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The Curve Fitting of Portable Wear Metal Analysis

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Abstract

This thesis describes the curve fitting algorithm that the Portable Wear Metal Analyzer used for calculating concentrations in ppm and compares this with some alternative algorithms. Each algorithm considered fits a curve to the three standards used, which were 20%, 50%, and 100% of the full scale for all nine wear metals. APL was used for all programs.

I. Introduction

Spectrometric oil analysis is used to determine the type and amount of wear metals in lubricating oil samples. The Portable Wear Metal Analyzer (PWMA) was developed for the USAF to perform engine oil analysis when aircraft are deployed away from their home bases. The analyzer can detect nine wear metals in parts per million concentration ranges. PWMA takes samples with known concentration to obtain absorbance areas, and uses those to determine a calibration curve. Absorbance areas obtained from unknown samples are compared to the calibration curve so that their concentration can be calculated.

This thesis describes the curve fitting algorithm that the PWMA used for calculating the concentration in ppm and compares this with some alternative algorithms for the curve fitting. We compare these algorithms to see which algorithm performs best. Each algorithm considered fits a curve to the three standards used 20%, 50%, and 100% of the full scale for all nine wear metals. APL was used for all programs.

Data gathered as the result of the field test of the PWMA are described in Chapter 2. Three rational functions, and polynomials which are quadratic in absorbance and quadratic in concentration

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are suggested as alternatives in Chapter 3. A squared error technique is employed to compare the algorithms' performances.

2. PWMA and Data Description

2.1 General

The PWMA test program was conducted at Naval Air Station, Pensacola FL, and three Air Force field test sites, Langley AFB, VA, Myrtle Beach AFB, SC, and Elmendorf AFB, AK in 1985. The purpose of this test plan was to determine the effectiveness and evaluate the functionality of the newly developed PWMA prototypes for measuring wear metal content in turbine engine lubricating oils under field conditions.

When aircraft are deployed from their home bases to austere sites where normal oil analysis capabilities are nonexistent, there still exists a requirement to determine wear metal concentration in turbine engine lubricants. Due to the critical nature of turbine engine lubrication system component wear, particularly in high performance systems such as the F-15, F-16, and A-10 aircraft, the requirement for oil analysis may be on an "after each flight" basis. Presently, the Air Force deploys Flame Atomic Absorption (FAA) spectrophotometers [Ref. 1: p. 50], which were not designed for mobile use. These instruments are sensitive and highly susceptible to damage when deployed for mobility exercises; such damage may lead to partial or complete loss of oil analysis capability in early stages of such exercises. In addition, the instruments require hazardous support accessories, such as compressed gases (nitrous oxide and acetylene) and solvents for dilution (and, in some past cases, acid solutions for digestion of wear metal particulates).

In 1980 HQ TAC issued TAF SON 305-80, establishing the requirement for a critically needed light-weight portable aircraft engine oil analysis unit. In response, AFWAL¹⁾ undertook a contractual effort to determine the feasibility of developing such a device (Contract Number F3361-80-C-2037). Since no such spectrometer with required light-weight portable features was commercially available, a major development program was initiated to ruggedize and miniaturize the conceptual hardware for mobility used. The actualization of the portable wear metal analyzer has been achieved under Contract Number F3361-81-C-2080 by Perkin-Elmer Corporation, Applied Science Division.

2.2 The Portable Wear Metal Analyzer

The PWMA features simultaneous measurement of nine wear metals in lubricating oils with an analysis cycle of four minutes (via air cooling): Silver (Ag), Aluminum (Al), Chromium (Cr), Copper

1) Air Force Wright Aeronautical Laboratory

(Cu), Iron (Fe), Magnesium (Mg), Nickel (Ni), Silicon (Si), and Titanium (Ti). Moreover, with the potential modification to water cooling on production units, this time can be reduced to two minutes. In additions, the PWMA may be operated on either 110/220 VAC, 50 or 60 Hertz, to accommodate use in both the U.S and Europe. The PWMA is packed in two aluminum "suitcases": the electronics/argon case, weighing forty pounds; and the furnace/optics case, weighing sixty pounds. The cases are readily set-up and interconnected by two multiconductor cables and one pneumatic hose. Developed for simple operation and reduced dependence on skill and labor of the operator, the PWMA is characterized as follow: ease of set-up and self-contained configuration; minimal consumables (sample tips, graphite tubes and argon gas supply); no hazardous gases or chemicals (inert compressed gas only); microprocessor-controlled software for calibration, diagnostic etc.; and elimination of transcription errors by automated read-out/print-out of data and results.

The PWMA operates on the principle of absorption of characteristic radiation by atoms of the wear metals of interest. Two multi-element hollow cathode lamps (HCLs), alternately pulsed for source combination and modulation, provide emission source lines for discrete line absorption by specific atoms, which are formed through heating in a preprogrammed ramped cycle (up to 3000° C) in the graphite furnace. All nine absorption lines can be separated simultaneously by the polychromometer and transmitted to respective discrete photomultiplier tubes (where the signal is transduced from energy to current). Next, each individual electrometer converts the current to a voltage signal, which is amplified and processed by the analog (A/D) converter. The output is printed in concentration (parts per million, ppm) for all measurements.

The operation of the PWMA is as follows. The operator first introduces an oil sample into the graphite tube of the Graphite Furnace Assembly . The PWMA start button, located on the control panel, is then depressed, and the entire analysis program is initiated and controlled by an "on board" microcomputer. As the graphite furnace executes the atomization cycles, the emission line spectra originating from the HCLs are focused through the graphite tube to the polychromometer where they are separated into individual spectral lines and are further conveyed to the exit slits. The spectral lines pass through their respective exit slits where their spectral intensities are detected and measured by individual Photomultiplier Tubes (PMTs). Wear metals present in the oil sample will absorb the light associated with each metal's spectral line, thus reducing the intensities reaching the PMTs. The amount of light absorbed is related to the concentration of metal in the oil sample.

The PWMA has several function modes. In the calibration mode, a prepared sample with known concentrations is used to get the absorbance data. Analysis mode is selected to analyze the unknown samples. The prototype PWMA prints out two types of data in the analysis mode, concentration data (computed by the on-board microprocessor) and absorbance data (in parentheses). These data can be used to compare analysis algorithms.

