TDMAFIT USER'S MANUAL

by

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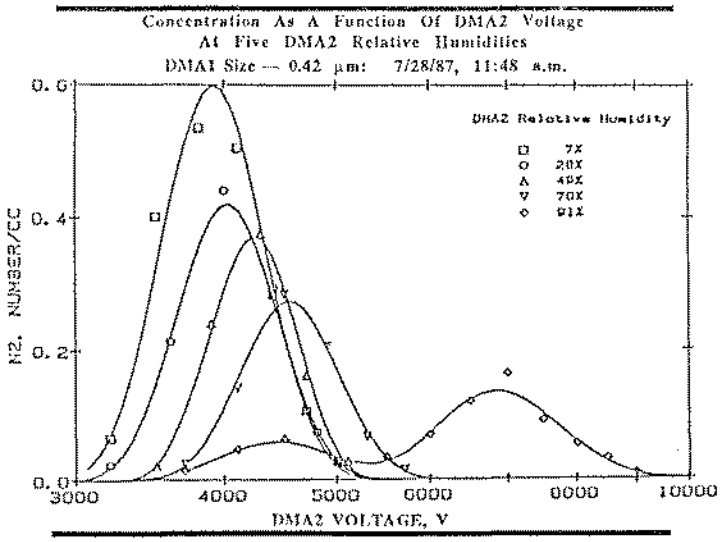

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TDMAFIT User's Manual

INTRODUCTION

The Tandem Differential Mobility Analyzer (TDMA) is an aerosol instrument system consisting of two DMAs, an aerosol conditioner, and an aerosol detector, as shown in Figure 1. The TDMA system can be used to study phenomena that lead to changes in particle size including:

- growth by chemical reaction (e.g., Gupta and McMurry, 1988)
- hygroscopic, deliquescent, and efflorescent properties of aerosol particles (e.g. Liu et al.,1977; McMurry, Takano and Anderson, 1983; McMurry and Stolzenburg, 1988)
- evaporation rates of aerosol particles (e.g., Rader, McMurry, and Smith, 1987; Tao and McMurry, 1988).

The TDMA system can also be used to check the performance of a DMA by determining whether the DMA-generated "monodisperse" aerosols have the correct mean size and size spread.

In performing measurements with a TDMA system, DMA1 is used to select "monodisperse"[1] aerosols from a polydisperse input aerosol (see Figure 1). This monodisperse aerosol flows into an "aerosol conditioner" which may consist of a reactor, a humidification or drying chamber, or an evaporator. (When a TDMA system is used to evaluate the performance of a DMA, the aerosol

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[1]The aerosols produced by DMA1 are not truely monodisperse. Rather, they typically have a triangular-shaped distribution as discussed by Knutson and Whitby (1975). Accounting for this distribution of sizes is essential in interpreting TDMA data.

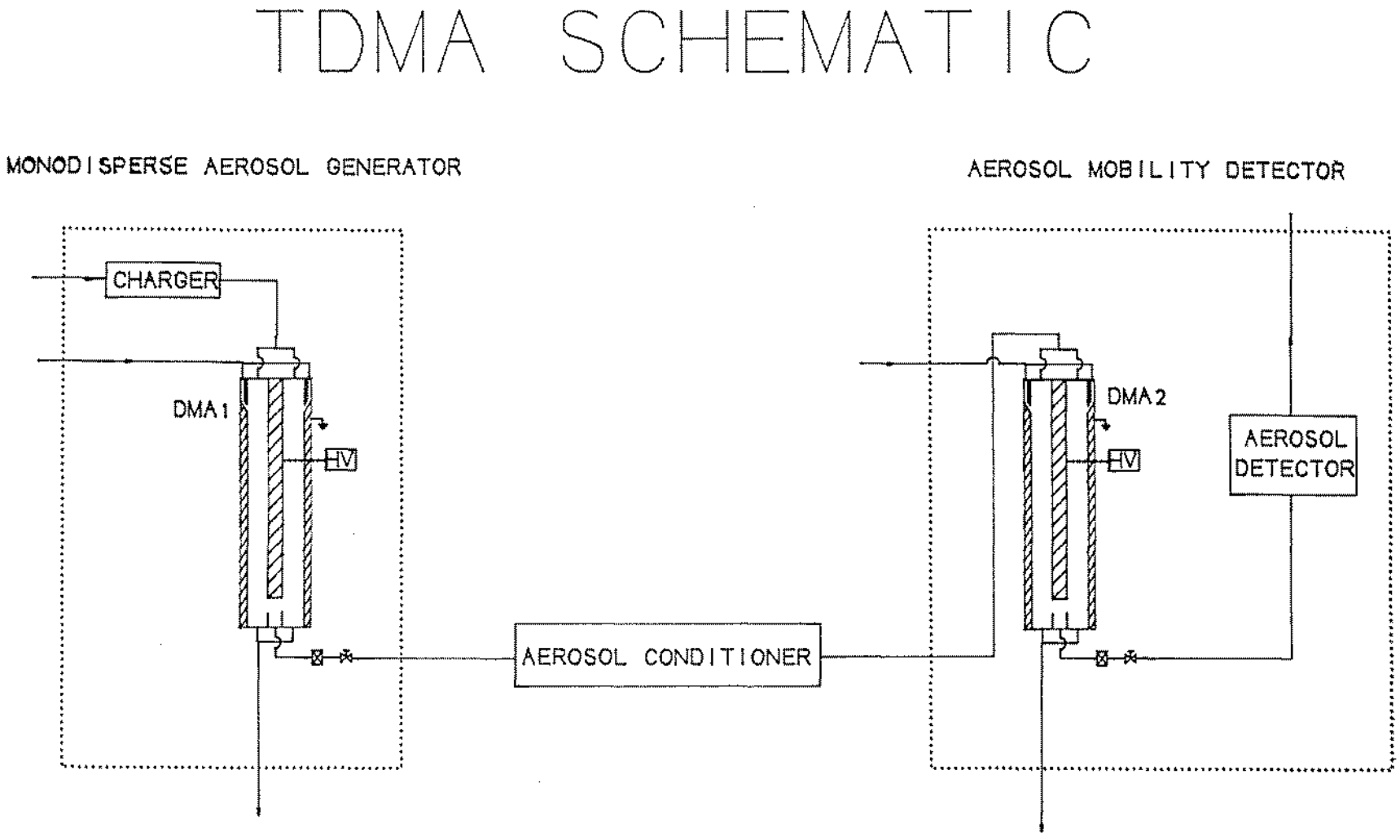

Figure 1. Schematic diagram of a TDMA system

conditioner is eliminated from the system). The "conditioned" aerosol then enters DMA2. The DMA2 collector rod voltage is adjusted until particles are detected downstream of DMA2, and the concentration of particles penetrating through DMA2 is then recorded as a function of DMA2 voltage at a minimum of 5 DMA2 voltage settings. Any suitable detector such as a condensation nucleus counter or an aerosol electrometer can be used downstream of DMA2.

Typical TDMA data are illustrated in Figure 2 where the concentration downstream of DMA2 (N_2) is shown as a function of the DMA2 collector rod voltage (V_2). In addition to the five data points shown in Figure 2 a smooth, bell-shaped curve passing through the data is also shown. The shape of this curve is predicted from theory (Rader and McMurry, 1986). Note that N_2 passes through a maximum as V_2 increases. The voltage at which this maximum occurs is related to the mean particle size entering DMA2. The width of the curve is determined by the distribution of particles generated by DMA1, by nonuniformities in growth or shrinkage of particles of a given size within the aerosol conditioner, and by diffusion within DMA1 and DMA2 (Stolzenburg, 1988).

The computer program TDMAFIT uses a least squares fitting procedure to fit theoretical TDMA transfer functions to $N_2(V_2)$ data. Three parameters are adjusted in fitting the theory to the data: f_N, f_V, and f_β. These parameters are defined as follows:

f_N = fraction of particles leaving DMA1 that are detected in a given DMA2 peak

f_V = mobility growth factor for a given DMA2 peak (ratio of centroid mobilities for DMA1 and DMA2)

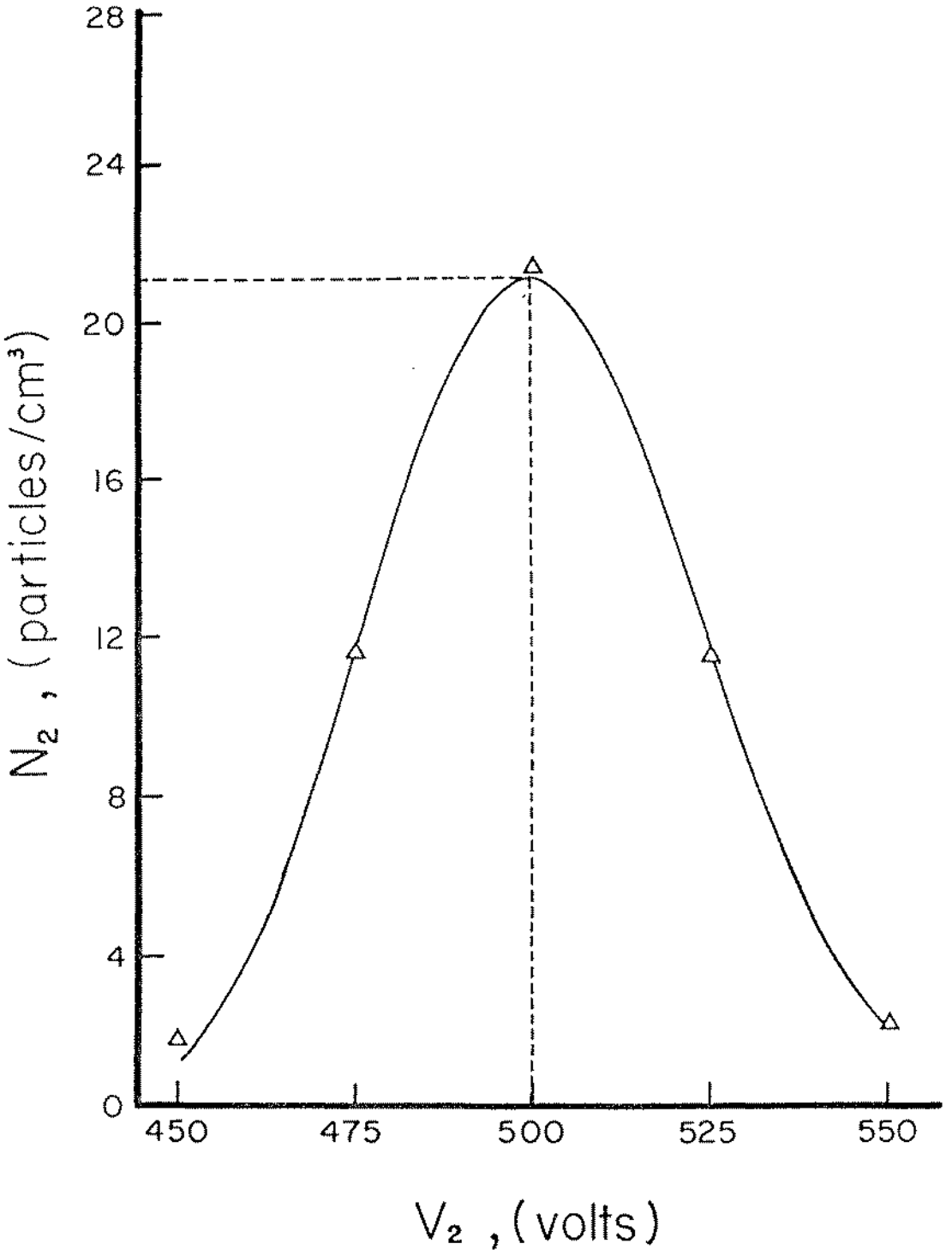

Figure 2. Typical data for number concentration measured downstream of DMA-2, N_2, versus DMA-2 voltage, V_2, in a TDMA system. The curve through the data was obtained by using TDMAFIT to fit theory to the data.

f_β = correction factor for width of $N_2(V_2)$; this parameter should equal 1.0 unless diffusion, inhomogeneities in aerosol chemical composition, or improper DMA performance lead to spreading.

After optimal values for these parameters are determined the program uses them to calculate sizes and size spreads; uncertainties in all calculated parameters are also determined.

The essential ideas behind this program are discussed by Rader and McMurry (1986). However, as described in the THEORY section of this manual, the approach of Rader and McMurry has been extended to include:

- the possibility of two peaks at the outlet from the aerosol conditioner as will happen, for example, if aerosol containing hydrophopic and hygroscopic particles is humidified

- the possibility that particles of a given size (and within a given DMA2 peak) grow by different amounts; we have treated this possibility by assuming that particle growth for particles of a given initial size follows a normal distribution characterized by a mean and standard deviation, both of which can be calculated with TDMAFIT.

The program is designed to operate either with manually entered data or with data files, and results can both be printed directly and stored in output files for further analysis.

In this manual the contents and formats for standard input and output files are first discussed followed by an explanation of how to use the program. The theory behind the analysis is discussed at the end of the manual.

TDMAFIT was developed for use on an IBM PC or compatible computer and was written in Microsoft Quick BASIC. Enclosed with this manual is a floppy disk that includes an executable version of the code (TDMAFIT.EXE) as well as source code (TDMAFIT.BAS and .QBS[2]) to facilitate modification. Also included is a copy of a sample data file (J208_S02.DAT) which is used in this manual with the tutorial on how to use the program.

FILE STRUCTURE FOR INPUT AND OUTPUT FILES

Data can be input into TDMAFIT with either ASCII data files or by hand. In either case an editor is built into the code to facilitate adding, deleting, or correcting data before transfer functions are fitted and before any processed results are stored in data files. For much of our work we use a data acquisition system to generate data files that can be read directly by TDMAFIT, although there are many instances where it is more convenient to acquire and input the data manually. The filename extension for input datafiles is .DAT.

