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**COMMENTS ON ANALYTICAL RUNS AND DATA REDUCTION
FOR THE TECHNICON AUTOANALYZER II SYSTEM**

Chemistries run on the Technicon AutoAnalyzer II System are frequently subject to baseline drift and/or change in analytical sensitivity. It is essential that a series of calibration standards and blanks be used to begin and end each analytical run, and that blanks and individual standards be distributed within the run if the importance of these two effects is to be evaluated and corrections made.

After an appropriate warm-up period (about 1 hour), the highest standard and a blank are used to set the Standard Calibrate and Baseline controls, respectively, on the spectrophotometer. The solution in the wash receptacle becomes contaminated to the point that it is often unsatisfactory for making adjustments of the Baseline control. This is especially true for chemistries where the analytical range is fairly low as in the case of PO₄ (1.0 - 0.0ppm).

Pairs of blanks are placed after the first calibration series and before and after the final calibration series of standards in the actual analytical run. Blanks and individual standards are used to separate unknown samples into groups of about 10 samples within the run. The following configuration (Fig. 1) represents the typical arrangement used in the analysis of 30 unknown samples for Cl or SO₄:

Blank
100 ppm Std
Blank
100 ppm Std
100 ppm Std
80 ppm Std
60 ppm Std
40 ppm Std
20 ppm Std
10 ppm Std
Blank
Blank
10 unknowns
Blank
60 ppm Std
Blank
Blank
10 unknowns
Blank
40 ppm Std
Blank
Blank
10 unknowns
Blank
Blank
100 ppm Std
100 ppm Std
80 ppm Std
60 ppm Std
40 ppm Std
20 ppm Std
10 ppm Std
Blank
Blank

Fig. 1, Example of an analytical run series
on the Technicon AutoAnalyzer II

Pairs of the high standard are used in each calibration series to help compensate for any lag in recorder pen response in going from zero to maximum analyte concentration. The concentration of unknowns is adjusted by dilution if necessary to bring the measured response into the mid-range of the calibration series in order to minimize the effect of recorder pen response.

Blanks are used to verify a 0.0 value for the baseline or adjust the baseline back to 0.0 during the course of a run. Drift in the baseline is assumed to change in a monotonic fashion. Any change in the baseline from 0.0 is divided by the number of determinations which cover the period of the run affected by the change to obtain an incremental "step size" for the drift. The baseline correction for a given peak on the stripchart is obtained by multiplication of the drift "step size" by the relative position number of the peak in that specific portion of the run under consideration for a given drift correction.

Corrections for changes in analytical sensitivity are considered after all adjustments for baseline drift have been made. The various determinations made using the Technicon AutoAnalyzer II System may exhibit no discernable change in peak heights for corresponding standards of the beginning and ending calibration series of a run, but frequently some systematic increase or decrease in peak heights of corresponding standards is noted. Changes of sensitivity are considered to be monotonic in nature over the course of the entire run.

If a change in sensitivity is noted, peak height values from the series exhibiting the greater set of values are divided by the values of corresponding standards in the series with the lesser peak heights. Ratios from the highest 3 or 4 standards, if exhibiting similar numerical values, are then used to obtain an average ratio for the change in sensitivity over the course of the analytical run. The decimal fraction of the "average ratio value" ($\bar{\Delta}$) is then divided by the number of sampling steps (n) necessary to reach corresponding positions of the standards in the two calibration series in order to ascertain the fractional change in sensitivity per sampling position ($\bar{\Delta}/n$). All sampling positions are numbered in a consecutive fashion beginning at the end of the run having the higher set of values for the calibration series. The increment change in sensitivity ($\bar{\Delta}/n$) is then multiplied by the sampling position number (X_i) and this value is added to 1.0 in order to obtain the sensitivity correction factor $[1 + X_i(\bar{\Delta}/n)]$ for a specific sample location in the analytical run. Multiplication of this factor by the measured peak height yields a value for the peak height which is normalized to the end sample in the calibration series having the greater set of peak heights. Adjusted peak heights of the individual standards which are dispersed in the run serve as checks on the validity of this correction process.

Once the corrections have been made for drift and/or sensitivity change, the peak height data are processed through a parabolic curve fitting routine. The

calibration series (high std.-blank) is broken into two segments. The lower curve is defined by the blank and the two lowest standards; the upper curve contains values for the highest standard down through the next to lowest standard, which provides a common link between the two curves at the next to lowest standard. For the Cl/SO₄ example cited above the curves would cover 100-20ppm and 20-0ppm.