2.3 Test Program and Data Collected

The four prototypes were tested at their respective field evaluation sites. The test followed the PWMA field test burn sequence, which is in Appendix A. The graphite tubes, used in the graphite furnace, deteriorate gradually with use, and should be replaced after every 160 sample burns. If a new graphite tube is being used, preconditioning of the tube is required. Laboratories were to follow the test sequence which included calibration samples, verification samples, correlation samples, random samples, reslope, and so on. Three calibration samples were prepared in MIN-L 7808 oil containing 20%, 50% and 100% of full scale for all nine metals. Perkin-Elmer provided these samples. Three verification samples were prepared in MIN-L 7808 oil containing 10%, 40% and 70% of full scale for all nine metals. Perkin-Elmer provided these samples, too. Correlation Samples used turbin engine oil samples. Each sample contained a minimum of 7 wear metals. Random samples were routine daily samples obtained at each evaluation site. This analysis employs only the calibration and verification samples.

The concentration data printed out by the PWMA are calculated by the microprocessor with the use of a calibration technique. Samples with known concentrations are analyzed first and the absorbance data obtained are used to construct calibration curves. Absorbance data obtained from unknown samples are then compared to the calibration curves so that their concentrations can be calculated. Later verification samples obtained from known samples give an indication of how valid the calibration curve is.

Table 1 shows data collected from one of the field test sites. P523 means "Pensacola May 23rd, 1985", the place and the date the data were collected, "401" is the tube sequential number. CAL IA and CAL IB stands for the calibration sample 20%. Cal II and Cal III are 50% and 100% of full scales respectively. In order to provide a more accurate result, a two-point average calibration was used for the field test, i.e., two CAL I samples were run at CAL I position; two CAL II samples at CAL II position; and two CAL III samples at CAL III position. For each calibration run, the numerical values are the absorbance data printed out (rounded to integers). The PWMA averaged the two samples at the same level, and stored them as the calibration points, but the average value was not printed out.

Part of the data for tube 401 is shown in Table 1. The complete data for tube 401 is attached in Appendix B. VERIF 10, VERIF 40 and VERIF 70 are the verification samples. The data in the first row of VERIF 10 is the computed concentration and the second row is absorbance data.

Table 2 shows all the data available for this study, Langley by location tested 6 tubes, Myrtle Beach tested 5 tubes, Pensacola tested 11 tubes, and Elmendorf tested 6 tubes. All 28 tubes were used during the field test program.

In the PWMA, three calibration standards of 20%, 50% and 100% are used to construct the calibration curve. The absorbance data in CAL IA through CAL IIIB are used to compute the calibration curve coefficients. A pair of two point rational equations were used to fit the calibration curves, one for each of the nine elements. The function used is given in equation 2.1.

Table 1. Absorbance Data of Tube 401

P523 401	Element								
	Fe	Ag	Al	Cr	Cu	Mg	Ni	Si	Ti
CAL IA	58	53	10	38	23	44	40	10	10
CAL IB	56	52	10	34	22	46	38	8	9
CAL IIA	115	98	19	83	47	60	92	28	30
CAL IIB	111	100	21	84	43	61	96	18	29
CAL IIIA	143	129	26	104	70	72	119	33	42
CAL IIIB	145	131	24	104	71	74	120	35	44
VERIF 10 CONC	9	1	2	1	4	3	3	2	5
VERIF 10 ABS	28	28	5	17	12	32	19	9	7
VERIF 40 CONC	44	4	10	4	18	9	12	9	7
VERIF 40 ABS	105	90	17	70	42	56	79	20	10
VERIF 70 CONC	70	7	9	6	28	17	20	12	10
VERIF 70 ABS	129	114	16	88	56	66	105	26	29

Table 2. Data of Each Laboratory

Lab.	Tubes			Total
Langley	PPM201 PPM204	PPM202 PPM206	PPM203 PPM207	6
Myrtle Beach	PPM302 PPM305	PPM303 PPM306	PPM304	5
Penscaloa	PPM401 PPM405 PPM409 PPM415	PPM403 PPM406 PPM412 PPM416	PPM404 PPM408 PPM413	11
Elmendorf	PPM501 PPM504	PPM502 PPM505	PPM503 PPM507	6

$$C = K_1 A / (K_2 A - 1) \tag{2.1}$$

where K_1 , K_2 are unknown coefficients, C is concentration in ppm, and A is absorbance data.

The first part of the curve uses absorbance values obtained from 20% and 50% samples and the second part of the curve uses values obtained from 50% and 100%. We will explain how the concen-

tration value of 9, the first line of the VERIF 10 in Table 1, was computed in the PWMA. Figure 2.1 shows the calibration technique used by the PWMA. In Figure 2.1, the first part of the curve for the FE is given by the solid line, the second part of the curve is given by the dashed line, and symbol + identifies the three calibration points. The verification absorption values of 129, 105 and 28 are applied to the curve, and the calibrated data computed by the PWMA are 70, 44 and 9 respectively.

