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Appendix A

Software created for data handling (Matlab R12)

1 Background subtraction

Program to subtract a five-point average (five lowest chromatographic values) from each second dimension chromatogram value. This baseline subtraction was done to ensure a same level baseline for the two-dimensional chromatogram.

```
function matrikstemp = backgroundsubtractionp(matriks)
% Program to subtract 5 low point average from 2nd dimension
% chromatograms to get stable baseline in two dimensions
% To use tipe in variable = backgroundsubtractionp(matrix)

[vertikaal,horisontaal] = size(matriks);
tic
versoek = 0;
h = timebar('Background Subtraction','Progress')
```

```
horsoek = 0;

maksimum = 0;

matrikstemp = matriks;


while versoek < vertikaal;                                          % while 1

    versoek = (versoek + 1);

    timebar(h,versoek/vertikaal)

    horsoek = 0;

    horsoektemp = 0;

    minimum1 = 9999999999999999;

    minimum2 = 9999999999999999;

    minimum3 = 9999999999999999;

    minimum4 = 9999999999999999;

    minimum5 = 9999999999999999;

    while horsoek < horisontaal;                                % while 2

        horsoek = (horsoek + 1);

        if matriks(versoek,horsoek) < minimum1;                     % if 1

            minimum1 = matriks(versoek,horsoek);

            horsoektemp = horsoek;

        end                                                         % end if 1

    end
```

```
horsoek = 0;
   while horsoek < horisontaal;
      horsoek = (horsoek + 1);
      if ((matriks(versoek,horsoek) < minimum2) & (matriks(versoek,horsoek) > minimum1))
                                                                              % if 2
                                                                              % if 3
           minimum2 = matriks(versoek,horsoek);
                                                                       % end if 3
      end                                                                     % end if 2
   end
   horsoek = 0;


while horsoek < horisontaal;
      horsoek = (horsoek + 1);
      if matriks(versoek,horsoek) < minimum3;                                 % if 4
        if matriks(versoek,horsoek) > minimum1;                               % if 5
           if matriks(versoek,horsoek) > minimum2;                            % if 6
             minimum3 = matriks(versoek,horsoek);
           end                                                                % end if 6
        end                                                                   % end if 5
      end                                                                     % end if 4
```

```
end
horsoek = 0;
while horsoek < horisontaal;
   horsoek = (horsoek + 1);
   if matriks(versoek,horsoek) < minimum4;                 % if 7
      if matriks(versoek,horsoek) > minimum1;              % if 8
         if matriks(versoek,horsoek) > minimum2;           % if 9
            if matriks(versoek,horsoek) > minimum3;        % if 10
               minimum4 = matriks(versoek,horsoek);
            end                                            % end if 10
         end                                               % end if 9
      end                                                  % end if 8
   end                                                     % end if 7
end
horsoek = 0;
while horsoek < horisontaal;
   horsoek = (horsoek + 1);
   if matriks(versoek,horsoek) < minimum5;                 % If 11
      if matriks(versoek,horsoek) > minimum1               % if 12
         if matriks(versoek,horsoek) > minimum2            % if 13
            if matriks(versoek,horsoek) > minimum3         % if 14
               if matriks(versoek,horsoek) > minimum4      % if 15
```

```
                minimum5 = matriks(versoek,horsoek);
              end                                           % end if 15
            end                                             % end if 14
          end                                               % end if 13
        end                                                 % end if 12
      end                                                   % end if 11
  end
                                                            % end while 2
  t = [minimum1 minimum2 minimum3 minimum4 minimum5];
  gemideld = ((minimum1 + minimum2 + minimum3 + minimum4 + minimum5) / 5);
  count1 = 0;
  for count1 = 1 : horisontaal
      matrikstemp(versoek,count1) = matrikstemp(versoek,count1) - gemideld;
  end
end                                                         % end while 1
close(h)
matrikstemp;
matriks;
toc
```

2 Program to reconstruct the one-dimensional chromatogram

Program for the reconstructing of a one dimensional chromatogram from a two-dimensional array by adding up all the values of any given second-dimension chromatogram, analogous to the reconstructed total ion chromatogram from GC-MS raw data

---

```
function onedimensionchrom(matriks)
% drawing one dimensional chromatogram from a dwo dimensional data set

[vertikaal,horisontaal] = size(matriks);
matrikstemp = matriks';
teller =   1:vertikaal;
i = 99999999;
while i > 99999
   i = input('What is the modulation period of the chromatogram in seconds ?: ');
   if i > 99999
      iii = input('The modulation period must be an interger between 0 and 99999 seconds !!! ');
   end
end
naam = input('What is the name of your chromatogram ?','s');
tottyd = (vertikaal*i)/60;
tydinkrement = tottyd/10;
```

```
onechrom=sum(matrikstemp(1:end,teller));

plot(onechrom)

inkrement = vertikaal/10;

set(gca,'XTick',inkrement:inkrement:vertikaal)

set(gca,'XTickLabel',{tydinkrement:tydinkrement:tottyd}),xlabel('minutes')

ylabel('intensity')

title(['1 Dimensional Plot of ',naam])
```