TDMAFIT generates two output files for each data set. One of these output files (filename extension .DTM) is identical in format to the input .DAT file (if an input file is used). This file contains the edited data that was actually used for data analysis. This file can be used as an input file to TDMAFIT (by changing the filename extension to .DAT) for further analysis of

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[2]TDMAFIT.BAS is in standard advanced BASIC format including all line numbers but exceeds the 64K byte limit of many BASIC interpreters and compilers. TDMAFIT.QBS is identical except that line numbers superfluous to Quick BASIC have been removed.

the edited data. The second output file (filename extension .DTR) contains information that can be read into a spreadsheet for further analysis.

Format for .DAT and .DTM files

The format for .DAT and .DTM files is shown in Table 1. The variables listed in Table 1 are defined in Table 2. A printout of a sample .DAT file is shown in Figure 3. Two types of data blocks are found in these files. Data in the six lines following "TdMaHeAdEr" are subsequently referred to as "header data" and include information about DMA operating parameters that typically remain constant during the course of measurements. Such information includes dates, input and output aerosol and sheath air flow rates for both DMAs, and pressures within the DMAs. If any of these variables changes during the course of an experiment, another complete block of "TdMaHeAdEr" data must be inserted in the data file.

In addition to the header data the .DAT and .DTM files include data blocks that begin with the string "RuN" and are referred to as "run data". A run involves a measurement of $N_2(V_2)$ at a fixed V_1, and with fixed aerosol conditioning. A given block of run data includes all of the additional information that is necessary to fit the TDMA theory to $N_2(V_2)$ data. The first two lines in the run data block include variables that typically change from run to run (DMA1 voltage, concentration downstream of DMA1, dew points, etc.) as well as those that may possibly change and so are updated from run to run (e.g. temperatures). The remainder of the run data block includes the "scan data". One line of scan data is recorded for each V_2. Program arrays will accept a maximum number of 30 data

TABLE 1

Format for .DAT and .DTM Files

filename.DAT

```
"TdMaHeAdEr"
DATE.BEG$,TIME.BEG$,FILENAME$,DATE.JUL,TIME.BAG$,START.NO
LOCAT$
EXPER$
K.DMA(1), QM!(1), QA!(1), QS!(1), DP.DMA!(1)
K.DMA(2), QM!(2), QA!(2), QS!(2), DP.DMA!(2)
QCNC!, P.AMB!
"RuN"
RUN.NO, TIME.RUN$, V.DMA1!, DP1!, N1!, NCNT1!, TIME.N1!, TINT.N1!, NPT.SCN
T.TC!(1), T.TC!(2), T.TC!(3), T.TC!(4), T.REF!, TDP1!, RH1!, TDP2!, RH2!
V2.SC!(1)     N2.SC!(1)     NCNT.SC!(1)     TIME.SC!(1)     TINT.SC!(1)
   :             :             :               :               :
V2.SC!(N)     N2.SC!(N)     NCNT.SC!(N)     TIME.SC!(N)     TINT.SC!(N)
```

Where N = NPT.SCN

NOTES

1. For the TSI Model 3071 DMA, K.DMA(1) = K.DMA(2) = 2
2. Optional data include:

Header data	Run data	if not required
FILENAME$	TIME.RUN$	use 0.0 for reals (1)
DATE.JUL*	DP1!*	use 0 for integers ( )
TIME.BAG$	TIME.N1!	use " " for strings ($)
START.NO	TINT.N1!	
LOCAT$	T.TC!(3)	
EXPER$	T.TC!(4)	
	T.REF!	
	TDP1!	
	RH1!*	
	TDP2!	
	RH2!*	
	TIME.SC!(1. . .N)	

* Calculated from other input data

Also, either NCNT.SC!(i) or TINT.SC!(i) may be set = 0.0 (see discussion of fitting procedure).

3. In the input data (.DAT) file, all values should be delimited by spaces or commas or any combination thereof. If a string value is delimited by spaces or contains a comma it must be enclosed in double quotation marks (e.g., "string").

   In the edited data output (.DTM) file, all string values including data section labels (i.e., "HeAdEr", "RuN") are enclosed in doubled quotation marks. All header data and the first two lines of each run data section are free format and the values therein are delimited by commas. The scan lines in each run data section are free format with values placed in five contiguous 14-column fields.

TABLE 2

DEFINITION OF SELECTED PROGRAM VARIABLES

Variable	Type	Symbol	Description [units or format]
BETA!(J)	R	β_j	DMAj flow ratio = $(Q_{sj} + Q_{aj})/(Q_{mj} + Q_{cj})$[ ]
BETA12!	R	β_{12}	β parameter for equiv. DMA1 at (T_2,p_2) [ ]
CHISQR!	R	$\hat{\chi}^2$	Reduced chi square of fit = $(\Sigma_{\text{fit } i} R_{si}^2)/n_f$ [ ]
DATE.BEG$	S		Experiment start date [mm-dd-yyyy or mm/dd/yy]
DATEJUL	I		Experiment start Julian date [1→ 365,366]
DELTA!(J)	R	δ_j	DMAj dim'less aerosol flow difference = $(Q_{sj}-Q_{aj})/(Q_{sj}+Q_{aj})$ [ ]
DLBP1!	R	a_1	-d(log B_p)/d(log D_p) at $\tilde{D}_{p1}$ and (T_1,p_1) [ ]
DLBP12!	R	a_{12}	-d(log Bp)/d(log Dp) at $\tilde{D}_{p12}$ and (T_2,p_2) [ ]
DLBP2!(K)	R	a'_{12}	-d(logBp)/d(log Dp) at $\tilde{D}'_{p12}$ and (T_2, p_2) [ ]
DP.DMA!(J)	R	Δp_j	DMAj over pressure (relative to p_{amb}) [cm H_2O]
DP1!	R	$\tilde{D}_{p1}$	Mean diameter of aerosol exiting DMA1 before conditioning [μm]
DP2!(K)	R	$\tilde{D}'_{p12}$	Mean diameter of aerosol in peak k after conditioning entering DMA2 [μm]
EXPER$	S		Experiment description [67 chars max]
FBET1!(K)	R	f_β	β_{12} multiplier fit parameter [ ]
FILENAME$	S		Original filename embedded within any raw data file
FLAMDA!	R	λ_f	Search method weighting parameter [ ]
GROWB!(K)	R	$f_V = G_B$	V_2^* multiplier fit parameter, mobility growth factor [ ]
GROWD!(K)	R	G_D	Diameter growth factor [ ]
INFILE$	S		Raw data input file name [filename.DAT]

Variable	Type	Symbol	Description [units or format]
IPK	I	k	Index of peak in conditioned aerosol distribution [1,2]
K.DMA (J)	I		DMAj type or dimension specifier [1-4]
L!	R	L	DMA classification section length [cm]
LOCAT$	S		Experiment location [69 chars max]
NCNT.SC!(I)	R	C_{2i}	Number of particles counted for N_{2i} measurement [#]
NCNT1!	R	C_1	Number of particles counted for N_1 measurement [#]
NFREE	I	n_f	Number of degrees of freedom of fit = $n'_s - n'_t$ [ ]
NPK	I		Number of peaks in conditioned aerosol distribution [1,2]
NPTS	I	n'_s	Number of fitted V_2 scan points [ ]
NPT.SCN	I	n_s	Number of V_2 scan points [ ]
NTERMF	I	n'_t	Number of fitted parameters [ ]
NTERMS	I	n_t	Number of parameters specifying conditioned distribution = 3*NPK [3,6]
N1!	R	N_1	Total measured aerosol concentration exiting DMA1 [#/cm^3]
N12!	R	N_{12}	Total aerosol concentration entering DMA2 assuming no losses [#/cm^3]
N2BAR!	R	$\overline{N}_{2i}$	$(N_{2i} + \hat{N}_{2i})/2$ [#/cm^3]
N2F.SC!(I)	R	$\hat{N}_{2i}$	Total predicted aerosol concentration exiting DMA2 at V_{2i} [#/cm^3]
N2.SC!(I)	R	N_{2i}	Total measured aerosol concentration exiting DMA2 at V_{2i} [#/cm^3]
OUTFILE$	S		Edited raw data output file name [filename.DTM]
P.AMB!	R	p_{amb}	Ambient absolute air pressure [mm H_g]
P.DMA!(J)	R	p_j	DMAj absolute air pressure = $p_{amb} + \Delta p_j/1.35955$ [mm H_g]

Variable	Type	Symbol	Description [units or format]
PENET!(K)	R	$f_N = P$	N_{12} multiplier fit parameter, aerosol fraction penetration factor [ ]
QA!(J)	R	Q_{aj}	DMAj polydisperse aerosol in flow [liters/min]
QC!(J)	R	Q_{cj}	DMAj clean air in flow [liters/min]
QCNC!	R	Q_{cnc}	CNC sample flow rate [liters/min]
QCONC!	R	Q_{conc}	Effective CNC sample flow rate for N_{2i} measurements = min (Q_{cnc}, Q_{s2})/ 0.06 [cm^3/sec]
QM!(J)	R	Q_{mj}	DMAj excess (main) air out flow [liters/min]
QS!(J)	R	Q_{sj}	DMAj monodisperse aerosol out [liters/min]
REDFILE$	S		Reduced data output file name [filename.DTR]
RESRMS!	R	$\overline{R}_s$	Root mean square normalized residual = $[\frac{(\Sigma_i R^2_{si})}{n_s}]^{1/2}$ [ ]
RES.SC!(I)	R	R_{si}	Normalized N_{2i} residual = $(N_{2i} - \hat{N}_{2i})/(w_i \bullet \bar{N}_{2i})^{1/2}$ [ ]
RH1!	R	RH_1	DMA1 relative humidity [%]
RH2!	R	RH_2	DMA2 relative humidity [%]
RUN.NO	I		Run # or nth set of run/scan data [1→99]
R1!	R	R_1	DMA outer radius of inner rod [cm]
R2!	R	R_2	DMA inner radius of outer cylinder [cm]
S.DP2!(K)	R	σ_{Dp}	Uncertainty in $\bar{D}'_{p12}$ [μm]
S.FBET1!(K)	R	$\sigma_{f\beta}$	Uncertainty in f_β [ ]
S.GROWB!(K)	R	$\sigma_{fV} = \sigma_{GB}$	Uncertainty in $f_V = G_B$ [ ]
S.GROWD!(K)	R	σ_{GD}	Uncertainty in G_D [ ]
S.PENET!(K)	R	$\sigma_{fN} = \sigma_P$	Uncertainty in $f_N = P$ [ ]
SPRDB!(K)	R	S_B	Mobility dispersion factor [ ]

Variable	Type	Symbol	Description [units or format]
SPRDD!(K)	R	S_D	Diameter dispersion factor [ ]
S.SPRDB!(K)	R	σ_{SB}	Uncertainty in S_B [ ]
S.SPRDD!(K)	R	σ_{SD}	Uncertainty in S_D [ ]
START.NO	I		nth experiment for given Julian date [0,1→99]
TDP1!	R	T_{dp_1}	DMA1 dew point temperature [°C]
TDP2!	R	T_{dp_2}	DMA2 dew point temperature [°C]
TIME.BAG$	S		Time of bag fill [8 chars max]
TIME.BEG$	S		Experiment start time [hh:mm:ss or hh:mm or hh]
TIME.DL!	R	t_d	Mean time delay between N_1 and fitted N_{2i} measurements [hr]
TIME.N1!	R	t_1	Time of day of N_1 measurement [hr]
TIME.RUN$	S		Time associated with run [13 chars max]
TIME.SC!(I)	R	t_{2i}	Time of day of N_{2i} measurement [hr]
TINT.N1!	R	Δt_1	Sample time for N_1 measurement [sec]
TINT.SC!(I)	R	Δt_{2i}	Sample time for N_{2i} measurement [sec]
T.REF!	R	T_{ref}	Thermocouple cold junction temperature [°C]
T.TC!(1)	R	T_1	DMA1 air temperature [°C]
T.TC!(2)	R	T_2	DMA2 air temperature [°C]
T.TC!(3)	R	T_{hum}	Aerosol humidity conditioner temperature [°C]
T.TC!(4)	R	T_{sat}	Water vapor saturator temperature [°C]
V.DMA1!	R	V_1	DMA1 classifier voltage [volts >0]
V2C1!	R	V^*_2	DMA2 voltage corresponding to $Z^*_{p2} = Z^*_{p12}$ [volts]
V2.SC!(I)	R	V_{2i}	DMA2 classifier voltage at i^{th} scan point [volts >0]
WTSIG!(I)	R	w_i	N_{2i}/C_{2i} or $1/(\Delta t_{2i} \cdot Q_{conc})$ if $N_{2i} = 0$ or $C_{2i} = 0$ [cm^{-3}]

```
"TdMaHeAdEr"
"07-27-1987","11:51:39","J208 S02.DTM",208,"11:48:00",2
"Seaver Laboratory (Chemistry Rm 223)  Pomona College  Claremont, CA"
"Dp dependence on relative humidity for ambient aerosols"
4,5.11,.5,.5,-3
3,3.06,.5,.5,-8.5
1.57,727.583
"RuN"
1,"15:11:15",7000.122,.419847,1.480955,1012,12.06472,84.12
24.00049,24.0793,24.10648,23.45074,24.2333,13.77092,52.76626,22.60095,91.46274
 3699.951        .0135998        17              14.37556        154
 4100.037        4.699933E-02    47              14.43403        123
 4499.97         6.239912E-02    52              14.47875        103
 5000            2.959957E-02    37              14.52639        154
 5500.031        .0343995        43              14.58361        154
 6000.061        6.869898E-02    229             14.68278        410
 6499.939        .1199982        190             14.77917        194
 6999.97         .1633823        177             14.83542        133
 7500            9.039869E-02    113             14.8875         154
 8000.031        5.457546E-02    161             14.97278        362
 8500.061        3.199954E-02    32              15.05375        123
 8999.94         9.142723E-03    16              15.11445        214
```

Figure 3. Printout of header and run data from a .DAT file.

points, and the minimum number should be at least five; if more than one peak is present at least 10-12 data points should be recorded. In addition to N_2 and V_2 this information includes the number of counts used to determine N_2 (assuming a single particle condensation nucleus counter was used), the time at which the measurement was made, and the time interval over which N_2 was measured.