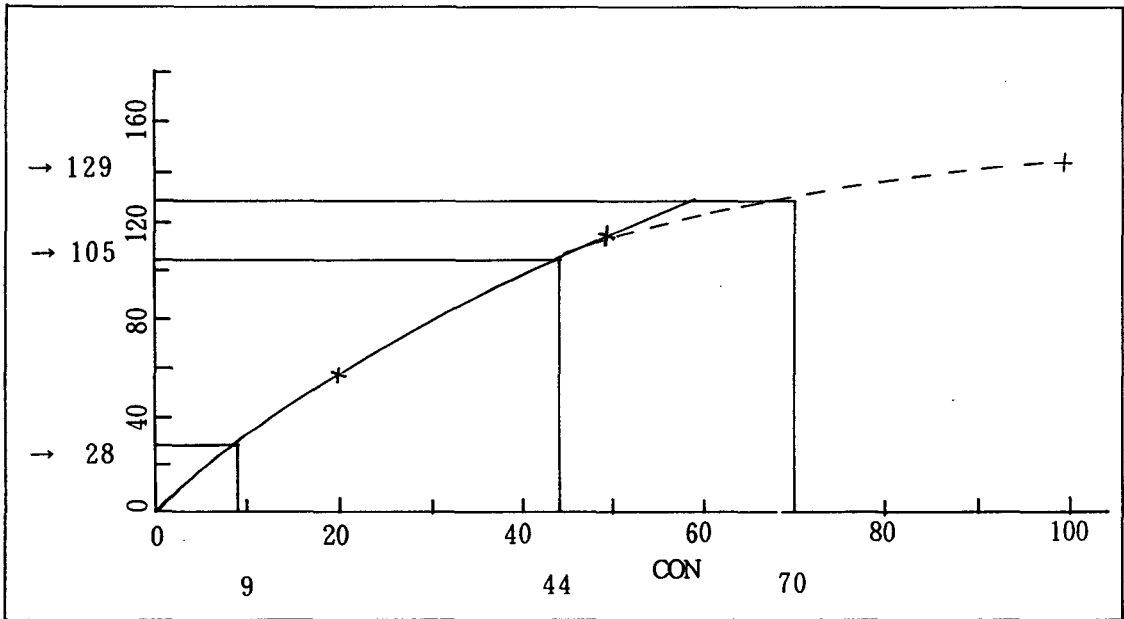


Figure 2.1 Calibration Technique used by the PWMA.

However, the correct values are 70, 40 and 10. Verification sample VERIF 10 which has known concentration should be close to 10. However, it shows some deviation because the curve point projected to the concentration axis makes concentration 9, as shown in Figure 2.1. When the observed absorbance is within the range of 0 to the absorbance value at 50% concentration, the first curve is applied to compute the concentration. For the absorbance data greater than this, the second curve is applied to compute the concentration. The computer selects the proper curve to calculate data, dependent upon the calibrating concentrations of all nine elements. [Ref. 2: p. 67]

The PWMA has a multi-element capability, the 9 elements already listed in Table 1, Iron, Silver, Aluminum, Chromium, Copper, Magnesium, Nickel, Silicon and Titanium.

The full scale capabilities for these elements are shown in Table 3. For example, the full scale value for Fe is 100, and is 10 for AG. The columns labeled 20%, 50% and 100% are CAL I, CAL II and CAL III samples respectively. The 10%, 40% and 70% columns are VERIF 10, VERIF 40 and VERIF 70 respectively. The concentration varies with the sample and the element.

Table 3. Table of Oil Sample Mixtures

METAL	Concentration (ppm)					
	10%	20%	40%	50%	70%	100%
FE	10	20	40	50	70	100
AG	1	2	4	5	7	10
AL	2.5	5	10	12.5	17.5	25
CR	1	2	4	5	7	10
CU	4	8	16	20	28	40
MG	2.5	5	10	12.5	17.5	25
NI	3	6	12	15	21	30
SI	2	4	8	10	14	20
TI	2	4	8	10	14	20
		CAL I		CAL II		CAL III

3. Algorithms

3.1 General

If one increment of concentration C causes an equal increment of absorbance A at all levels of C , then we say that there is no curvature in the analytical curve expressing the relation between C and A . In reality, in the presence of stray light the analytical curve bends towards the concentration axis. [Ref. 3: p. 681]

Calibration curvature can be controlled to an extent by the instrument design. The degree of curvature for iron at the 248.3-nm wavelength, for example, is partially controlled by the spectral bandwidth since most of the curvature can be attributed to overlap of nearby nonabsorbed lines in the iron spectrum. This curvature effect is analogous to stray light interferences observed in molecular spectroscopy. However, at practical instrument settings, it is not possible to eliminate this curvature completely.

B. E. Limbeck investigated transformations of the data from AA (Atomic Absorption) instruments to forms that would produce more easily handled curves. Graphic trials on several possible transformations revealed that a plot of A/C vs A or C/A vs C produced pseudocalibrations that were much less curved than the A vs C calibrations, even for the extreme cases. He concluded that over a limited concentration range, two or three standards were sufficient to produce excellent fits for AA calibrations with the rational algorithm. [Ref. 4: p. 96]

As already mentioned, the PWMA uses a rational function which uses two standards; to cover the full range this equation is used twice. This same function will be used twice in the following analysis. The PWMA on board computer uses single precision arithmetic and establishes its calibration curve internally. The data available for this study was printed out in the PWMA paper tapes, which rounded the observed absorbance numbers. Thus, if one uses the PWMA equation to establish a curve, and then reads the rounded absorbance figures back through this curve, one does not exactly arrive at the concentration printed out. Thus the first algorithm should give essentially the same results as those labeled PWMA, which were the rounded figures from the internal curve. The other two rational functions have three unknown coefficients so that they are used one time with three calibration standards. We will examine three rational functions and two quadratic functions, which are defined below.

$$\text{Algorithm 1 : } C = A / (K_1 + K_2 A)$$

$$\text{Algorithm 2 : } C = (K_1 A + K_3 A^2) / (K_2 A - 1)$$

$$\text{Algorithm 3 : } C = A / (K_1 + K_2 A + K_3 A^2)$$

$$\text{Algorithm 4 : } C = K_1 + K_2 A + K_3 A^2$$

$$\text{Algorithm 5 : } A = K_1 + K_2 C + K_3 C^2$$

3.2 Algorithm 1

This is useful when a simple linear approximation gives a good fit to the plot of A/C versus A. The following rational function was chosen as algorithm 1:

$$A / A / C = K_1 + K_2 A \tag{3.1}$$

It is clear by a simple rearrangement of the formula that the concentration is a function of absorbance:

$$C = A / (K_1 + K_2 A) \tag{3.2}$$

For brevity, the calibration algorithm using this linear rational function is referred to as the "rational method" and is the one actually employed in the PWMA. This algorithm uses a pair of two-point rational equations 3.2 to fit data for all nine elements. The first part of the curve uses absorbance data obtained from 20% and 50% samples, and the second part of the curve uses data obtained from 50% and 100% samples.

3.3 Algorithm 2

William B. Barnett found that the equation,

$$C = K_0 \frac{K_1 A + K_3 A^2}{K_2 A - 1} \tag{3.3}$$

was applicable in fitting the analytically useful concentration range of atomic absorption calibration

curves. [Ref. 5: p. 829]

In this equation, C is the concentration, A is the observed absorbance, and the K_i 's are coefficients which must be determined during calibration. The coefficient K_0 is the reslope constant which is set equal to 1.0 during the initial standardization, which gives

$$C = \frac{K_1 A + K_3 A^2}{K_2 A - 1} \quad (3.4)$$

In equation 3.4, concentration has been expressed as a function of absorbance. This is the reverse of the usual representation where absorbance is considered to be a function of the standard concentrations. However, expressing concentration as the dependent variable facilitates its computation without the need for extracting roots of equations as others had done. Equation 3.4 can actually be used in three forms: as shown in the PWMA, with K_3 being set equal to zero,

$$C = K_1 A / (K_2 A - 1) \quad (3.5)$$

or with K_2 and K_3 both being set equal to zero. This latter case is, of course, the equation for a straight line which passes through the origin.