3 Program to extract individual second-dimension chromatograms

This program was designed to extract individual second-dimension chromatograms from the two-dimensional data array and plot it in a one-dimensional chromatogram.

```
function matrikstwee = twodimensionchrom(matriks)
% drawing two dimensional chromatogram from a one dimensional data set

[vertikaal,horisontaal] = size(matriks);
matrikstemp = matriks';
teller =   1:(vertikaal-1);
i = 99999999;
t = 99999999;
col = 99999999;
while i > 99999
   i = input('What is the modulation period of the chromatogram in seconds ?: ');
   if i > 99999
      iii = input('The modulation period must be an interger between 0 and 99999 seconds !!! ');
   end
end
while t > 99999
   t = input('What is the sampling rate in Hz ?: ');
```

```
    if t > 99999
        ttt = input('The sampling rate must be between 0 and 99999 Hz !!! ');
    end
end
while col > 99999
    col = input('What is the column you whish to plot -- amu = column + 1 + minmass exported ---:
');
    if col > 99999
        colll = input('The column must be between 0 and 99999  !!! ');
    end
end
inkrement = i * t
aantalchroms = vertikaal/inkrement
herstel = round(aantalchroms)

tydelik = matriks([1:inkrement], col);


teller = 0;
while teller < (herstel - 1);
    teller = (teller + 1);
    volg = inkrement;
    volg = (volg * teller);
```

```
    h = (volg + 1);
    n = (volg + inkrement);
    tydelik2 = matriks([h:n], col);
    tydelik = [tydelik tydelik2];
end
matrikstwee = tydelik';
```

Appendix B

Calculations

Equations used

a) Linear flow rate of the first-dimension

u = (column length) / (dead time measured)

b) Resolution

$$R = \frac{2(t_{R2} - t_{R1})}{4\sigma_1 + 4\sigma_2}$$

t_{R1} and t_{R2} are respectively the retention times of the two chromatographic peaks

$$\sigma_1 = \frac{hw_1}{2.355}$$

$$\sigma_2 = \frac{hw_2}{2.355}$$

Where hw the width at half height for the respective peaks represent.

c) Plate number

$$N_1 = 5.54\left(\frac{t_{R1}}{hw_1}\right)^2$$

d.) Plate height, H

$$H = \frac{L}{N}$$

where L is the column length and N is the plate number

Calculations of the respective linear flow rates of the two dimensions						
Inlet pressure (kPa)	Dead Time First-dimension (s)	Linear flow rate first-dimension (cm/s)	Iterated pressure between the two dimensions (kPa)	Dead time calculated for seond-dimension (ms)	Linear velocity at second column exit (cm/s)	Average linear velocity calculated for second-dimension (cm/s)
320	60	47.617	343.00	139	2093	753
280	68	42.015	310.20	157	1686	664
220	80	35.713	258.50	201	1120	520
190	82	34.841	230.31	237	865	442
185	85	33.612	226.85	242	835	432
175	89	32.101	218.80	256	767	409
170	90	31.744	214.30	264	730	396
150	100	28.570	198.60	300	607	350
130	114	25.061	183.20	344	495	304
125	117	24.419	179.10	358	467	292
120	121	23.612	175.15	374	440	281
115	125	22.856	171.15	391	414	269
110	130	21.977	167.00	410	387	256
100	143	19.979	160.00	447	344	234
90	156	18.314	152.00	500	296	210
80	173	16.514	144.59	561	255	187
60	224	12.754	129.58	751	177	140

The calculation for the second-dimension resolution and plate numbers										
Inlet pressure (kPa)	Width at half height hw_1 (ms)	Width at half height hw_2 (ms)	Second-dimension column "dead time" (ms)	Peak 1 retention time t_{R1} (ms)	Peak 2 retention time t_{R2} (ms)	Plate number for peak 1 N2	Plate number for peak 2 N2	Peak 1 width at baseline $4\sigma_1$ (ms)	Peak 2 width at baseline $4\sigma_2$ (ms)	Resolution of peaks R
60	72	90	751	2626	2926	7369.44	5855.63	122.3	152.9	2.18
80	57	65	561	2151	2401	7889.34	7559.05	96.8	110.4	2.41
90	55	61	500	2025	2270	7509.91	7671.88	93.4	103.6	2.49
100	55	60	447	1872	2107	6417.95	6831.82	93.4	101.9	2.41
110	55	60	399	1744	1964	5570.28	5935.95	93.4	101.9	2.25
120	55	60	374	1654	1864	5010.20	5346.86	93.4	101.9	2.15
130	55	60	344	1594	1803	4653.30	5002.63	93.4	101.9	2.14
150	70	75	300	1600	1800	2894.37	3191.04	118.9	127.4	1.62
190	90	90	237	1574	1754	1694.47	2104.19	152.9	152.9	1.18

The calculations for the resolution in the first-dimension							
Inlet pressure (kPa)	Peak 1 retention time t_{R1} (s)	Peak 2 retention time t_{R2} (s)	Width at half height of peak 1 hw_1 (s)	Width at half height of peak 2 hw_2 (s)	Width at baseline Peak 1 $4\sigma_1$ (s)	Width at baseline Peak 2 $4\sigma_2$ (s)	Resolution between peaks 1 and 2
60	74686	81582	704	727	1328	1369	5.674382
80	59889	65575	483	496	905	999	6.838882
100	48408	53114	365	383	680	730	7.408175
110	45955	50441	320	358	585	653	7.790951
120	42281	46433	291	308	530	580	8.161903
130	39972	43920	283	296	498	530	8.028964
150	35254	38763	228	249	470	435	8.662154
190	28783	31675	185	203	379	362	8.776624
220	25365	27922	160	174	320	335	9.014573
280	20502	22582	140	150	286	291	8.445517
320	18065	19889	125	138	250	300	8.166388

Calculations of the square root N value				
P	k term	α term	R	sqrt N
60	0.7433	0.1379	2.181	85.0707
80	0.7663	0.1359	2.413	92.6943
90	0.7797	0.1384	2.487	92.1698
100	0.7879	0.1416	2.406	86.2954
110	0.7968	0.1406	2.253	80.4386
120	0.7994	0.1409	2.150	76.343
130	0.8192	0.1315	2.099	77.9403
150	0.8333	0.1333	1.624	58.469
190	0.8649	0.1187	1.178	45.8963