The file structure that was set up for the run data was designed for studies of the sensitivity of particle size to relative humidity (McMurry and Stolzenburg, 1988). For other TDMA applications some of this data may be irrelevant. Furthermore, some of this information is optional and is not absolutely essential for the program to operate. The notes at the bottom of Table 1 identify variables that are optional.

TDMAFIT has algorithms to calculate several of the variables in the .DAT and .DTM files from other input data. These include the Julian date (calculated from the mm/dd/yy calendar date), DMA1 size (Dp1) (from flow rates, temperatures, and pressures), and DMA1 and DMA2 relative humidities (from temperatures and dew points). Therefore, it is not necessary for the user to include correct values for these parameters in the .DAT files (although some value must be included to ensure that the file is read correctly). We have found it convenient to use Julian dates to identify data files, although the user has the option of using his own file identification scheme.

Format for .DTR files

The .DTR files are generated to facilitate further data analysis by some other program. We have used the RS/1 package

developed by BBN Software Products Corp.,[3] but many other spreadsheet-type programs could also be used. The .DTR files consist of rows of numbers with 37 columns. There is a row for every peak; for runs where two peaks were detected, a separate row is included for each peak. In addition to information pertaining to the experiment (date, time, etc), and DMA operating parameters (DMA1 voltage, flow ratios, etc.), the .DTR files also include results that were obtained when the TDMA transfer function was fit to the data. A complete summary of information that is included in .DTR files is given in Table 3. Variables are defined in Table 2.

USING TDMAFIT: A Tutorial

In this section the use of TDMAFIT is explained. The explanation is designed in the format of a tutorial to be used in conjunction with the program and data file that are included on the enclosed floppy disk. A rudimentary knowledge of DOS, default drives and directories, etc. is assumed. The program is menu driven and provides prompts, and so is reasonably self-explanatory. Therefore, an attempt has been made to keep this tutorial brief. It is useful to know that data files are always closed after data are recorded. This ensures that data will not be lost if the computer is turned off (accidentally or intentionally) during data processing.

---

[3] A copy of the layout table (RH_LAYT.ARK) that is used to read .DTR files into RS/1 is included on the floppy disk.

TABLE 3

Format for .DTR Files

Parameter (units)	Variable Name	BASIC Format	Format Length	Starting Column
Julian Date	DATE.JUL	# # #	3	1
Time Bag	TIME.BAG$	\ \	8	5
Start No.	START.NO	# #	2	14
Run No.	RUN.NO	# #	2	17
Peak No.	IPK	#	1	20
RH_1 (%)	RH1!	# # . # #	5	22
RH_2 (%)	RH2!	# # . # #	5	28
β_1	BETA!(1)	# . # # # #	6	34
δ_1	DELTA!(1)	# . # # # #	6	41
β_2	BETA!(2)	# . # # # #	6	48
δ_2	DELTA!(2)	# . # # # #	6	55
$\bar{D}_{p1}$ (μm)	DP1!	# . # # # #	6	62
a_1	DLBP1!	# . # # # #	6	69
a_{12}	DLBP12!	# . # # # #	6	76
β_{12}	BETA12!	# . # # # #	6	83
V_1 (volts)	V.DMA1!	# # # # # . # #	8	90
V_2^* (volts)	V2C1!	# # # # # . # #	8	99
N_1 (#/cm^3)	N1!	# # . # # # # ^ ^ ^ ^	10 (11)*	108*
N_{12} (#/cm^3)	N12!	# # . # # # # ^ ^ ^ ^	10(11)*	119*
$\hat{\chi}^2$	CHISQR!	# # . # # # # ^ ^ ^ ^	10(11)*	130*
n_f	NFREE	# #	2	141
t_d (hr)	TIME.DL!	# # . # #	5	144

Parameter (units)	Variable Name	BASIC Format	Format Length	Starting Column
$\bar{D}'_{p12}$ (μm)	DP2!(IPK)	#.####	6	150
σ_{D_p} (μm)	S.DP2!(IPK)	#.####	6	157
a_{12}	DLBP2!(IPK)	#.####	6	164
f_β	FBET1!(IPK)	##.####	7	171
$\sigma_{f\beta}$	S.FBET1!(IPK)	##.####	7	179
P	PENET!(IPK)	#.####	6	187
σ_P	S.PENET!(IPK)	#.####	6	194
G_B	GROWB!(IPK)	#.####	6	201
σ_{GB}	S.GROWB!(IPK)	#.####	6	208
G_D	GROWD!(IPK)	#.####	6	215
σ_{GD}	S.GROWD!(IPK)	#.####	6	222
S_B	SPRDB!(IPK)	#.####	6	229
σ_{SB}	S.SPRDB!(IPK)	#.####	6	236
S_D	SPRDD!(IPK)	#.####	6	243
σ_{SD}	S.SPRDD!(IPK)	#.####	6	250

1. All values in the reduced data output file are formatted as indicated above with single spaces separating format fields. String values are not enclosed in quotation marks.

2. * Note that these parameters are > 0. Therefore, following conventions in BASIC, the first character is always blank and has been used as the delimeter in the .DTR files. The starting column represents the location of the first non blank character.

Proceed as follows:

COPY the **TDMAFIT.EXE** and **J208_S02.DAT** files to another floppy disk or to a subdirectory on the hard disk, and set the default directory to the location of these files.

Load the DOS utility "**GRAPHICS**" to facilitate screen dumps of plots to printer.

Startup and Setting Output Data Files

Type **TDMAFIT** to start the program.

Type **208** when asked for new or existing Julian Date. (If data is to be typed in by hand rather than read from an existing data file this may be a new Julian Date.) Note that initially all files of the type JnnnSnn.* are listed at the top of the screen. After entering the Julian date, all files of the type J208_Snn.* are shown.

Type **2** when asked for start number. The program will then know to use J208_S02.DTM and DTR as the output files. If present, J208_S01.DAT will be set as the initial input file. (While it is not always necessary to use more than one data file per day, we have found it helps with bookkeeping to use separate data files for different experiments. We normally identify the first data file as start 1 (*S01.DAT), etc. Note that it is possible to use other schemes for identifying input file names (e.g., another possible input file name is INPUT.DAT). If a different naming scheme is used, the user can follow prompts on the screen to access the file.)

After the output (and input) data files have been identified, the main menu appears as follows:

```
Edited data output file: J208_S02.DTM      Current input file: J208_S02.DA
Reduced data output file: J208_S02.DTR     Last Run Number read: 0
Next Run Number to record: 1               Next data to read: HEADER

                          MAIN MENU

                Please choose one of the following
            Make your selection by typing the appropriate key

                Change input file        ----   key [C]
                Read input file          ----   key [I]
                Header Data edit/record  ----   key [H]
                Run Data edit/record     ----   key [R]
                Exit program             ----   key [X]
```

Checking and Editing Header Data

Note that the input and output files are identified at the top of the screen. Because data are edited and recorded one block at a time, no data are initially loaded into the program. The information at the top of the screen tells us, however, that the first data that can be edited in J208_S02.DAT is HEADER data. Note that the program requires the user to at least look at the header data before proceeding with the RUN data. To edit the HEADER data press:

I

H

The program then loads the header data and displays the "Current Header Data" screen. An example of a "Current Header Data" screen is shown in Figure 4. The cursor can be moved to selected data values with the arrow keys. Variables that cannot be accessed with the cursor are calculated by the program. To change the value of a variable **move the cursor to that variable**, press **ENTER** (carriage return), and type in the new value of the variable. After the header data have been corrected press **Q** and respond appropriately to queries about disk storage and printer output. The program then returns to the Main Menu.

Checking and Editing Run Data

To edit and record the data for run 1 proceed by pressing:

I
R

The program will then display the "Current Run Data" screen. An example of this screen is shown in Figure 5. Again, selected data values can be modified by following the procedure that was used to edit the "Current Header Data" screen. The scan data can then be checked and edited by pressing:

S

Again, the procedure for editing this screen is like that used with the current header screen. In addition, however, one can delete or add rows of data to the scan data by using the **D** or **I** commands, as indicated at the bottom of the screen.

Current Header Data

Start Date: 07-27-1987 Start time: 11:51:39 Data File: J208_S02.DTM
Julian Date: 208 Bag Fill Time: 11:48:00 Start No. = 2
Location: Seaver Laboratory (Chemistry Rm 223) Pomona College Claremont, CA
Experiment: Dp dependence on relative humidity for ambient aerosols

DMA Parameter	Variable	Upstream (DMA1)	Downstream (DMA2)	Units
Type index	(K.DMA)	4	3	
Clean sheath flow	(QC!)	5.110	3.060	liters/min
Main outlet flow	(QM!)	5.110	3.060	liters/min
Aerosol inlet flow	(QA!)	0.500	0.500	liters/min
Aerosol sample flow	(QS!)	0.500	0.500	liters/min
Beta - flow ratio	(BETA!)	0.0978	0.1634	
Delta - flow ratio	(DELTA!)	0.0000	0.0000	
Over pressure	(DP.DMA!)	-3.000 (-1.181)	-8.500 (-3.346)	cm(in) H20
Total pressure	(P.DMA!)	725.38	721.33	mm Hg

Ambient pressure (P.AMB!) = 727.58 mm Hg (28.645 in Hg)
CNC flow (QCNC!) = 1.570 liters/min

To change data, select item with cursor keys and press RETURN.
Press [H] to redisplay Header data. Press [Q] to quit.

Figure 4. Copy of "Current Header Data" screen.

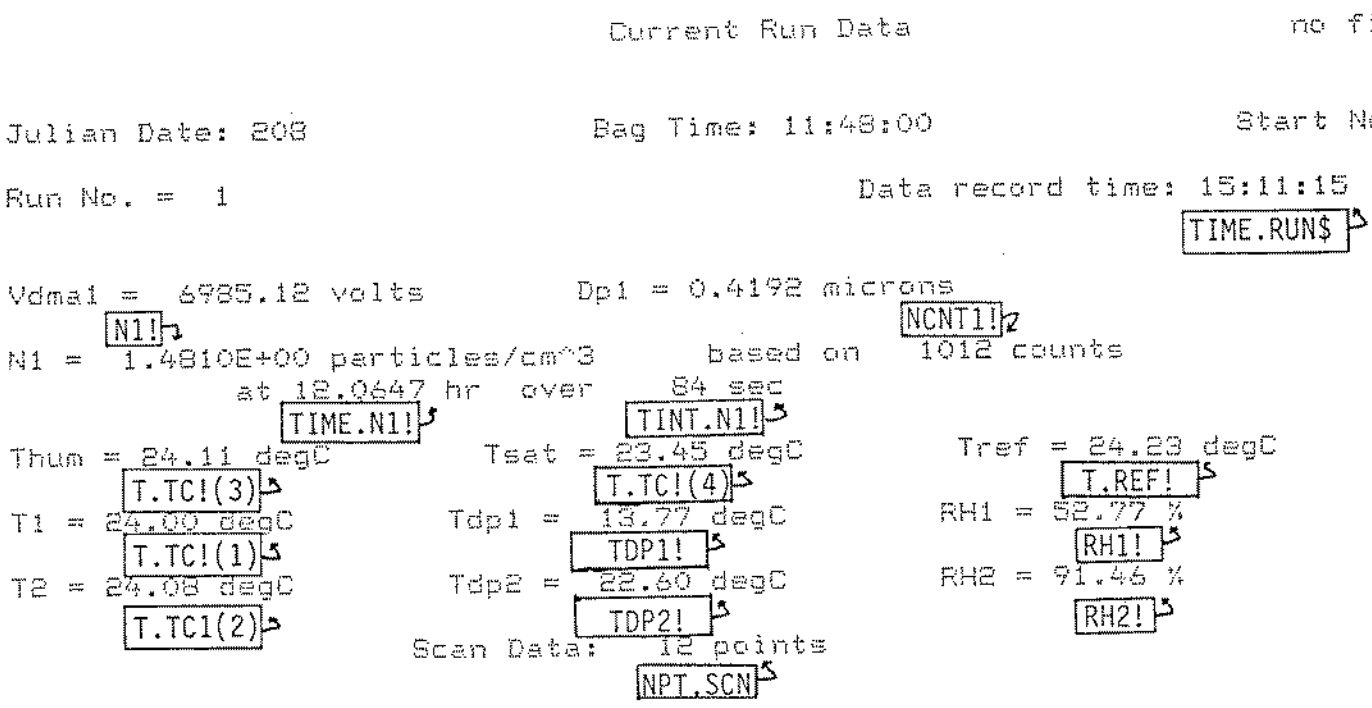

Figure 5. Copy of "Current Run Data" screen. Note that variable definitions are enclosed in boxes. See Table 2 for additional information.

Fitting TDMA Transfer Functions to Peak Data

After the run data have been edited they can be fit with the TDMA transfer function. The program will use the data to make a first guess about the shape of the transfer function. To determine whether this first guess is likely to be reasonable press:

G

to display a graph of the data and the initial guess for the fitting curve. For well-behaved aerosols with a single peak you will often find that the program's initial estimate was a reasonable initial starting point. In that case proceed by pressing any key to clear the graph followed by **F** to initiate the curve fitting procedure to find the best fit . In the data file that was supplied with the program, however, the first run contains two peaks. The program's initial guess is a reasonable approximation to the larger peak, but completely misses the smaller peak.

There are several approaches that can be used to fit data with two peaks, and the user will naturally identify a variety of options as he/she works with the program. In this tutorial we proceed by first approximately fitting the two peaks separately by trial and error (the fit for the larger peak is already a reasonable first guess). These trial and error estimates are then used as initial guesses for the two-peak TDMA transfer function fit.