When the number of standards matches the number of coefficients to be determined, it is a simple matter to determine the coefficients by the solution of simultaneous equations. We will employ simultaneous equations, to show how to get the coefficients in APL.

Suppose

$$C = (c_1, c_2, c_3), \quad A = (a_1, a_2, a_3).$$

If we express both sides of equation 3.4 in terms of components and then equate corresponding components, we obtain the system

$$c_i = \frac{K_1 a_i + K_3 a_i^2}{K_2 a_i - 1} \quad i = 1, 2, 3 \quad (3.6)$$

which leads to

$$K_2 a_i c_i - c_i = K_1 a_i + K_3 a_i^2 \quad i = 1, 2, 3 \quad (3.7)$$

i.e.,

$$c_i = -K_1 a_i + K_2 a_i c_i - K_3 a_i^2 \quad i = 1, 2, 3 \quad (3.8)$$

Define

$$K = (K_1, K_2, K_3), \text{ and } P = \|P_{ij}\|$$

with

$$\begin{aligned} P_{i1} &= -a_i, \\ P_{i2} &= a_i c_i, \\ P_{i3} &= -a_i^2. \end{aligned}$$

Then

$$C = PK \tag{3.9}$$

The solution for K is

$$K \leftarrow C \boxed{\ominus} P$$

where $\boxed{\ominus}$ is the matrix inverse operator in APL [Ref. 6: pp. 82, 83].

While this curve may well faithfully represent the Absorbance - Concentration relationship over the useful range, there are certain possible observed values where it does not. For example algorithm 2 will not perform well when the observed pairs (c_i, a_i) lead to $K_2 = 1/a$, where $a_1 < a < a_3$, since the denominator of equation 3.6 becomes zero. For example, with $C = (20, 50, 100)$, $A = (43, 117, 152)$, the calibration coefficients K are $(-0.4693, 0.00694, 0.00322)$. The fitted curve defined by these coefficients is shown in Figure 3.1. The horizontal line is an asymptote line at A equal to 144.16, which is the reciprocal of K_2 . If the observed absorbance is slightly less than 144.16, the computed concentration will be a large negative number, and when the absorbance data is slightly greater than 144.16, then the computed concentration will be a large positive number, a behavior which would not be acceptable.

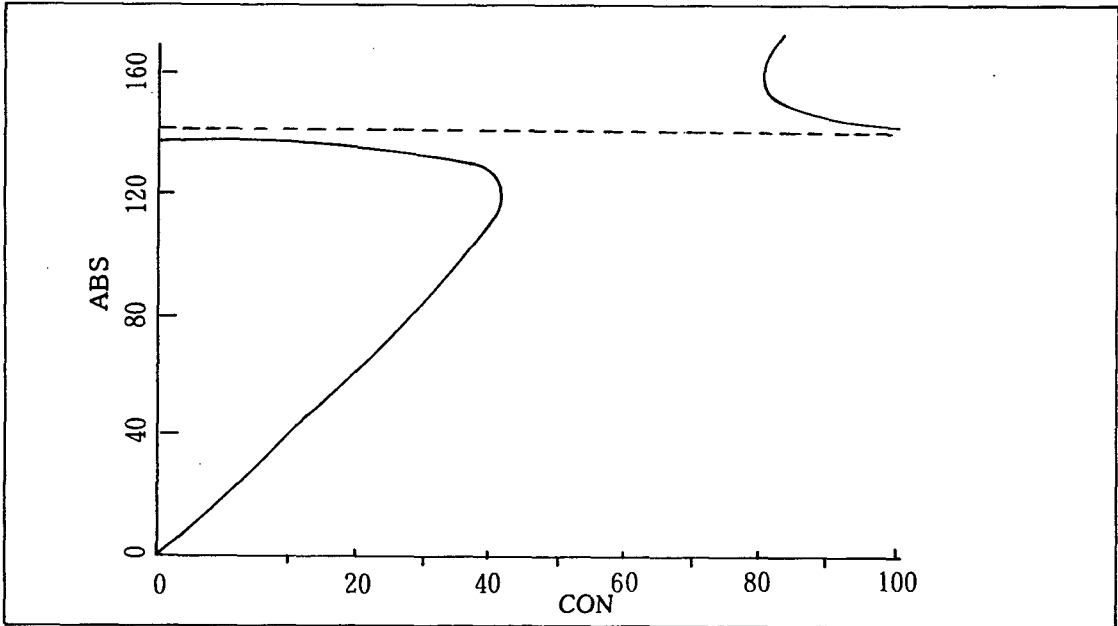


Figure 3.1 An Asymptote Line in Algorithm 2.

3.4 Algorithm 3

This algorithm was suggested by Limbeck [Ref. 4: p. 96].

$$C = \frac{A}{K_1 + K_2 A + K_3 A^2} \tag{3.10}$$

This is a different extension of algorithm 1, namely, $A/C = K_1 + K_2 A$. In equation 3.10, the quadratic term is included. To get the coefficients in APL, we again employ the notation of simultaneous equations.

$$K_1 + K_2 a_i + K_3 a_i^2 = a_i/c_i \quad i = 1, 2, 3 \quad (3.11)$$

Now, let

$$C = (a_1/c_1, a_2/c_2, a_3/c_3) \text{ with}$$

$$P_{i1} = 1,$$

$$P_{i2} = a_i,$$

$$P_{i3} = a_i^2.$$

and again $C = P K$, so the solution is

$$K \leftarrow C \begin{bmatrix} \boxplus \\ \boxminus \\ \boxtimes \end{bmatrix} P$$

This algorithm can also produce a curve with an interior asymptote, like algorithm 2, when the denominator is zero.