Several of the chemistries employed in the Technicon AutoAnalyzer II System exhibit noticeable departure from linearity over the range of the calibration series of standards plus the blank. Thus, a division of the calibration data into two curves, both of which employ a parabolic fit, provides better results than those obtained from a single curve based upon a simple linear regression of the data.

The following worksheet for a PO₄ analytical run demonstrates the correction of peak heights taken from the stripchart record for baseline drift and a change in analytical sensitivity over the course of the run. Information is also shown for the two calibration curves used to evaluate the peak height data.

Curve: 1.0 - 0.2 ppm
 $r^2 = 0.9999$
 $a_0 = 0.001469$
 $a_1 = 0.009864$
 $a_2 = 0.000004$

Curve: 0.2 - 0.0 ppm
 $r^2 = 1.0000$
 $a_0 = -0.000001$
 $a_1 = 0.009976$
 $a_2 = 0.000002$

Sample	Chart Peak Height	Drift Position Number	Peak Height (χ_i) Drift Corrected	Sensitivity Position Number	Peak Height Sensitivity Corrected	PO4 ppm	Reported PO4 ppm
Blank	0.0		—		—		
1.0 ppm PO4	94.8	1	—		—		
1.0 ppm	95.5	2	95.5	38	97.3		
0.8 ppm	76.9	3	76.8	37	78.2		
0.6 ppm	58.3	4	58.2	36	59.3		
0.4 ppm	38.9	5	38.8	35	39.5		
0.2 ppm	19.8	6	19.6	34	19.9		
0.1 ppm	10.0	7	9.8	33	10.0		
Blank	0.2	8	0.0	32	0.0		
Blank	0.0		0.0	31	0.0		
900480	20.1	1	20.1	30	20.4	0.204	0.20
481	1.8	2	1.8	29	1.8	0.018	0.02
482	6.0	3	6.0	28	6.1	0.061	0.06
483	0.1	4	0.0	27	0.0	0.000	0.00
484	14.1	5	14.0	26	14.2	0.143	0.14
485	12.1	6	12.0	25	12.2	0.123	0.12
486	2.6	7	2.5	24	2.5	0.025	0.02
487	2.9	8	2.8	23	2.8	0.029	0.03
488	2.6	9	2.5	22	2.5	0.025	0.02
489	21.7	10	21.6	21	21.8	0.219	0.22
Blank	—	11	—	20	—		
0.4 ppm PO4	39.2	12	39.0	19	39.4		
Blank	0.2	13	0.0	18	0.0		
Blank	0.0		0.0	17	0.0		
490	33.9	1	33.9	16	34.2	0.344	0.34
491	36.5	2	36.4	15	36.7	0.369	0.37
492	7.8	3	7.7	14	7.8	0.078	0.08
493	8.0	4	7.9	13	8.0	0.080	0.08
494	20.0	5	19.9	12	20.0	0.200	0.20
495	2.2	6	2.0	11	2.0	0.020	0.02
496	9.1	7	8.9	10	8.9	0.090	0.09
Blank	0.2	8	0.0	9	0.0		
Blank	0.0		0.0	8	0.0		
1.0 ppm	96.9		—	7	—		
1.0 ppm	97.0		97.0	6	97.3		
0.8 ppm	78.0		78.0	5	78.2		
0.6 ppm	59.2		59.2	4	59.3		
0.4 ppm	39.8		39.8	3	39.9		
0.2 ppm	19.9		19.9	2	19.9		
0.1 ppm	10.0		10.0	1	10.0		
Blank	0.0		0.0		0.0		
Blank	0.0		0.0		0.0		

Calib. Series 2

	Series 2	Series 1
1.0 ppm	97.0	95.5
0.8 ppm	78.0	76.8
0.6 ppm	59.2	58.2
0.4 ppm	39.8	38.8
0.2 ppm	19.9	19.6

Ratio 2/1
 1.015707
 1.015625
 1.017182
 1.025773
 1.015306
 1.016171 ave. ratio

$\bar{\Delta} = 0.016171$ $n = 32$ $\bar{\Delta}/n = 0.000505$ (Sensitivity Step size)