To proceed with the trial and error fits press any key to clear the graph followed by

P

This brings us to the "Current Peak Data" screen. An example of this screen is shown in Figure 6. Move the cursor to the asterisk (*) to the left of "Peak 1" and press **ENTER**. The message "MASKED" now appears on the Peak 1 data. Move the cursor to the triangle one space to the right and press **ENTER**. Peak 2 data now appear. Move the cursor one space to the left (to the bullet (•)) and press **ENTER**. This will unmask the Peak 2 data. Note that there are also bullets in front of each of the three Peak 2 variables. **These variables will be treated as fixed (not variable) during the fitting procedure unless the bullets (•) are changed to asterisks (*) by moving the cursor to that point and pressing ENTER.** Proceed by changing the screen so that all Peak 2 parameters can be fitted.

The default values for the three Peak 2 variables may or may not be reasonable initial guesses. To find out press **G**. Indeed, the estimated peak height is far too large. Return to the "Current Peak Data" screen by pressing any key. To reduce the initial estimate for the Peak 2 peak height move the cursor **one space to the right of the asterisk** located in front of the variable labelled Peak 2 Aerosol Fraction. Press **ENTER** followed by **M**. Type in 0.06 (to reduce peak height by about a factor of 16) and return to the graphical output (**G**) to see if this is a better guess. Indeed, it is pretty good.

We could now proceed by unmasking Peak 1 and finding the best 2-peak fit for the data. It is occasionally found, however, that it is better to obtain least squares fits to the individual peaks before proceeding with the bimodal fit. We will proceed by finding the least squares best fit for Peak 1. To do this press any key to clear the graph and redisplay the "Current Peak Data" screen, and use the cursor and ENTER keys to mask Peak 2 and unmask Peak 1. Now press **S** to return to the scan data. Note

RH1!	BETA!(1)	DELTA!(1)	V.DMA1!	DP1!	DLBP1!	N1!
	BETA12!	DELTA!(1)	V2C1!	DP1!	DLBP12!	N12!
RH2!	BETA!(2)	DELTA!(2)				

Current Peak Data no fit

	RH(%)	Beta	Delta	Vdma(V)	Dp(μm)	d.lnBp	Conc(#/cc)
DMA1:	52.77	0.0978	0.0000	7000.12	0.4198	1.3279	1.4810E+00
DMA12:		0.0980	0.0000	4305.08	0.4198	1.3296	1.4723E+00
DMA2:	91.46	0.1634	0.0000				

DMA12 corresponds to null conditioning d.lnBp = -d(logBp)/d(logDp)

			Peak 1		
Mean Diameter(μm) after cond	=		0.6139 ± 0.0000	DP2!	± S.DP2!
-d(logBp)/d(logDp) @ Dp2	=		1.2333	DLBP2!	
Beta-12 Multiplier	=	*	1.0000 ± 0.0000	FBET1!	± S.FBET1!
Aerosol Fraction	=	*	0.1387 ± 0.0000	PENET!	± S.PENET!
Mobility Growth Factor	=	*	1.6260 ± 0.0000	GROWB!	± S.GROWB!
Diameter Growth Factor	=		1.4681 ± 0.0000	GROWD!	± S.GROWD!
Mobility Spread Factor	=		0.0000 ± 0.0000	SPRDB!	± S.SPRDB!
Diameter Spread Factor	=		0.0121 ± 0.0000	SPRDD!	± S.SPRDD!

(Chi)²/(0 deg free) = 0.0000E+00 (@ 0.00 hr) RMS Residual = 0.0000E+00

CHISQR! NFREE RESRMS!

To change data, select item with cursor keys and press RETURN.

Options: Display [R]un, [S]can, [P]eak or [G]raph data. [F]it peak. [Q]uit.

Figure 6. Copy of "Current Peak Data" screen. Note that Variable definitions are enclosed in boxes. See Table 2 for additional information.

that the first column of each row contains an asterisk. Any asterisk can be deleted by moving the cursor to that spot and pressing **ENTER**. Data points without asterisks in column 1 are excluded during the fitting procedure. Since, in our example, Peak 1 involves only the last eight data points, delete the asterisks for the first four data points. The "Current Scan Data" screen then appears as shown in Figure 7.

To initiate the peak fitting procedure press **F** and **ENTER** to accept the default of 25 maximum iterations. The screen displays updated values of Chi Squared $\hat{\chi}^2$ and Lambda λ_f (for explanations see curve fitting discussion) as well as the least squares fitted parameters. A copy of the information that is displayed on the screen during the fitting procedure is shown in Figure 8. When the convergence criteria are met the message "Converged Fit" appears at the top of the screen.[4] Proceed by pressing any key to display a graphical representation of the fit. An example of this display is shown in Figure 9. Note that data points that were not used during the fitting procedure are displayed as open circles. Press any key to return to the "Current Peak Data" screen where the new values of the fitted parameters are displayed. A similar procedure can be used to separately fit Peak 2 if necessary.

To obtain the best bimodal fit proceed by returning to the scan data **[S]** and unmask the four data points that were excluded in fitting Peak 1 (i.e., change " " to "*"). Then switch to the

---

[4]While editing and fitting a set of run data, the current status of the fit parameters - "converged", "unconverged" or "no fit" - is always displayed in the upper right corner of the screen. Editing data or fit parameters after obtaining a converged fit may nullify the fit producing a "no fit" status indicator. See FITTING PROCEDURE section for more information.

Current Scan Data no fit

Pt. No.	Fit Pt.	Vdma2 (volts)	N2meas (#/cm^3)	N2fit (#/cm^3)	Weighted Residual	No. of Counts	Day Time (hr)	Time Int (sec)
1		3699.95	1.3600E-02	0.0000E+00	+0.0000	17	14.3756	154
2		4100.04	4.6999E-02	0.0000E+00	+0.0000	47	14.4340	123
3		4499.97	6.8399E-02	0.0000E+00	+0.0000	52	14.4788	103
4		5000.00	8.9600E-02	0.0000E+00	+0.0000	37	14.5264	154
5	*	5500.03	3.4399E-02	0.0000E+00	+0.0000	43	14.5836	154
6	*	6000.06	6.8699E-02	0.0000E+00	+0.0000	229	14.6828	410
7	*	6499.94	1.2000E-01	0.0000E+00	+0.0000	190	14.7792	194
8	*	6999.97	1.6339E-01	0.0000E+00	+0.0000	177	14.8354	133
9	*	7500.00	9.0399E-02	0.0000E+00	+0.0000	113	14.8875	154
10	*	8000.03	5.4575E-02	0.0000E+00	+0.0000	161	14.9728	362
11	*	8500.06	3.2000E-02	0.0000E+00	+0.0000	32	15.0538	123
12	*	8999.94	9.1427E-03	0.0000E+00	+0.0000	16	15.1145	214
		V2.SC!	N2.SC!	N2F.SC!	RES.SC!	NCNT.SC!	TIME.SC!	TINT.SC!

To change data, select item with cursor keys and press RETURN.
Press [D] to delete or [I] to insert row at cursor.
Options: Display [R]un, [S]can, [P]eak or [G]raph data. [F]it peak. [Q]uit.

Figure 7. Copy of "Current Scan Data" screen. Note that variable definitions are enclosed in boxes. See Table 2 for more information.

Peak Fitting Procedure converged fit

ITER	CHISQR	LAMDA	PENET(1)	GROWB(1)	FBET1(1)	PENET(2)	GROWB(2)	FBET1(2)
0	0.0000E+00	1E-02	0.1387	1.6260	1.0000	0.0000	1.0000	1.0000
1	9.6585E+00	1E-03	0.1467	1.6088	1.9673	0.0000	1.0000	1.0000
2	4.0751E+00	1E-04	0.1616	1.5996	2.2262	0.0000	1.0000	1.0000
3	3.7975E+00	1E-05	0.1644	1.5967	2.3034	0.0000	1.0000	1.0000
4	3.7902E+00	1E-06	0.1646	1.5961	2.3185	0.0000	1.0000	1.0000
5	3.7900E+00	1E-07	0.1646	1.5960	2.3209	0.0000	1.0000	1.0000

Press any key to continue.

Figure 8. Copy of "Peak Fitting Procedure" screen. Additional information about variables is given in Table 2 and in the section entitled "FITTING PROCEDURE".

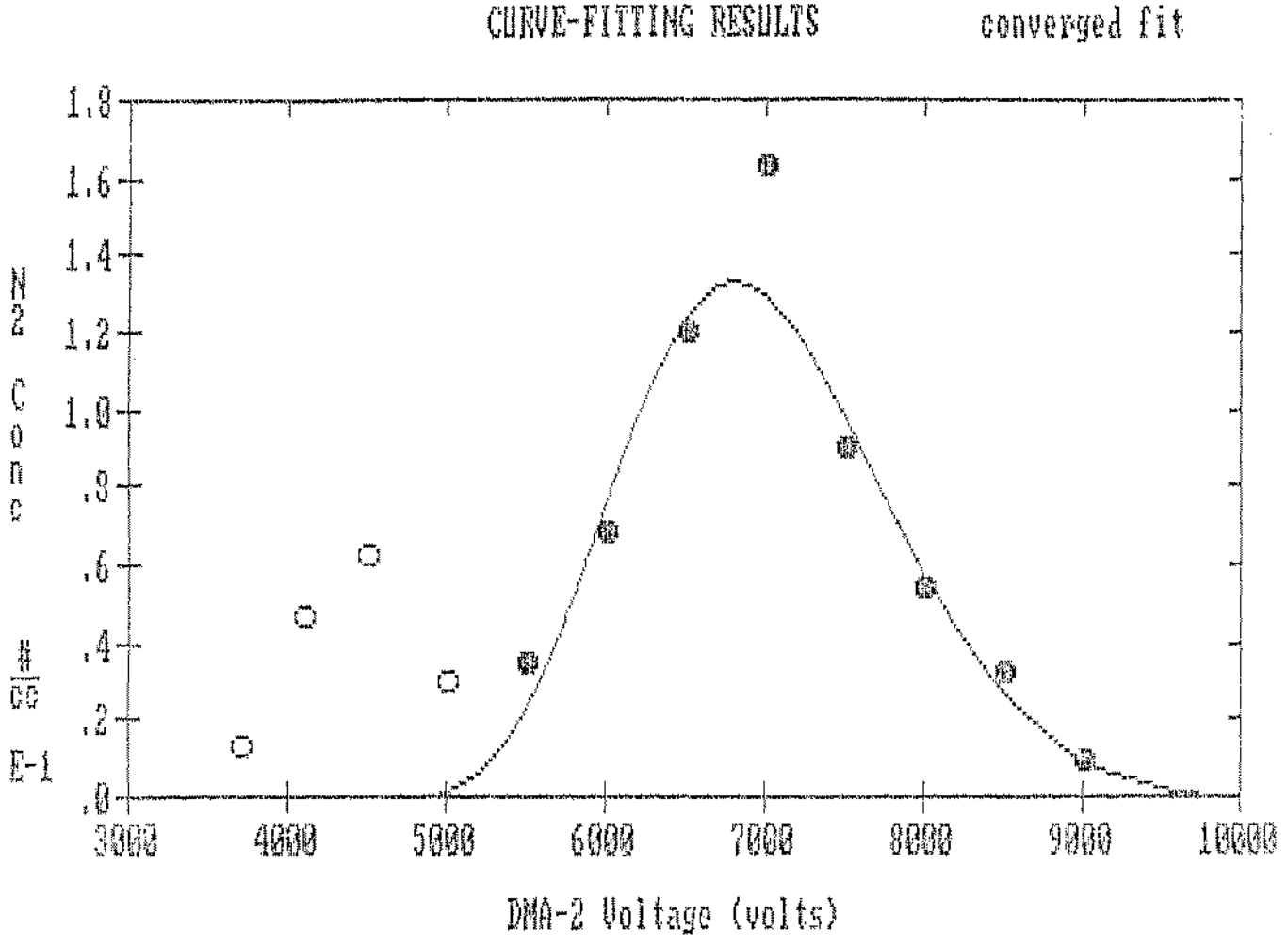

Figure 9. Copy of screen showing TDMA data for concentration downstream of DMA-2, N_2, versus the DMA-2 collecting rod voltage, V_2. Note that in this example particles leaving the aerosol conditioner were bimodal. TDMAFIT was used to fit the TDMA transfer function to the larger peak (solid data points). The open points were masked, and were not used.

"Current Peak Data" screen [**P**] and unmask both peaks. The program provides the user with the option of fixing any of the three (one peak) or six (two peaks) curve fitting parameters. A variable is held fixed if there is a "•" rather than a "*" in front of the variable when the curve fitting procedure [**F**] is called. (Use the cursor and **ENTER** to change from "•" to "*" and back). We have found this option to be especially valuable with data containing two peaks that are close together, or where there are insufficient data points to define one of the peaks adequately. Based on previous experience with similar data the user may know, for example, that one of the peaks did not grow (Mobility Growth Factor = 1.0) or that the width of the $N_2(V_2)$ curve is equal to the theoretically expected value (Beta-12 Multiplier = 1.0). Fixing these parameters at the expected values may help the program to find the least squares best fit.

A copy of the "Current Peak Data" screen that was obtained after fitting the bimodal TDMA transfer function to the data is shown in Figure 10. Note that in obtaining this fit the mobility growth factor for Peak 2 (the smaller peak) was held fixed at 1.0. A graphical display of the two-peak fit is shown in Figure 11. Deviations of individual data points from the bimodal fit are represented as weighted residuals, R_{si}, on the "Current Scan Data" screen [**S**].

When a satisfactory fit has been obtained (with "converged fit" displayed in upper right corner of screen) press **Q** and respond appropriately to queries about disk storage and printer output. This fitting procedure is repeated for each Run. In cases where the Header data was changed during the course of an experiment, the program requires the user to input and check the new Header data before proceding to the next Run.