Another type of undesirable shape can occur with this case (as well as algorithm 2). This is illustrated by taking

$$C = (20, 50, 100).$$

$$A = (43, 75, 152).$$

Then, we find

$$K = (3.632, -0.0425, 0.000188).$$

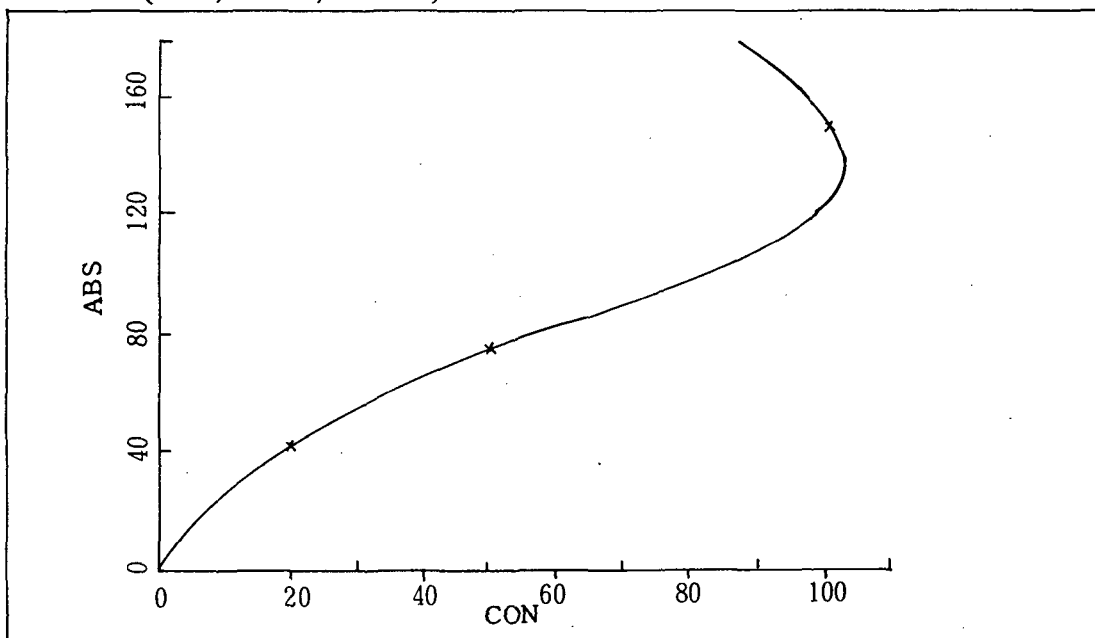


Figure 3.2 Possible Observed Curve from Algorithm 3.

The resulting curve is pictured in Figure 3.2. Increased absorbance will cause lower estimated concentration for $A > 140$ with this example.

3.5 Algorithm 4

A simple quadratic equation

$$C = K_1 + K_2 A + K_3 A^2 \quad (3.12)$$

might be a reasonable alternative for a calibration curve.

Equation 3.12 has been expressed as a function of absorbance. This is the reverse of the usual representation where absorbance is considered to be a function of the standard concentrations. However, expressing concentration as the dependent variable facilitates its calculation without the need for extracting roots of equations as is needed for algorithm 5.

This algorithm may give a satisfactory shape, depending on the A values which occur during calibration burns.

It has an undesirable shape for

$$\begin{aligned} C &= (20, 50, 100), \\ A &= (40, 130, 170), \\ K &= (43.3, -0.865, 0.007). \end{aligned}$$

Pictured in Figure 3.3, here decreasing A, for $A < 60$, gives increasing C.

When

$$\begin{aligned} C &= (20, 50, 100), \\ A &= (40, 60, 170), \\ K &= (-59.3, 2.3, -0.008), \end{aligned}$$

algorithm 4 gives the curve shown in Figure 3.4, in which increasing A, for $A > 140$, leads to decreasing C.

Note that neither of these two curves pass through the origin, since the polynomial equation will not necessarily give zero concentration with zero absorbance.

In APL the coefficients K are given by

$$K \leftarrow C \begin{bmatrix} + \\ + \\ + \end{bmatrix} A \circ . * 012$$

where $C = (c_1, c_2, c_3)$ are the concentrations used and $A = (a_1, a_2, a_3)$ are the observed absorbance numbers.

3.6 Algorithm 5

The final curve to be considered is

$$A = K_1 + K_2 C + K_3 C^2 \quad (3.13)$$

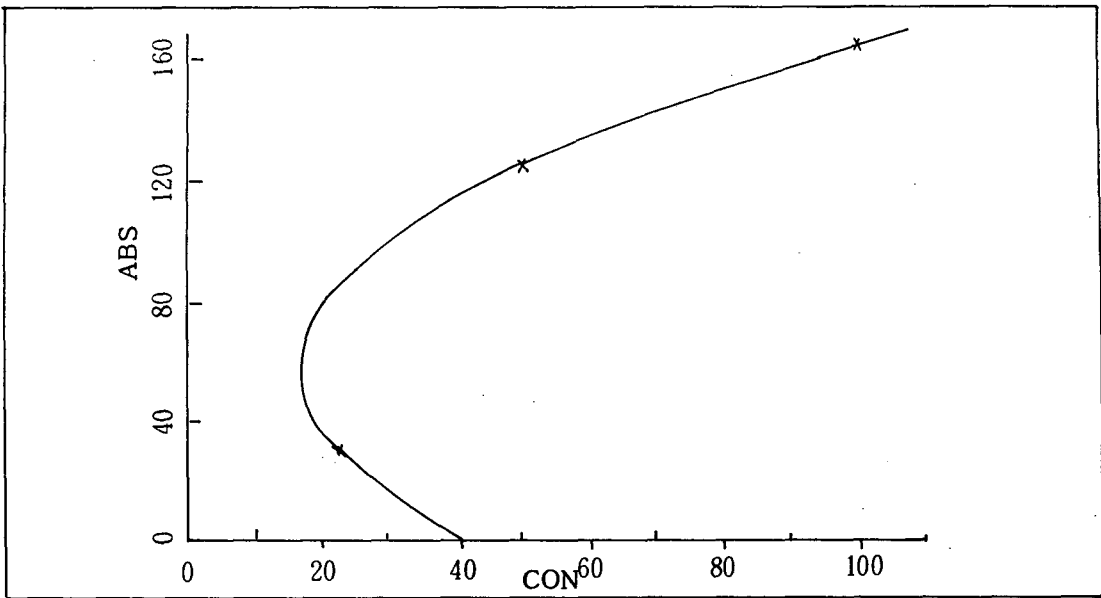


Figure 3.3 The Curve Bending Downward at Lower Concentration by Algorithm 4.

