculate peak intensity ratios and retention time differences. As illustrated in Figure 1, this repetitive process was easily performed by a computer.

Using the Hewlett-Packard ChemStation software, extracted ion chromatograms were integrated and the abundance and the retention time for each integrated peak were tabulated. An HP ChemStation macro opened Excel and automatically started an Excel macro. Data interpretation, results reformatting and printing were all performed using Excel macros. Several macro assisted spreadsheets were designed for sample quantitation.

The homologue specific area counts were taken from a data interpretation spreadsheet (Figure 2), and copied to another sheet for addition (Figure 3). The totals were then transferred to a final spreadsheet for quantitative results calculations. The transfer of data between spreadsheets was achieved using "button" accessed macros. As shown in Figure 4, the quantitation spreadsheet was divided into three sections: Section "A" contained the response data from the daily calibration standard solution; Section "B" calculated the average RRFs of the daily calibration standard and compared it to the established five point calibration results; Section "C" received all of the sample data, including sample size, area responses, and calculated homologue and total PCB concentrations.

DISCUSSION

The RRFs calculated using the calibration standard solutions were generally in good agreement with those of individual congeners in the NRC CLB-1 standard solution set

Figure 1 Flowchart of macro assisted data processing.

(A-D) (Table 3). Each solution in the series contained a different set of PCB congeners. The average for the RRF ratios of the calibration standard (CS3) to the NRC standard (CLB-1) was 1.02. Of the twenty three values, three were greater than 1.20. Quantitative results and theoretical values of Aroclors and Aroclor mixtures are presented in Table 4. For total PCBs with a concentration range of 0.5 ng/μL to 10.0 ng/μL, a maximum difference of 10% was observed.

With the proper GC operating conditions the degree of M + 2Cl overlap was greatly reduced (Figure 4). Automated macros and macro assisted spreadsheets significantly reduced sample quantitating and reporting times and minimized the possibility of error during data manipulation. The spreadsheet used for results calculations also contains

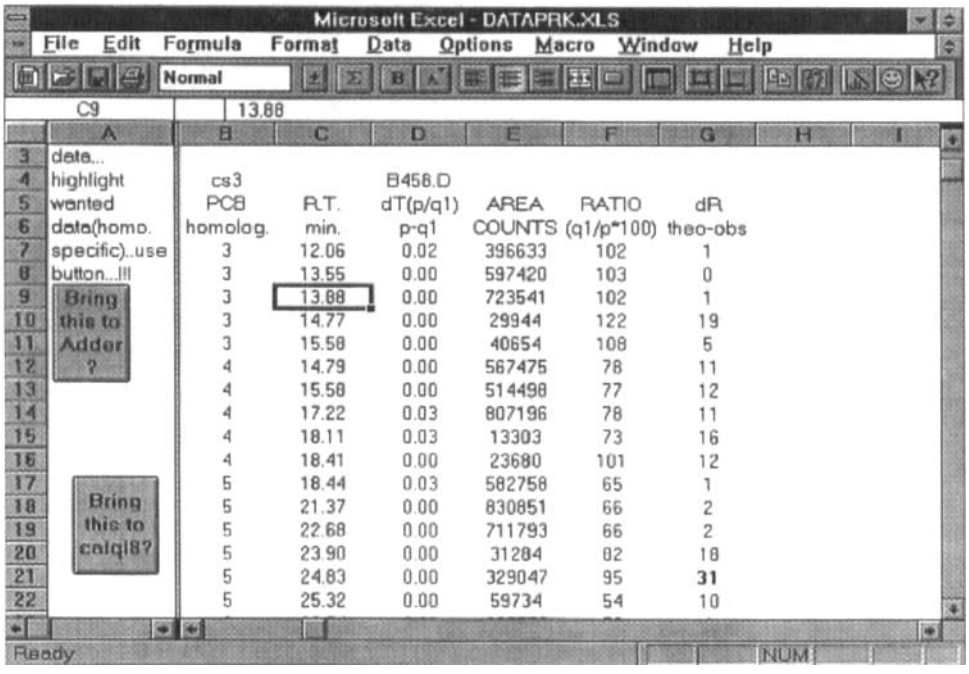

Figure 2 Spreadsheet for data interpretation.