Current Peak Data converged fit

	RH(%)	Beta	Delta	Vdma(V)	Dp(μm)	d.lnBp	Conc(#/cc)
DMA1:	52.77	0.0978	0.0000	7000.12	0.4198	1.3279	1.4810E+00
DMA12:		0.0980	0.0000	4305.08	0.4198	1.3296	1.4723E+00
DMA2:	91.46	0.1634	0.0000				

DMA12 corresponds to null conditioning d.lnBp = -d(logBp)/d(logDp)

		*	Peak 1	*	Peak 2
Mean Diameter(μm) after cond	=		0.6053 ± 0.0020		0.4198 ± 0.0000
-d(logBp)/d(logDp) @ Dp2	=		1.2365		1.3296
Beta-12 Multiplier	=	*	2.2934 ± 0.0997	*	1.9761 ± 0.3110
Aerosol Fraction	=	*	0.1639 ± 0.0054	*	0.0631 ± 0.0054
Mobility Growth Factor	=	*	1.5979 ± 0.0064	-	1.0000 ± 0.0000
Diameter Growth Factor	=		1.4417 ± 0.0047		1.0000 ± 0.0000
Mobility Spread Factor	=		0.0825 ± 0.0044		0.0682 ± 0.0145
Diameter Spread Factor	=		0.0678 ± 0.0035		0.0513 ± 0.0109

$(Chi)^2$/(7 deg free) = 3.8263E+00 (@ 2.66 hr) RMS Residual = 1.4940E+00

To change data, select item with cursor keys and press RETURN.
Options: Display [R]un, [S]can, [P]eak or [G]raph data. [F]it peak. [Q]uit.

Figure 10. Copy of "Current Peak Data" screen for a bimodal fit to TDMA data. For variable definitions see Figure 6 and Table 2.

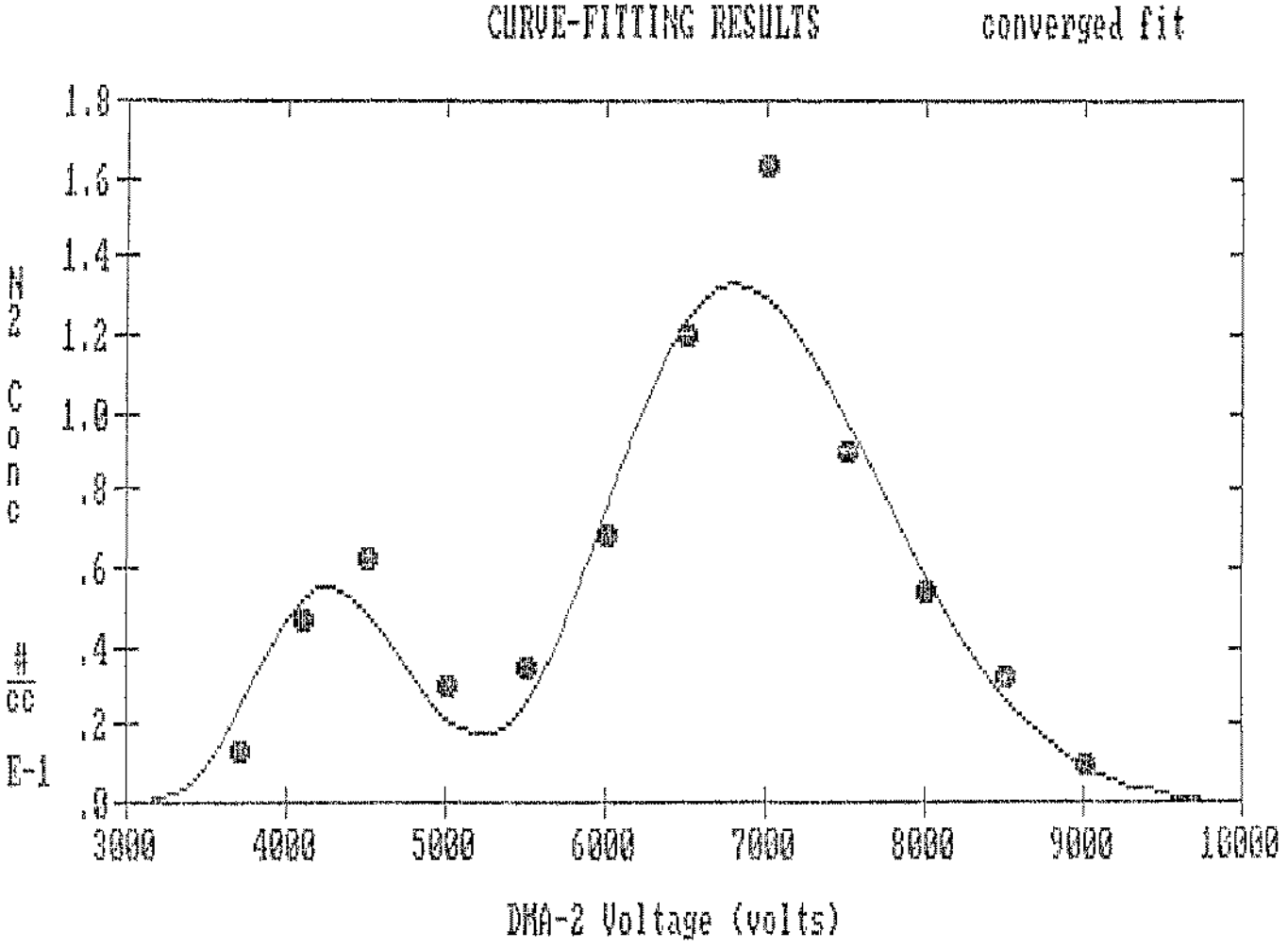

Figure 11. Copy of screen showing TDMA data for concentration downstream of DMA-2, N_2, versus the DMA-2 collecting rod voltage, V_2. The smooth curve through the data points was obtained with TDMAFIT, and represents the least squares best fit for a bimodal aerosol entering DMA-2.

EVALUATING DMA TRANSFER FUNCTIONS WITH A TDMA SYSTEM

There are two ways to measure DMA transfer functions. If the DMA is used to classify a perfectly monodisperse, nondiffusing aerosol, then the relationship between concentration downstream of the DMA and the DMA voltage (N(V)) will be triangular in shape, as predicted by Knutson and Whitby (1975). The nondiffusing constraint can be met by working with 'large' ($\geq$0.2 μm) particles at 'high' flow rates ($\geq$10 lpm). Unfortunately, perfectly monodisperse aerosols do not exist, and the finite variability in particle size for monodisperse aerosol standards such as PSL can lead to significant discrepancies between the measured and theoretical N(V) response. Therefore, the use of monodisperse aerosol standards is not usually a good approach for evaluating DMA performance.

The second approach for evaluating DMA performance involves using the TDMA technique, as described in this section. With this approach DMA2 is used with a suitable detector to measure the mobility distribution of aerosols produced by DMA1. Measurements are done with stable aerosols to ensure that particle sizes remain constant during transport through the TDMA.[5] Measurements are compared with theoretical expectations to obtain a quantative evaluation of the system performance. The discussion below is based on the assumption that the following constraints are met:

---

[5]Suitable aerosol materials include DEHS (diethylhexyl sebacate) and dry salt particles. Oleic acid and dioctyl phthalate (DOP) are not suitable because evaporative shrinkage is measureable during transport through the TDMA system.

1. The effects of diffusion on particle transport through the DMAs is negligible (otherwise the measured transfer functions will appear to be incorrect). As a rule of thumb particles larger than 0.2 μm will not diffuse significantly if the total flow rate is ≥ 10 lpm (Stolzenburg, 1988).

2. The aerosol concentration at the inlet to DMA1 is constant during a measurement of the transfer function.

3. The dimensionless slope of the polydisperse aerosol distribution entering DMA1 can be assumed constant over the width of the DMA1 mobility window. The effect of the input aerosol variability has been discussed by Rader (1985). For lognormal distributions the dimensionless slope increases monotonically as particle sizes move away from the geometric mean diameter. As a rule of thumb, particles produced by DMA1 should fall within two standard deviations of the geometric mean diameter for lognormal distributions entering DMA1.

Rader (1985) recommends measuring concentrations downstream of DMA2 at <u>at least</u> 5 voltages. For a flow ratio of 0.1, the nominal voltages should be:

$$0.9 * V_{max},\ 0.95*V_{max},\ 1.0*V_{max},\ 1.05*V_{max},\ 1.1*V_{max}$$

where V_{max} is the voltage corresponding to the peak concentration downstream of DMA2.

After acquiring the $N_2(V_2)$ data downstream of DMA2, the performance of DMA1 can be determined by using TDMAFIT. To evaluate the TDMA performance a user must:

1. Input data into the program. This can be done either by using the program to read a standard input file (***.DAT; see section II.A) or by manually entering data from the keyboard by use of the editor provided with TDMAFIT.

2. Fit theoretical transfer functions to the data (see TUTORIAL, section III.D)

3. Compare least squares parameters f_β, f_N, and f_V (or equivalently G_D) with theoretically expected value of 1.0 (see discussion below).

The parameter f_β is the ratio of the measured to expected mobility distribution width. For an ideally performing TDMA system operating under the constraints outlined above, this parameter should equal 1.0. Errors in measurement of flow ratios or excessive diffusion effects lead to errors in f_β. f_β should never be less than 1.0 (to within experimental counting uncertainties, which are calculated by TDMAFIT). f_β will exceed 1.0 if flow within either of the DMAs is not laminar and radially symmetric. Common causes of flow disturbances include improperly installed flow straightening screens in the sheath air inlet and plugged holes in the flow straightener at the sheath air outlet. Also, excessive flow rates degrade DMA performance. We have seen some indication that transfer functions are broader than expected for flow rates of $\geq$20 lpm.

Flow disturbances in either DMA1 or DMA2 will lead to incorrect values of f_β. Unfortunately, when this occurs there is no a priori way to determine which DMA is operating improperly, and flows in both may need to be adjusted until f_β is brought adequately close to 1.0. After the instruments are found to operate properly with stable particles a TDMA system can be used to investigate phenomena involving size changes. In this case values of f_β exceeding 1.0 are valid and provide useful information about size transformations in the aerosol conditioner (see Figure 1). McMurry and Stolzenburg (1988) have used such information to infer the variability of particle growth/shrinkage during humidification/dehumification of ambient aerosols.

The parameter f_N accounts for aerosol depositional losses in DMA2. We have found that f_N is typically several percent less

than 1.0, depending on particle size; f_N = 1.0 indicates no depositional losses.

The parameter f_V is the ratio of centroid mobilities for DMA1 and DMA2. Because mobilities of singly charged, spherical particles are uniquely dependent on size, the diameter ratio G_D contains equivalent information. Incorrect flow rates or voltages lead to errors in f_V. Also, f_V will be different from 1.0 if the polydisperse inlet distribution changes significantly over the size range included in the DMA1 mobility window.

The performance of five DMAs was evaluated with TDMAFIT, and the results of these measurements is summarized in Table 4. These DMAs were geometrically similar to the design described by Liu and Pui (1974) and to the TSI Model 3071 electrostatic classifier. Aerosol and sheath air flow rates were held fixed and 1.0 and 10.0 lpm, and the flows exiting DMA1 were fed directly into DMA2 to ensure that the total flow through both instruments were identical. Note that f_β was about 5% greater than the theoretically expected value of 1.0. This seems to be typical. About 3% of the aerosol was lost by deposition in DMA2 (f_N = 0.97), on average, and particle sizes measured with DMA2 were about 0.7% larger than those produced by DMA1. Size discrepancies for the individual measurements appear to be in excess of estimated measurement uncertainty. Reasons for these discrepancies are unknown.

TABLE 4

DATA FROM TDMAFIT EVALUATIONS OF FIVE DMAs

	Unit No.	f_β	f_N	f_V	G_D
	4	1.06 ± 0.02	0.98 ± 0.01	1.016 ± 0.001	1.011 ± 0.001
	5	1.04 ± 0.04	0.98 ± 0.02	1.011 ± 0.001	1.008 ± 0.001
	0	1.03 ± 0.03	0.95 ± 0.02	1.007 ± 0.001	1.005 ± 0.001
	2	1.09 ± 0.04	0.96 ± 0.02	1.010 ± 0.002	1.007 ± 0.001
	3	1.05 ± 0.04	0.95 ± 0.02	1.007 ± 0.001	1.005 ± 0.001
	3	1.02 ± 0.06	0.97 ± 0.03	1.005 ± 0.002	1.004 ± 0.002
low		1.02	0.95	1.005	1.004
high		1.09	0.98	1.016	1.011
mean		1.05 ± 0.03	0.97 ± 0.02	1.009 ± 0.004	1.007 ± 0.003

THEORY

A schematic diagram of the DMA is shown in Figure 12. R_1 and R_2 are the rod and inner cylinder radii, respectively, and L is the axial separation of the aerosol entrance and exit slits. Q_a and Q_s are the aerosol inlet and outlet flows whereas Q_c and Q_m are the sheath air inlet and outlet flows, respectively. The outer cylinder is grounded while the inner analyzer rod is held at voltage V.

The behavior of the DMA is characterized by its transfer function $\Omega(Z_p)$ representing the fraction of aerosol particles with electric mobility Z_p which are successfully transferred from the Q_a inlet flow to the Q_s outlet flow. The transfer function can be expressed as (Stolzenburg, 1988)

$$\Omega = \frac{1}{2\beta(1-\delta)} \cdot \left[|\tilde{Z}_p-(1+\beta)| + |\tilde{Z}_p-(1-\beta)| - |\tilde{Z}_p-(1+\beta\delta)| - |\tilde{Z}_p-(1-\beta\delta)| \right] \quad (1)$$

and is depicted graphically in Figure 13. The non-dimensional

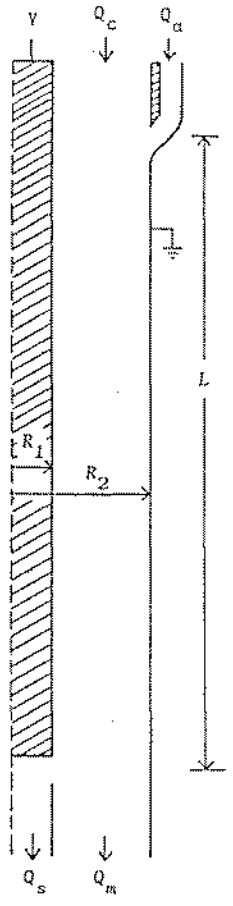

Figure 12: Schematic of DMA.