In equation 3.13, absorbance has been expressed as a function of concentration which is the natural representation. However, expressing absorbance as the dependent variable requires the solution of a quadratic equation to find concentration. Equation 3.13 can be expressed like this,

$$K_3C^2 + K_2C + K_1 - A = 0 \quad (3.14)$$

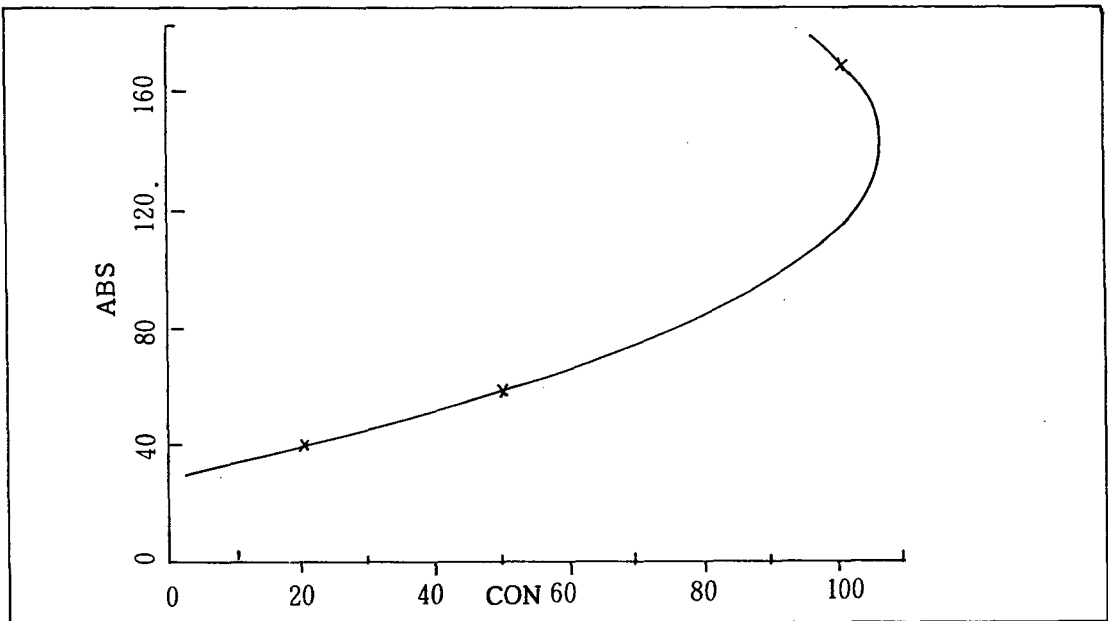


Figure 3.4 The Curve Bending Upward at High Concentration by Algorithm 4.

Solving the resulting equation for C, we obtain the formula,

$$C = \frac{-K_2 \pm \sqrt{K_2^2 - 4K_3(K_1 - A)}}{2K_3} \quad (3.15)$$

Whenever $K_2^2 - 4K_3(K_1 - A)$ is negative, there is no concentration value C for the given absorbance A.

As with algorithm 4, two different undesirable shapes may occur; if the initial calibration data is

$$C = (20, 50, 100),$$

$$A = (40, 140, 170),$$

then

$$K = (-60.8, 5.7, -0.03),$$

giving the curve pictured in Figure 3.5.

If the initial data is

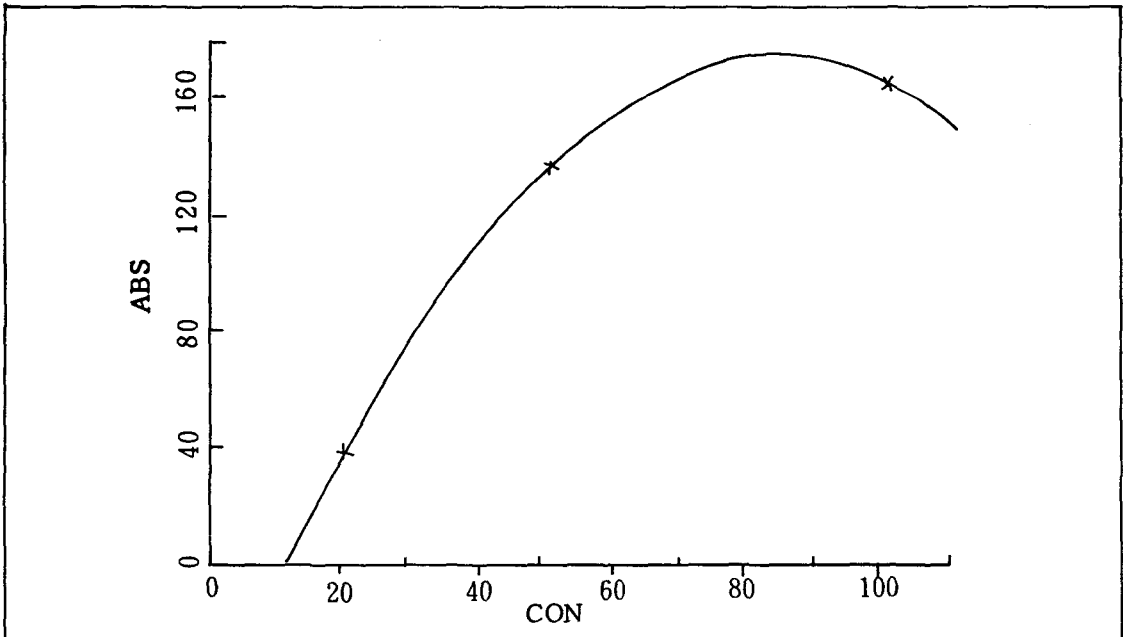


Figure 3.5 The Curve Bending Downward at High Concentration by Algorithm 5.