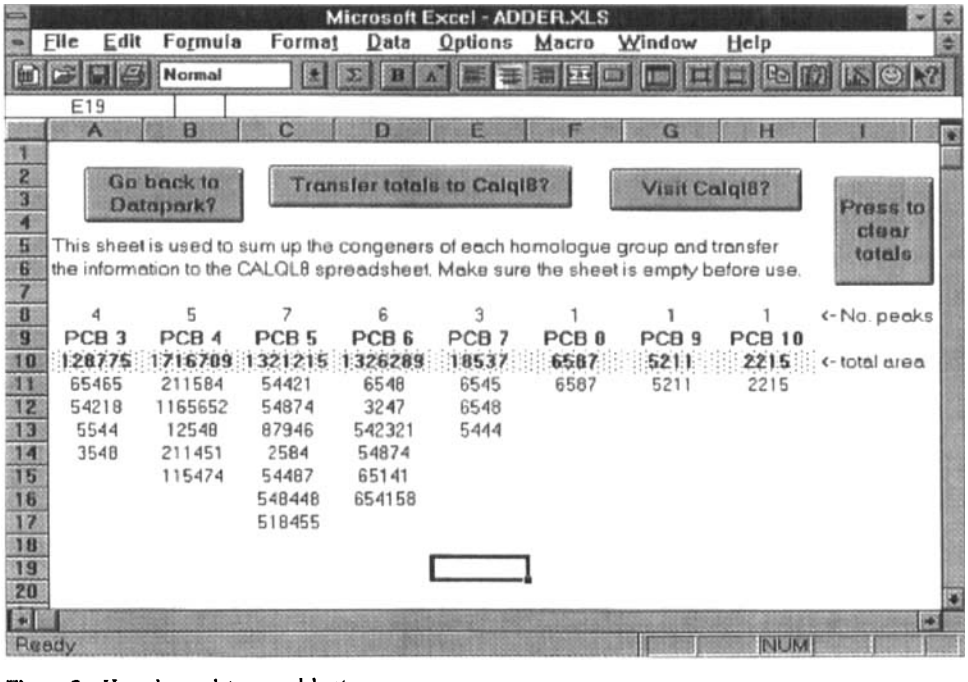

Figure 3 Homologue data spreadsheet.