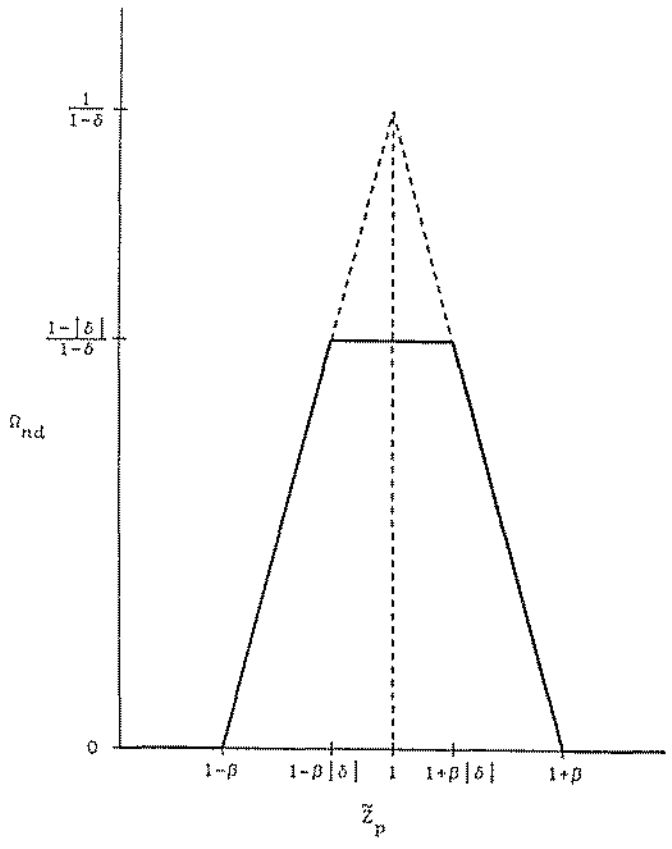

Figure 13: DMA transfer function.

parameters $\tilde{Z}_p$, β and δ are defined as

$$\tilde{Z}_p \equiv Z_p/Z_p^* \tag{2}$$
$$\beta \equiv (Q_s+Q_a)/(Q_m+Q_c) \tag{3}$$
$$\delta \equiv (Q_s-Q_a)/(Q_s+Q_a) \tag{4}$$

where

$$Z_p^* \equiv (Q_m+Q_c)\cdot\log(R_2/R_1)/4\pi LV \tag{5}$$

is the electric mobility corresponding to the centroid of the transfer function. In normal operation the DMA aerosol flows are equal (δ=0) so that the transfer function forms a triangle with apex at the centroid $Z_p=Z_p^*$ ($\tilde{Z}_p$=1) and Ω=1.

Suppose now that the aerosol entering DMA1 has a differential number distribution as a function of electric mobility represented by dN_0/dZ_p. The distribution exiting the classifier is given by

$$dN_1/dZ_p = \frac{Q_{a1}}{Q_{s1}}\cdot\Omega_1(Z_p)\cdot dN_0/dZ_p \ . \tag{6}$$

The total number concentration exiting the DMA can be calculated as

$$N_1 = \int_0^\infty (dN_1/dZ_p)dZ_p = \frac{Q_{a1}}{Q_{s1}}\cdot\int_0^\infty \Omega_1(Z_p)\cdot(dN_0/dZ_p)dZ_p \ . \tag{7}$$

The arithmetic mean of the exiting distribution is given by

$$\bar{Z}_{p1} = \frac{1}{N_1}\cdot\frac{Q_{a1}}{Q_{s1}}\cdot\int_0^\infty Z_p\cdot\Omega_1(Z_p)\cdot(dN_0/dZ_p)dZ_p \tag{8}$$

and the arithmetic standard deviation is

$$\Delta Z_{p1} = \left[\frac{1}{N_1}\cdot\frac{Q_{a1}}{Q_{s1}}\cdot\int_0^\infty (Z_p-\bar{Z}_{p1})^2\cdot\Omega_1(Z_p)\cdot(dN_0/dZ_p)dZ_p\right]^{1/2} \ . \tag{9}$$

If the classifier inlet distribution can be treated as

essentially constant ($dN_0/dZ_p \simeq dN_0/dZ_p$ @ Z^*_{p1}) over the relatively narrow width of the DMA transfer window then the output distribution takes on the same triangular shape as the transfer function. In this case, using Eqs. (1)-(4), Eqs. (7)-(9) reduce to

$$N_1 = (dN_0/dZ_p)\cdot Z^*_{p1}\cdot I_1 = (dN_0/dZ_p)\cdot Z^*_{p1}\cdot \beta_1(1-\delta_1) \tag{10}$$

$$\bar{Z}_{p1} = Z^*_{p1} \tag{11}$$

$$\Delta Z_{p1}/\bar{Z}_{p1} = \left[\frac{1}{6}\beta_1^2(1+\delta_1^2)\right]^{1/2} \tag{12}$$

where

$$I_1 \equiv \frac{Q_{a1}}{Q_{s1}}\cdot\int_0^\infty \Omega_1 d\tilde{Z}_{p1} = \beta_1(1-\delta_1) \ . \tag{13}$$

It is generally of more interest to express aerosol size distributions in terms of particle diameter D_p. Z_p and D_p are related via the following formulas (Allen and Raabe, 1982):

$$Z_p = n_p\cdot e_c\cdot B_p \tag{14}$$

$$B_p = C_s/(3\pi\mu D_p) \tag{15}$$

$$C_s = 1+Kn[1.155+0.471\exp(-0.596/Kn)] \tag{16}$$

where B_p is the particle (dynamic) mobility, n_p is the number of elementary charges e_c on the particle, C_s is the Cunningham slip correction and $Kn\equiv 2\lambda/D_p$ is the Knudsen number. μ and λ are the dynamic viscosity and mean free path of air, respectively, and are calculated from the Sutherland formulas

$$\mu = \mu_o\cdot\left[\frac{T}{T_o}\right]^{3/2}\cdot\left[\frac{T_o+S}{T+S}\right] \tag{17}$$

and

$$\lambda = \lambda_o \cdot \left[\frac{T}{T_o}\right] \cdot \left[\frac{p_o}{p}\right] \cdot \left[\frac{1+(S/T_o)}{1+(S/T)}\right] \qquad (18)$$

where T and p are absolute temperature and pressure, S=110.4°K, T_o=293.15°K, p_o=760mmHg, μ_o=1.819×10^{-4}g/(cm·sec) and λ_o=6.64×10^{-6}cm.

The number distribution of the aerosol exiting the DMA in terms of diameter is related to that in terms of mobility by

$$dN_1/dD_p = (dN_1/dZ_p)\cdot(dZ_p/dD_p) \ . \qquad (19)$$

The total number concentration N_1, arithmetic mean $\bar{D}_{p1}$ and standard deviation ΔD_{p1} of this distribution are determined from equations analogous to Eqs. (7)-(9). If the relationship between mobility and diameter given by Eqs. (14)-(16) can be treated as essentially linear ($dZ_p/dD_p \simeq dZ_p/dD_p$ @ Z^*_{p1}) over the relatively narrow width of the DMA transfer window then dN_1/dD_p is shaped just like dN_1/dZ_p. With this approximation and $dN_0/dZ_p \simeq$ const., the parameters of the diameter distribution can be expressed simply as

$$\bar{D}_{p1} = D_p(\bar{Z}_{p1})_1 \qquad (20)$$

$$\Delta D_{p1}/\bar{D}_{p1} = (\Delta Z_{p1}/\bar{Z}_{p1})/a_1 \ . \qquad (21)$$

The notation $D_p(\bar{Z}_{p1})_1$ indicates the diameter corresponding to electric mobility $\bar{Z}_{p1}$ using Eqs. (14)-(16) at conditions (T_1,p_1) in DMA1. Similarly, a_1=$a(\bar{D}_{p1})_1$ is the derivative

$$a \equiv d(\log Z_p)/d(\log D_p) = d(\log B_p)/d(\log D_p) \qquad (22)$$

evaluated at $\bar{D}_{p1}$ at DMA1 conditions. The total number concentration N_1 is, of course, the same for both mobility and

diameter distributions and is given by Eq. (10).

The aerosol distribution exiting the first classifier, DMA1, has now been fully characterized. In the TDMA technique it is this aerosol which is conditioned (in this case by changing the relative humidity), causing the particles to grow or shrink. The resulting altered distribution is then analyzed using the second classifier, DMA2. Because DMA2 does not measure particle diameter directly but rather particle mobility, it is necessary to consider differences in air conditions between DMA1 and DMA2. That is, changes in the mobility distribution in going from DMA1 to DMA2 are due not only to diameter growth (or shrinkage) caused by the conditioning but also to changes in temperature and pressure.

To account for these secondary (T,p) effects, the mobility distribution exiting DMA1 at DMA1 conditions may be converted to an equivalent mobility distribution at DMA2 conditions corresponding to no change in the diameter distribution. This conversion process is illustrated in Figure 14. The upper left graph indicates the DMA1 transfer function $\Omega_1(Z_p)$. The mobility dN_1/dZ_p and diameter dN_1/dD_p distributions exiting DMA1 at (T_1,p_1) as derived above are shown below that. The lower right graph is the diameter distribution dN_{12}/dD_p as it would appear entering DMA2 at (T_2,p_2) for the case of no growth. The shape and, consequently, the mean $\bar{D}_{p12}$ and standard deviation ΔD_{p12} of the distribution are unchanged from those of dN_1/dD_p. Above that is the corresponding mobility distribution dN_{12}/dZ_p at (T_2,p_2) with mean $\bar{Z}_{p12}$ and standard deviation ΔZ_{p12} derived by the reverse of the process used above. The upper right graph depicts the transfer function $\Omega_{12}(Z_p)$ of a hypothetical DMA12, equivalent to DMA1 but at (T_2,p_2), which would produce the distributions dN_{12}/dZ_p and dN_{12}/dD_p. Using the relationships from the figure the parameters of DMA12 can be expressed as

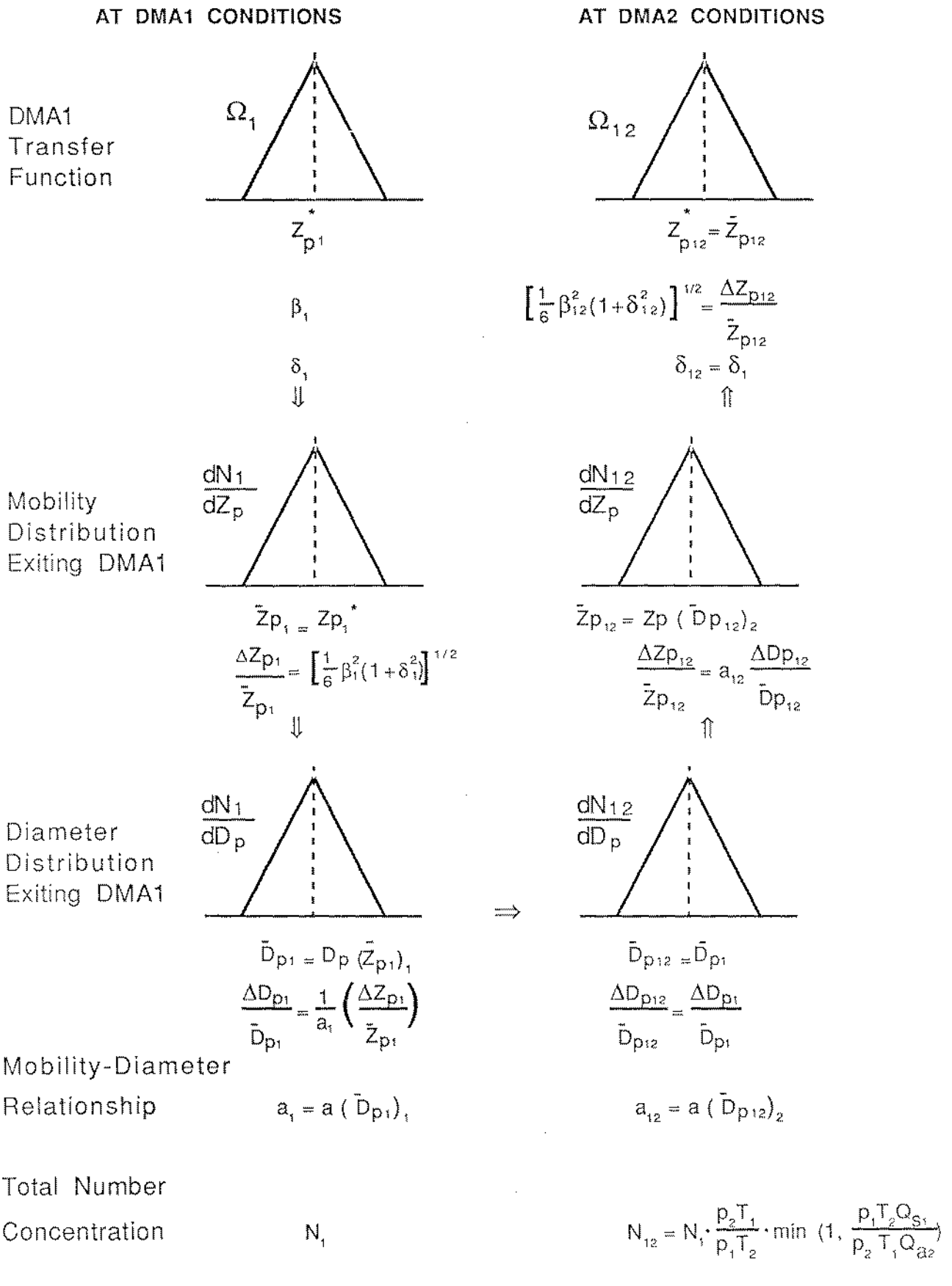

Figure 14: Conversion of DMA1 transfer function and exiting distribution to their equivalents at DMA2 conditions.

$$Z^{*}_{p12} = Z_p(D_p(Z^{*}_{p1})_1)_2 \tag{23}$$

$$\beta_{12} = (\alpha_{12}/\alpha_1)\cdot\beta_1 \tag{24}$$

$$\delta_{12} = \delta_1 \ . \tag{25}$$

As can be seen from Figure 13, $|\delta|$ is just the ratio of the top to the base of the trapezoidal transfer function and should remain constant even though the overall width, measured by β, changes.