$$C = (20, 50, 100),$$

$$A = (40, 50, 170),$$

then

$$K = (59.2, -1.5, 0.03),$$

giving the curve in Figure 3.6. With A and C as defined earlier, the coefficients K are given by

$$K \leftarrow A \frac{H}{C} \cdot 0.012$$

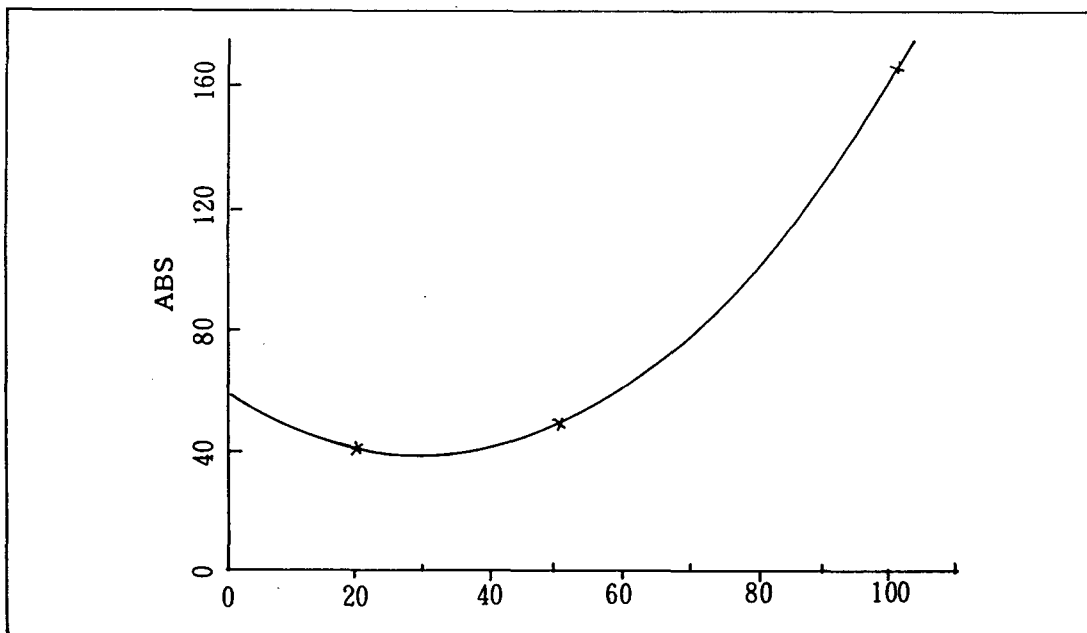


Figure 3.6 The Curve Bending Upward at Lower Concentration by Algorithm 5.

4. Algorithm Comparison

4.1 General

We have mentioned how algorithms are used to fit the curve and each algorithm has defects for specific A values. Recall that the field test program included the concentrations: 10%, 20%, 40%, 50%, 70% and 100% of full scale for each element. Calibrating the tube consisted of two analyses each using the 20%, 50% and 100% samples; these samples were used to fix the absorbance - concentration curve for all analyses performed until the next calibration. During the planned sequence of burns, each of the 10%, 40%, and 70% verification samples were analyzed twice, once just after the calibration curve was established and then a second time about 30 analyses later. Ideally, the established calibration curve should give 10%, 40% and 70% of full scale respectively for these samples; the different possible algorithms can be compared by using these 10%, 40% and 70% samples, in terms of how close the resulting calibration curve result is to the known concentration, for the various tubes used.

Specifically, each algorithm can be used to establish a calibration curve using the observed absorbance numbers for the 20%, 50% and 100% samples. Since these curves are not, in general, exactly the same for all algorithms, the difference between the returned concentration for a 10% sample, $e_{1.0}$

say, can be compared with the expected result c_{10} . We will introduce the sum of squares method to compare the algorithms. Thus, for a given algorithm, we will have two e_{10} , two e_{40} , and two e_{70} values from which we will compute the sum of the 6 squared differences. The algorithm which has the smallest mean sum of squares will be selected as the rank 1, with ranks 2, 3, ..., 5 assigned the larger mean sum of squares. The number of rank 1 and rank 2 for each element throughout all tubes will be considered as the comparing tool for that rank. The algorithm which produces the most rank 1 and rank 2 scores will be designated the best one.

4.2 Sum of Squares Method.

We will explain the sum of squares method by an example. For tube 401, for element Fe, the fitted curve is shown in Figure 4.1 where the coefficients are computed by algorithm 2.

The residuals E are defined by

$$E = C - C'$$

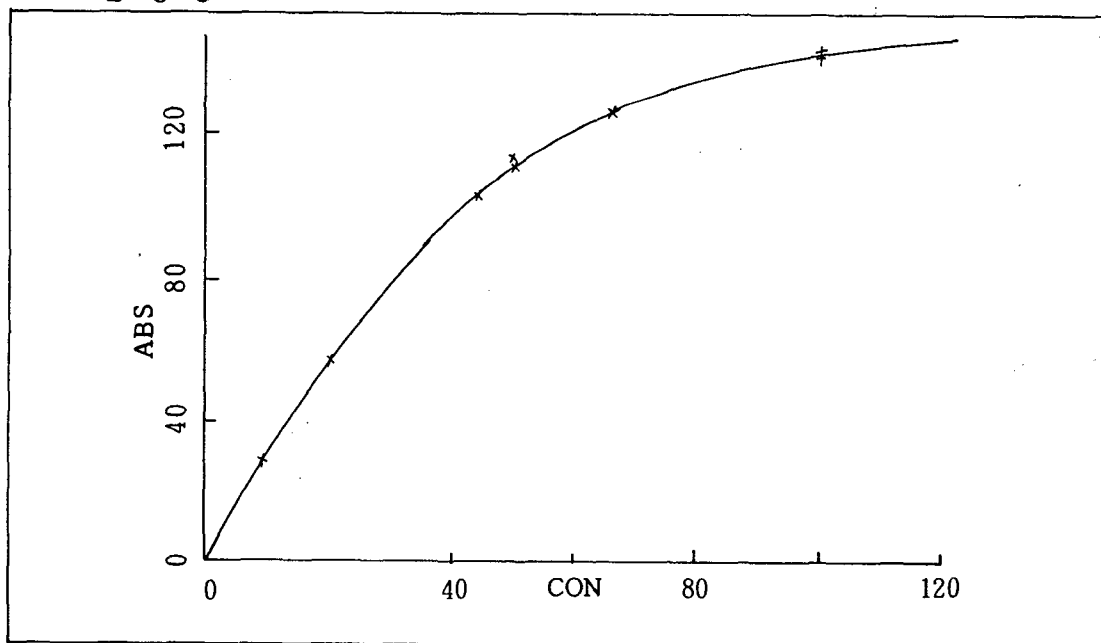


Figure 4.1 The Horizontal Deviation of Residual by Algorithm 2.

where C is a known concentration and C' is the estimated concentration produced by the algorithm.