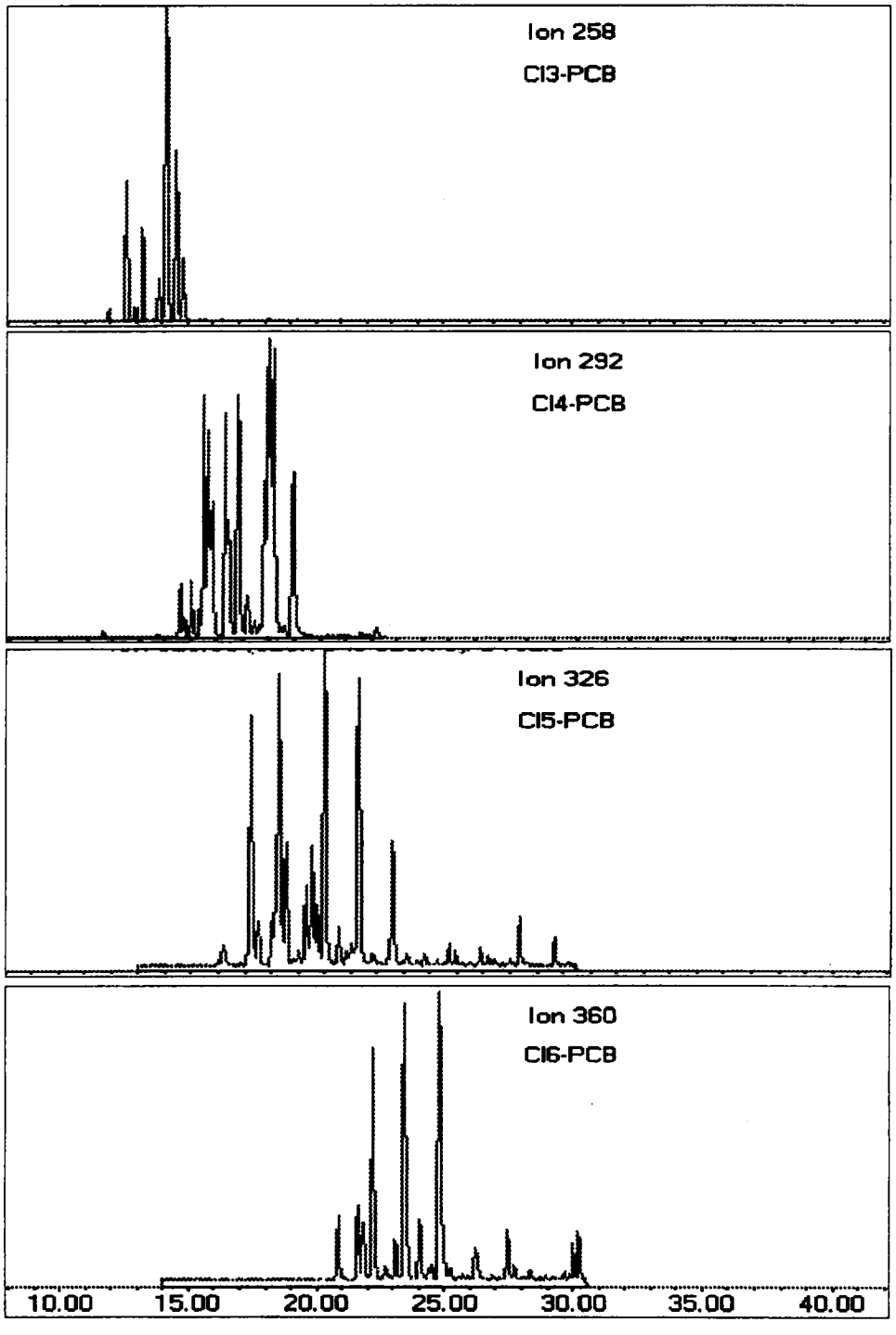

Figure 4 Tri, tetra, penta, hexa chlorinated biphenyls.

Table 3 Average relative response factors from CS3 and CLB-1 standards.

	Average relative response factors					*Average relative response factor ratios*			
Homologue	*cs-3*	*clb1-a*	*clb1-b*	*clb1-c*	*clb1-d*	*cs3/ clb1-a*	*cs3/ clb1-b*	*cs3/ clb1-c*	*cs3/ clb1-d*
3	0.89 (3)	0.66 (2)	–	–	–	1.36	–	–	–
4	1.12 (3)	1.07 (5)	1.16 (2)	–	–	1.05	0.96	–	–
5	0.90 (3)	0.68 (3)	0.92 (2)	1.09 (1)	0.82 (2)	1.32	0.98	0.83	1.10
6	0.89 (3)	0.83 (3)	0.92 (3)	0.84 (3)	0.86 (4)	1.08	0.97	1.06	1.03
7	1.01 (3)	–	1.03 (2)	1.14 (5)	0.93 (3)	–	0.98	0.89	1.08
8	0.98 (2)	–	1.17 (2)	0.96 (3)	0.91 (4)	–	0.84	1.02	1.07
9	0.98 (1)	–	0.91 (2)	0.77 (1)	–	–	1.07	1.28	–
10	1.01 (1)	0.97 (1)	1.21 (1)	1.17 (1)	1.19 (1)	1.04	0.84	0.86	0.85

Value in brackets represents the number of congeners.

Table 4 PCB Concentrations (ng/μL) for Aroclors 1242, 1254, 1260.