In the bottom line of Figure 14, N_1 indicates the total aerosol number concentration (per unit volume air) exiting DMA1 in Q_{s1} at (T_1,p_1). N_{12} is the concentration that should enter DMA2 in Q_{a2} at (T_2,p_2) if there are no losses in the conditioning system. The factor $\min(1,p_1T_2Q_{s1}/p_2T_1Q_{a2})$ indicates the necessary dilution that must take place if the air mass flow entering DMA2 is greater than that exiting DMA1. The factor p_2T_1/p_1T_2 is the dilution due to the change in specific air volume.

The converted distributions and transfer function (designated by subscript 12) in Figure 14 represent a reference state relative to which aerosol growth due to conditioning may now be analyzed. This growth may be expressed in terms of particle diameter or mobility. The diameter growth model used is explained in detail below. The mobility growth model follows by analogy.

Due to variations in chemistry or other factors all particles of size D_p exiting DMA1 may not necessarily grow to the same size D_p' after conditioning. Some dispersion in particle size may occur during the growth process which can be characterized by the function

$$f_D(D_p',D_p)dD_p' \equiv \text{fraction of particles of initial size } D_p$$

which grow into the size range D_p' to $D_p'+dD_p'$.

Using this growth function the aerosol number distribution dN'_{12}/dD_p after growth entering DMA2 is determined by

$$dN'_{12}/dD_p = \int_0^\infty f_D(D'_p, D_p) \cdot (dN_{12}/dD_p) dD_p \quad . \tag{26}$$

The arithmetic mean $\bar{D}'_{p12}$ and standard deviation $\Delta D'_{p12}$ of this distribution can be calculated by the appropriate integrals.

In this work a geometric growth model is used with normal dispersion:

$$f_D(D'_p, D_p) dD'_p = \frac{1}{\sqrt{2\pi} \cdot S_D G_D D_p} \cdot \exp\left[-\frac{1}{2}\left[\frac{D'_p - G_D D_p}{S_D G_D D_p}\right]^2\right] dD'_p \quad . \tag{27}$$

G_D and S_D are the average diameter growth and dispersion factors, respectively, such that the arithmetic mean and standard deviation of diameter after growth of particles of initial size D_p are $\bar{D}'_p = G_D \cdot D_p$ and $\Delta D'_p = S_D \cdot \bar{D}'_p = S_D \cdot G_D \cdot D_p$, respectively. Performing the usual integrations over the resulting aerosol distribution dN'_{12}/dD_p after growth yields

$$\bar{D}'_{p12} = G_D \cdot \bar{D}_{p12} \tag{28}$$

$$\Delta D'_{p12}/\bar{D}'_{p12} = \left[(\Delta D'_{p12}/\bar{D}'_{p12})^2 + S_D^2\left[1 + (\Delta D'_{p12}/\bar{D}'_{p12})^2\right]\right]^{1/2} \tag{29}$$

$$\simeq \left[(\Delta D'_{p12}/\bar{D}'_{p12})^2 + S_D^2\right]^{1/2} \quad \text{if } (\Delta D'_{p12}/\bar{D}'_{p12})^2 \text{ or } S_D^2 \ll 1.$$

The last approximation is valid if either the width of the distribution before growth or the degree of dispersion during growth is relatively small.

The results of the growth process are illustrated in Figure 15. The left column indicates the DMA1 transfer function and exiting distribution in the reference state, that is, at (T_2, p_2) before growth. In the column to its right are shown the mobility and diameter distributions predicted theoretically assuming geometric

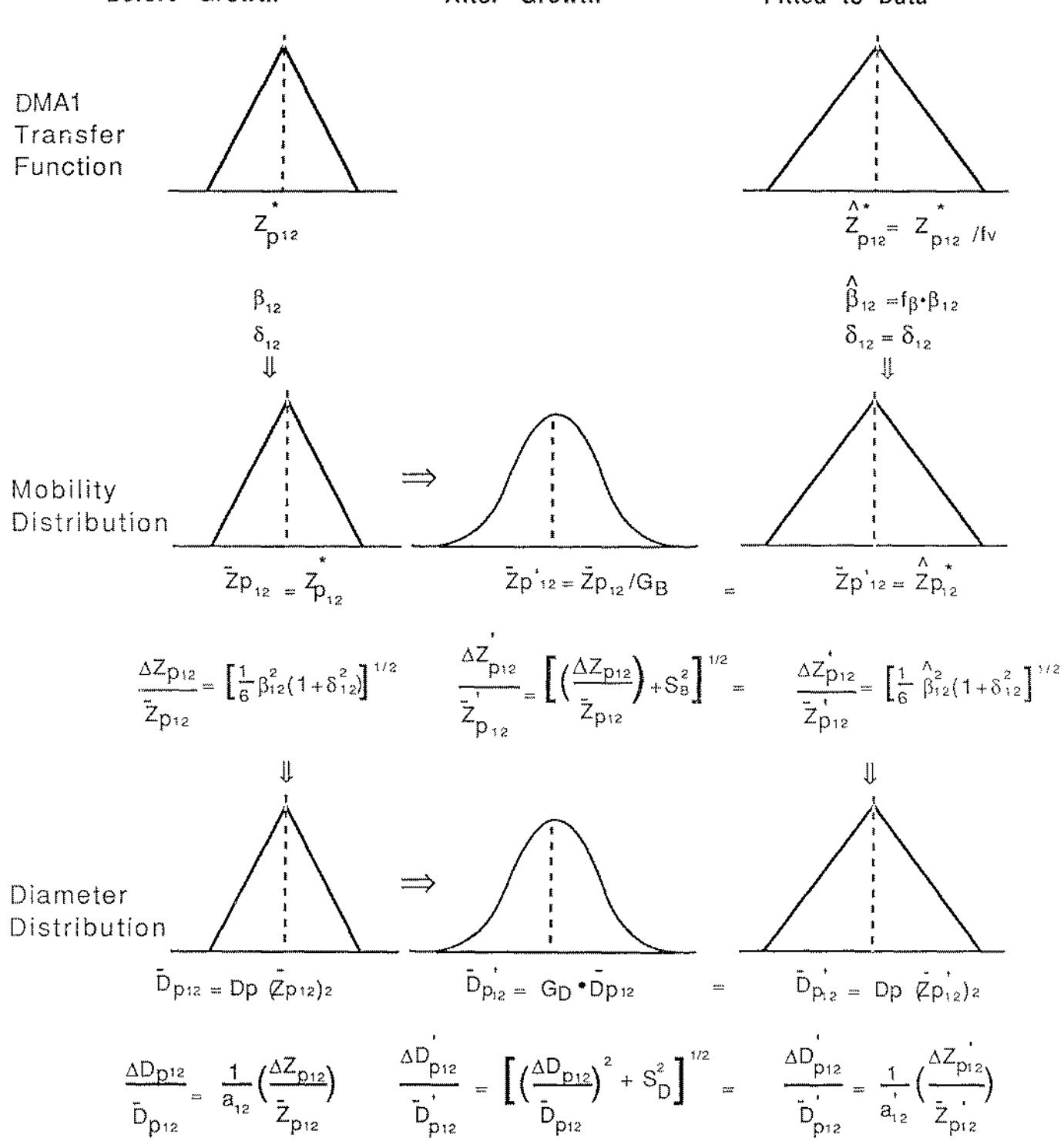

Figure 15: Modeling and measurement of aerosol growth of DMA1 output distribution.

growth with normal dispersion. The mobility distribution dN'_{12}/dZ_p after growth is derived from dN_{12}/dZ_p and mobility growth and dispersion factors G_B and S_B in a manner analogous to that used for diameter above. G_B is defined such that it is greater than unity when diameter increases and mobility decreases during conditioning. In the bottom line of Figure 15, N_{12} represents the total aerosol number concentration in the reference state (*i.e.* assuming no losses in the conditioner) whereas N'_{12} is the actual concentration entering DMA2 corrected for the penetration efficiency P through the aerosol conditioner. The factors G_B, S_B, G_D, S_D and P are considered unknowns and are to be determined from experimental data as explained below.

In the TDMA technique the second classifier, DMA2, is used to measure the aerosol mobility distribution dN'_{12}/dZ_p after growth. This is done by making measurements of N_2, the total aerosol concentration exiting DMA2, versus V_2, the DMA2 analyzer voltage, as the DMA2 transfer window is scanned across the entering distribution. A fitting procedure is then used to determine the DMA2 inlet mobility distribution for which the theoretically predicted responses calculated from

$$N_2 = \int_0^\infty (dN_2/dZ_p)dZ_p = \frac{Q_{a2}}{Q_{s2}} \cdot \int_0^\infty \Omega_2(Z_p) \cdot (dN'_{12}/dZ_p)dZ_p \qquad (30)$$

most closely match the measured responses at the selected V_2 settings. Once dN'_{12}/dZ_p is determined the growth parameters G_B, S_B, G_D, S_D and P may also be determined.

When the data set (V_2, N_2) is finite, as is usually the case, assumptions concerning the shape of dN'_{12}/dZ_p must be made before Eq. (30) can be inverted. The growth model proposed above provides a mobility distribution of a well-defined shape (a "dispersed triangle" as shown in the second column of Figure 15) with only three unknown parameters G_B, S_B (or G_D, S_D) and P. It is possible then to carry out the fitting procedure as described to obtain best-fit values for these growth parameters. However,

the analytic computation of the integral in Eq. (30) is extremely complicated for the proposed form of dN'_{12}/dZ_p and numerical integration is too time consuming to be used in the fitting procedure. Thus, the "dispersed" triangle (or trapezoid if $\delta \neq 0$) is approximated by a true triangular (trapezoidal) distribution (third column of Figure 15). This distribution could be produced by a hypothetical DMA1 (with parameters $\hat{Z}^*_{p12}$, $\hat{\beta}_{12}$, δ_{12}) at DMA2 conditions with no growth taking place. With this approximation the integral in Eq. (30) may be calculated as a relatively simple algebraic expression. The derivation of this expression is shown below. The fitting procedure is described in a later section.

Consider the case in which there is no change in the aerosol mobility distribution in going from the exit of DMA1 to the entrance of DMA2. Then the mobility distribution exiting DMA2 is given by

$$dN_2/dZ_p = \frac{Q_{a2}}{Q_{s2}} \cdot \Omega_2(Z_p) \cdot \frac{Q_{a1}}{Q_{s1}} \cdot \Omega_1(Z_p) \cdot dN_0/dZ_p \qquad (31)$$

with total concentration

$$N_2 = \int_0^\infty (dN_2/dZ_p) dZ_p = \frac{Q_{a2}}{Q_{s2}} \cdot \frac{Q_{a1}}{Q_{s1}} \cdot \int_0^\infty \Omega_2(Z_p) \cdot \Omega_1(Z_p) \cdot (dN_0/dZ_p) dZ_p \; . \qquad (32)$$

If the source mobility distribution dN_0/dZ_p can again be considered uniform within the width of the DMA1 transfer window, then, using Eq. (10), Eq. (32) reduces to (Rader and McMurry, 1986, and Stolzenburg, 1988)

$$N_2 = (dN_0/dZ_p) \cdot Z^*_{p1} \cdot I_2 = N_1 \cdot I_2/I_1 \qquad (33)$$

where

$$I_2 \equiv \frac{Q_{a2}}{Q_{s2}} \cdot \frac{Q_{a1}}{Q_{s1}} \cdot \int_0^\infty \Omega_2 \cdot \Omega_1 \, d\tilde{Z}_{p1}$$

$$= \frac{1}{12\beta_1(1+\delta_1)\beta_2(1+\delta_2)} \cdot \tilde{V}_2^{-2}$$

$$\cdot \sum \sum \left[|\tilde{V}_2(1\pm\beta_1)-(1\pm\beta_2)|^3 + |\tilde{V}_2(1\pm\beta_1\delta_1)-(1\pm\beta_2\delta_2)|^3 \right.$$

$$\left. -|\tilde{V}_2(1\pm\beta_1)-(1\pm\beta_2\delta_2)|^3 - |\tilde{V}_2(1\pm\beta_1\delta_1)-(1\pm\beta_2)|^3 \right] . \quad (34)$$

The non-dimensional parameter $\tilde{V}_2$ is defined as

$$\tilde{V}_2 \equiv Z^*_{p1}/Z^*_{p2} = V_2/V^*_2 \quad (35)$$

where

$$V^*_2 \equiv [(Q_m+Q_c)\cdot\log(R_2/R_1)/4\pi L]_{DMA2}/Z^*_{p1} \quad (36)$$

is the DMA2 voltage corresponding to $Z^*_{p2}=Z^*_{p1}$. The double summation in Eq. (34) indicates that each of the terms within the square brackets represents four terms corresponding to the four possible arrangements of signs.