Homologue	*mix*	*mix*	*mix*	*1242*	*1254*	*1260*	*1254*
3	0.07	0.28	0.75	0.80	0.01	–	0.11
4	0.06	0.30	0.77	0.62	0.25	0.01	1.82
5	0.12	0.42	1.09	0.12	0.92	0.17	4.66
6	0.11	0.47	1.17	–	0.54	0.79	2.67
7	0.07	0.24	0.66	–	0.08	0.68	0.31
8	–	0.04	0.12	–	–	0.13	–
9	–	–	0.01	–	–	0.01	–
10	–	–	–	–	–	–	–
Total PCB	0.43	1.75	4.57	1.54	1.80	1.79	9.57
Theoretical	0.47*	1.89*	4.75*	1.70*	2.00	2.00	10.0
% Recovery	91	93	96	91	90	90	96

*Aroclor % from Environ. Sci. Technol. Vol 23, No. 7, 1989
mix- equal concentrations of Aroclor 1242, 1254, 1260.

several quality assurance features (Figure 5). The averaged RRFs for a daily calibration standard solution and the deviation from the calibration curve were included in the spreadsheet. The dates of the last updated calibration curve and surrogate standard spiking solution concentrations were also recorded with each sample processed.

Occasionally manual interpretation and/or integration may be required. Integration problems (misdrawn baseline, split peaks, etc.) may result in the mis-interpretation of peaks due to incorrect ion ratios or retention times. These types of problems could typically arise in samples with very high or very low PCB loadings or high levels of matrix background.

Accurate PCB results can be obtained by using this method with adequate cleanup procedures, freedom from cross-contamination, accurate calibration standards and proper interpretation of ion chromatograms.

Quantitation Spreadsheet

A.

VALUES FROM DAILY STANDARD (CS3)

Sample =	Native Area B421	Average Area	Native (ng) 0.25 RF native
3	401736	566296	2265185
	567505		
	729648		
4	525490	549443	2197771
	443736		
	679102		
5	578757	669518	2678073
	766709		
	663089		
6	635156	568355	2273421
	592642		
	477268		
7	487992	524887	2099549
	502973		
	583697		
8	407688	581026	2324104
	754364		
9	390643	390643	1562572
10	383297	383297	1533188
			Surrogate (ng)
			0.4
			RF surr
3'	1255643		3139108
4'	919201		2298003
5'	1533002		3832505
6'	1084655		2711638
7'	867658		2169145
8'	806308		2015770
10'	529593		2015770
REC STD	1173768		1323983
			2934420

B.

DAILY CS3 RRF VALUES (D)			RRF Values(C) From Calibration Curve*			% DEVIATION (D-C)/C	
RRF n/s	RRF s/rs		RRF n/s	RRF s/rs		RRF n/s	RRS r/rs
0.72	1.07	3	**0.69**	**1.09**	3	4.58	–1.86
0.96	0.78	4	**0.96**	**0.77**	4	–0.38	1.70
0.70	1.31	5	**0.66**	**1.38**	5	5.88	–5.36
0.84	0.92	6	**0.76**	**0.86**	6	10.32	7.45
0.97	0.74	7	**0.88**	**0.65**	7	9.99	13.72
1.15	0.69	8	**1.15**	**0.69**	8	0.26	–0.44
0.78	0.69	9	**0.84**	**0.69**	9	–7.72	–0.44
1.16	0.45	10	**1.19**	**0.45**	10	–2.69	0.26

* Calibration Curve Updated: **May 3, 1994**

C.

Calculated PCB Homologue Concentrations for Sample ID: t-142-dh

	Sample Surr Area	ism28.2d-A conc. ** ng/ul	Sample Surr. Rec %	Sample Native Area	Native conc.	No. of Peaks	PCB Homologues
3'	304886	2.62	69	5226837	13.02	8	**3**
4'	266182	2.61	86	4550085	9.29	15	**4**
5'	466955	2.81	78	2963310	5.40	16	**5**
6'	339109	2.86	89	7185132	15.95	20	**6**
7'	255072	2.97	86	4827535	12.78	17	**7**
8'	234209	3.07	72	989039	2.25	8	**8**
10'	50000	2.79	26	73047	0.21	3	**9**
REC STD	308142	4		2796	0.04	1	**10**

TOTAL ng/uL 58.94

Volume ism28*2d added (uL)	**100**
Volume pcb101 added (uL)	**50**
Sample Size (g, uL, etc.)	**500**
Dilution/Conversion Factor	**1**

** ism28.2d calibrated: **May 5, 1994**

Figure 5 Spreadsheet for sample quantitation.

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