The values of N_2 predicted by Eqs. (33)-(36) and (13) are for the case in which the mobility distribution is unchanged in going from the exit of DMA1 to the entrance of DMA2. When there is no growth but a difference in air conditions between the two DMAs, N_{12}, Z^*_{p12}, β_{12} and δ_{12} must be substituted for N_1, Z^*_{p1}, β_1 and δ_1, respectively, in the equations. To accommodate growth N_{12}, Z^*_{p12} and β_{12} may be replaced by

$$N'_{12} \equiv f_N \cdot N_{12} \quad (37)$$

$$\hat{Z}^*_{p12} \equiv Z^*_{p12}/f_V \quad (38)$$

$$\hat{\beta}_{12} \equiv f_\beta \cdot \beta_{12} \ , \quad (39)$$

respectively, where f_N, f_V and f_β are variable non-dimensional factors. $f_N=f_V=f_\beta=1$ represents the reference case of no growth and no loss in the conditioning system. δ_{12} is left fixed at $\delta_{12}=\delta_1$.

The dN'_{12}/dZ_p distribution can now be determined from (V_2, N_2) data by varying f_N, f_V and f_β to obtain the best fit between values of N_2 predicted from Eq. (33) and measured values. The arithmetic mean and relative standard deviation of the fitted mobility distribution after growth are given by

$$\bar{Z}'_{p12} = \hat{Z}^*_{p12} = \bar{Z}_{p12}/f_V \tag{40}$$

$$\Delta Z'_{p12}/\bar{Z}'_{p12} = \left[\tfrac{1}{6}\hat{\beta}^2_{12}(1+\delta^2_{12})\right]^{1/2} = f_\beta \cdot \Delta Z_{p12}/\bar{Z}_{p12} \ . \tag{41}$$

The arithmetic mean and relative standard deviation of the corresponding diameter distribution are

$$\bar{D}'_{p12} = D_p(\bar{Z}'_{p12})_2 \tag{42}$$

$$\Delta D'_{p12}/\bar{D}'_{p12} = (\Delta Z'_{p12}/\bar{Z}'_{p12})/\alpha'_{12} \tag{43}$$

where $\alpha'_{12}=\alpha(\bar{D}'_{p12})_2$. The total concentration of the fitted distribution is given by Eq. (37).

The second column of Figure 15 shows the theoretical prediction of the aerosol distribution after growth while the third column shows that obtained from the data. Since the fitted distribution was assumed to be triangular (trapezoidal) its shape does not exactly match that of the theoretical dispersed distribution. Since the distribution before growth is triangular, if the degree of dispersion is not too great this shape discrepancy should be small. In any case, the fitted values for the moments $\bar{Z}'_{p12}$, $\Delta Z'_{p12}$, $\bar{D}'_{p12}$, $\Delta D'_{p12}$ and N'_{12} should fairly accurately represent the true values for the grown distribution and, as such, can be equated to the theoretical expressions in the second column. The

growth parameters can then be found as functions of the fit parameters:

$$P = N'_{12}/N_{12} = f_N \tag{44}$$

$$G_B = \bar{Z}_{p12}/\bar{Z}'_{p12} = V_2^*(\hat{Z}^*_{p12})/V_2^*(Z^*_{p12}) = f_V \tag{45}$$

$$G_D = \bar{D}'_{p12}/\bar{D}_{p12} = D_p(Z^*_{p12}/f_V)_2/D_p(Z^*_{p12})_2 \tag{46}$$

$$S_B^2 = \left[\frac{\Delta Z'_{p12}}{\bar{Z}'_{p12}}\right]^2 - \left[\frac{\Delta Z_{p12}}{\bar{Z}_{p12}}\right]^2 = \left[f_\beta^2 - 1\right]\left[\tfrac{1}{6}\beta_{12}^2(1+\delta_{12}^2)\right] \tag{47}$$

$$S_D^2 = \left[\frac{\Delta D'_{p12}}{\bar{D}'_{p12}}\right]^2 - \left[\frac{\Delta D_{p12}}{\bar{D}_{p12}}\right]^2 = \left[\left[\frac{f_\beta}{\alpha'_{12}}\right]^2 - \left[\frac{1}{\alpha_{12}}\right]^2\right]\left[\tfrac{1}{6}\beta_{12}^2(1+\delta_{12}^2)\right] \tag{48}$$

Due to experimental uncertainties or non-linearities in the growth function, the fitted value of f_β may occasionally be so small that S_B^2 and/or S_D^2 is less than zero. Dispersion factors in the program are therefore calculated as

$$S_B = \mathrm{sgn}(S_B^2)\cdot|S_B^2|^{1/2} \tag{49}$$

$$S_D = \mathrm{sgn}(S_D^2)\cdot|S_D^2|^{1/2} \tag{50}$$

where sgn(x) is the sign of x. Negative dispersion values represent a narrowing of the aerosol distribution during growth.

In the growth model described above (Eq. (27)) all aerosol of a particular size is treated as being of essentially one type. That is, all particles of a given size are assumed to have nearly identical properties such as shape and chemical composition. Variations in these properties are small and normally distributed resulting in small degrees of dispersion during growth.

There are situations, however, when the aerosol being studied may consist of more than one distinct type. For instance, experiments with atmospheric aerosols indicate that some samples contain both hygroscopic and hydrophobic particles.

Upon humidifying the aerosol exiting DMA1 the hygroscopic fraction of the aerosol grows significantly while the balance remains essentially unchanged. The resulting conditioned distribution exhibits a bimodal nature, sometimes with two easily distinguishable peaks.

In such cases, each aerosol type (corresponding to a peak in the conditioned distribution) may be treated in the manner of the single component growth model. That is, each aerosol type k has its own unique set of growth and dispersion factors G_{Bk}, G_{Dk}, S_{Bk}, S_{Dk}. The factor P_k associated with each type represents the product of the conditioner penetration efficiency and the fraction of the aerosol belonging to type k. The conditioned distributions from each of the different types are then added together to form the overall distribution of the conditioned aerosol entering DMA2. Using this technique of adding distributions the fitting procedure can be used to simultaneously solve for multiple sets of growth parameters associated with an external mixture of aerosol types.

FITTING PROCEDURE

In the TDMA technique the aerosol mobility distribution $dN_{12}^{\prime}/dZ_p$ after growth is determined by matching the DMA2 exit aerosol concentrations predicted from Eq. (30) to measured values obtained at various DMA2 analyzer voltages. This is done by a search routine which locates the set of values of f_N, f_V and f_β (or one set for each aerosol type/peak) which gives the best fit between the theoretical values $\hat{N}_{2i}$ predicted from Eq. (33) and the measured values N_{2i} at the selected measurement voltage settings V_{2i}.

The best fit is defined as that set of fit parameters which minimizes the reduced chi-square function

$$\hat{\chi}^2 \equiv \frac{1}{n_f} \cdot \sum_{i_{fit}} R_{si}^2 \quad . \tag{51}$$

n_f is the number of degrees of freedom of the fit and is equal to the number n_s' of fitted V_2 scan points minus the number n_t' of fitted parameters. The normalized residual R_{si} is defined as

$$R_{si} \equiv (N_{2i} - \hat{N}_{2i}) / (w_i \cdot \bar{N}_{2i})^{1/2} \tag{52}$$

where

$$\bar{N}_{2i} \equiv (N_{2i} + \hat{N}_{2i})/2 \quad . \tag{53}$$

The denominator in the definition of R_{si} represents an estimate of the experimental uncertainty in the N_{2i} measurement based on Poisson statistics. The weighting factor w_i is defined as

$$w_i \equiv N_{2i}/C_{2i} \tag{54}$$

where C_{2i} is the number of particles counted for the N_{2i} measurement. When C_{2i} is not available the weighting factor is calculated in the equivalent form

$$w_i \equiv 1/(\Delta t_{2i} \cdot Q_{conc}) \qquad \text{if } N_{2i}=0 \text{ or } C_{2i}=0 \tag{55}$$

where Δt_{2i} is the sample time for the N_{2i} measurement and $Q_{conc} \equiv \min(Q_{cnc}, Q_{s2})$ is the effective CNC sample flow rate for the N_{2i} measurements. This latter definition is also used when the measured concentration is zero so that the uncertainty is calculated as if one particle were counted.

If N_{2i} measurement uncertainties due to counting statistics are the only major source of error in the fitting procedure then the behavior of the fit parameter $\hat{\chi}^2$ as defined above should be reasonably well described by the theoretical probability distribution for the reduced chi-square random variable. That

is, $\hat{\chi}^2$ should be on the order of one for most fits. If it is significantly greater than one this may indicate other major sources of experimental uncertainty or errors in the theoretical model. For instance, aerosols undergoing extensive dispersion during conditioning are not modeled particularly well in the fitting procedure which may lead to unusually large values of $\hat{\chi}^2$.

The least squares fitting algorithm used to minimize $\hat{\chi}^2$ is one adapted from the FORTRAN program CURFIT in Bevington (1969). The program is based on the gradient-expansion algorithm of Marquardt (1963) which combines the methods of gradient search and linearization of the fitting function. Far from the minimum the algorithm is most heavily weighted toward the method of searching in the reverse direction of the gradient of $\hat{\chi}^2$. As the minimum is approached the algorithm favors the method of linearly extrapolating the fitting function $\hat{N}_2$ to estimate the location of the apex (minimum) of the paraboloid $\hat{\chi}^2$ surface which is a second-order function of $\hat{N}_2$. The relative weighting of the two methods is determined by the dimensionless parameter $\lambda_f > 0$. When λ_f is large the gradient search method is dominant, and as λ_f goes to zero the algorithm reduces to the method of linearization. λ_f is automatically adjusted by the algorithm to optimize the search path.

To assure physically reasonable results from the fitting procedure, the fitted parameters are constrained to the following ranges at each step of the search:

$$0.001 \leq f_N \leq 9.9999$$
$$0.1 \leq f_V \leq 9.9999$$
$$0.5 \leq f_\beta \leq 20 \ .$$

In addition, f_V is so constrained such that mean of the fitted mobility distribution falls within the range of DMA2 centroid

mobilities corresponding to the V_2 values of the fitted points.

A number of convergence criteria are used to determine when the minimum solution has been obtained. These criteria are based on changes of parameters in successive steps of the search algorithm. The solution is considered converged when $\hat{\chi}^2$ changes by less than 0.1% and each of the fitted parameters changes by less than 10% of its respective estimated uncertainty. These uncertainties are calculated by the algorithm from a sensitivity analysis of the $\hat{\chi}^2$ function to the fitted parameters. This calculation is based on the method of linearization of the fitting function, so, to assure its validity, $\lambda_f \leq 10^{-7}$ is also a requirement at convergence. All of the above criteria must be met for a solution to be accepted as converged. Even then, there is no guarantee that the result represents a global minimum of $\hat{\chi}^2$ and not just a local minimum.

The search procedure terminates when a "converged fit" is attained or when the search exceeds a user-defined maximum number of iterations or when the user issues a quit command. In the latter two cases the results of the search are designated as an "unconverged fit". (Original or edited data for which "no fit" has been attempted are designated as such.)

Upon termination the fitting algorithm provides the final $\hat{\chi}^2$ value as well as values for f_N, f_V, f_β and their respective uncertainties σ_{fN}, σ_{fV}, $\sigma_{f\beta}$ for each aerosol peak fit. The mean diameter $\bar{D}'_{p12}$ of each peak of the conditioned distribution is calculated as $\bar{D}'_{p12}=D_p(Z^*_{p12}/f_V)_2$ with uncertainty

$$\sigma_{Dp} = \bar{D}'_{p12} \cdot \alpha'^{-1}_{12} \cdot (\sigma_{fV}/f_V) \qquad (56)$$

computed by the usual derivative formulas for propagation of errors. Growth parameters P, G_B, G_D, S_B, S_D are calculated for

each peak according to Eqs. (44)-(50) with respective uncertainties

$$\sigma_P = \sigma_{fN} \tag{57}$$

$$\sigma_{GB} = \sigma_{fV} \tag{58}$$

$$\sigma_{GD} = G_D \cdot (\sigma_{Dp} / \bar{D}'_{p12}) \tag{59}$$

$$\sigma_{SB} = \frac{1}{2} \cdot \left[S_B(f_\beta + \sigma_{f\beta}) - S_B(f_\beta - \sigma_{f\beta}) \right] \tag{60}$$

$$\sigma_{SD} = \frac{1}{2} \cdot \left[S_D(f_\beta + \sigma_{f\beta}) - S_D(f_\beta - \sigma_{f\beta}) \right] \tag{61}$$

Because of the infinite derivatives of the $S_B(f_\beta)$ and $S_D(f_\beta)$ functions near f_β=1, uncertainties for these parameters are calculated by the indicated difference formulas.

Besides the statistically important $\hat{\chi}^2$ parameter, the goodness of any fit may also be measured by the root mean square normalized residual:

$$\bar{R}_s \equiv \left[\frac{1}{n_s} \cdot \sum_i R_{si}^2 \right]^{1/2} . \tag{62}$$

This is a measure of the average number of Poisson standard deviations with which the N_{2i} measurements deviate from the fitted response curve. Unlike the $\hat{\chi}^2$ parameter which only considers the fitted points, this is an average over all of the scan points.

Because the aerosol source must be stable over the course of a V_2 scan, many TDMA experiments are carried out while sampling from a bag. Though this arrangement provides stability over short time intervals, there tends to be a gradual decrease in aerosol concentration over longer periods as particles are lost to the walls. Frequently, the concentration N_1 exiting DMA1 is measured at the beginning of an experiment but then decreases during subsequent V_2 scans and measurements of N_2. If this

single measured value of N_1 is used in reducing data from a number of scans executed over a lengthy time interval, the apparent penetration factor P through the TDMA aerosol conditioner will slowly decrease. This decrease is a reflection of the time-dependent aerosol concentration in the bag rather than any change in the aerosol conditioner. As such it is useful to know the time elapsed between the N_1 measurement and the N_{2i} scan measurements associated with any P value. This time delay is calculated as

$$t_d \equiv \frac{1}{n_s'} \cdot \sum_{i_{fit}} (t_{2i} - t_1) \qquad (63)$$

where t_1 is the time of the N_1 measurement and t_{2i} is the time of an N_{2i} measurement. (Time units are in fractional hours and time differences are corrected for clock wrap-around at midnight.) This average is computed after execution of the fitting procedure and uses only those points involved in the fit.

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