For tube 401, for Fe, the absorbance data of the verification sample A are,

$$A = (28, 105, 129)$$

and the known concentrations are,

$$C = (20, 50, 100)$$

Then we find K by algorithm 2,

$$K = (-0.3211, 0.00602, 0.00159)$$

We can compute the estimated concentration C' from equation 3.4 with (28, 105, 129) in place of A.

That is

$$C' = (9.315, 44.004, 67.040).$$

Suppose $E = (e_1, e_2, e_3)$. The residual E is

$$E = C - C' = (0.685, -4.004, 2.96)$$

and the sum of squares SS is defined as the sum of the squares of these residuals, i.e.,

$$SS = \sum_{i=1}^3 e_i^2 = 0.685^2 + 4.004^2 + 2.96^2 = 25.263. \quad (4.1)$$

Then the mean sum of squares MSS is defined as,

$$MSS = \frac{SS}{3}, \quad (4.2)$$

giving

$$MSS = 25.263 / 3 = 8.42.$$

Residuals at each point are shown in Figure 4.1 where the residual is indicated by the horizontal line between symbol 'X' and 'o'. Estimated concentration C' is indicated by the symbol 'X' and concentration is indicated by symbol 'o'.

When we are using algorithm 4 with the same data, then

$$K = (79.237, -1.775, 0.013)$$

This curve is shown in Figure 4.2. Horizontal deviation is the distance between symbol 'X' and 'o', which is shown as a horizontal line. The estimated concentrations are

$$C' = (39.75, 36.57, 67.184).$$

As we see, the estimated concentration at absorbance 28 is larger than at absorbance 105, because the curve is bent downward at the lower concentration with this algorithm. Therefore, the residuals are larger. Also, algorithm 2 is considerably better than algorithm 4 for this set of data.

Accordingly,

$$E = (-29.75, 3.43, 2.816),$$

$$SS = (-29.75)^2 + 3.43^2 + 2.816^2 = 735.257,$$

and

$$MSS = 735.257/3 = 245.086.$$

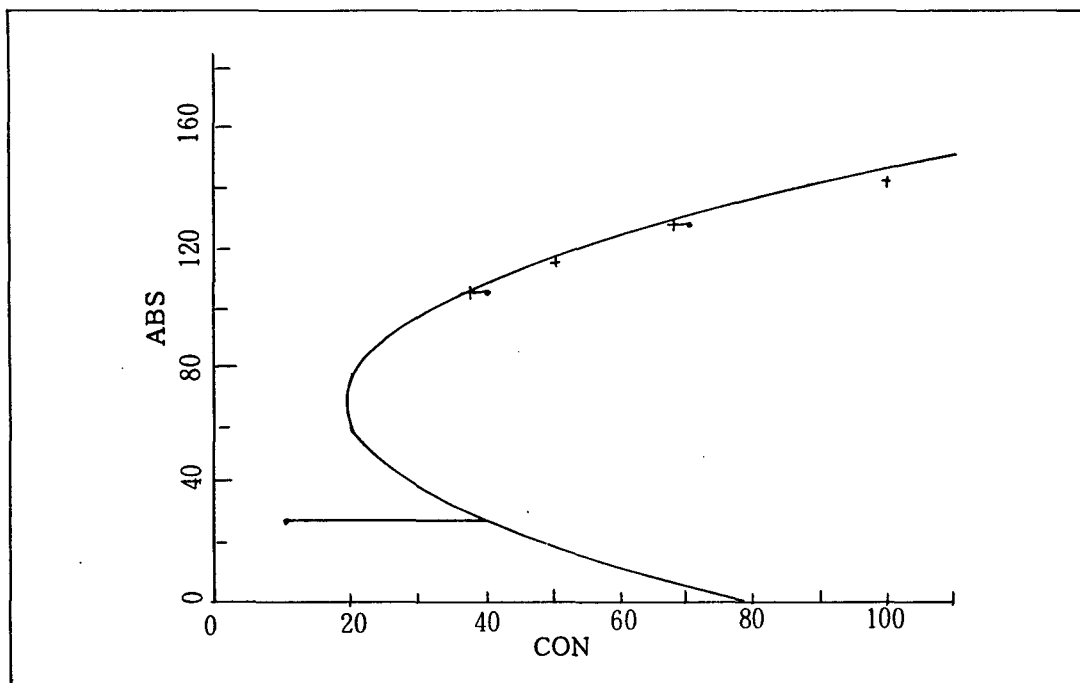


Fig 4.2 The Horizontal Deviation of Residual Algorithm 4.

For these data with these two algorithms,

MSS by algorithm 2 = 8.42,

MSS by algorithm 4 = 245.086,

and algorithm 2 is better than algorithm 4.

Estimated concentrations C' by 6 algorithms for Fe are summarized in Table 4. Known concentrations C , shown in the first column, were used 4 times 105%, 40% and 70% of full scale. After the calibration curve was established, each of the 10%, 40%, and 70% verification sample was analyzed twice. For tube 401 this calibration was done twice, so that 12 verification data are gathered in Table 4. Notice the differences between the estimated concentrations in column 2 and 3 in Table 4. The estimated concentrations by PWMA and by algorithm 1 are very close. Since algorithm PWMA and algorithm 1 are exactly the same as noted earlier; the PWMA concentration values are those printed out by the microprocessor, while the algorithm values are computed from the curve established from the rounded absorbance values. Since algorithms 2 through 5 must be employed with the rounded absorbance values, rather than the single precision values available to the microprocessor the rank comparisons will be restricted to only algorithms 1 through 5. The mean square residuals will be computed for the PWMA, but they will not be used in comparison with the others; cases in which

the PWMA actually gives the smallest mean square will be denoted by an asterisk(*). We might expect that algorithm PWMA and algorithm 1 should perform very similarly. In the last column, .00 means we can not obtain acceptable estimated concentrations with this algorithm. If $K_2^2 - 4K_3(K_1 - A)$ was negative, the estimated concentration was forced to be .00 for all verification samples with this calibration. The estimated concentration in the first three rows of algorithm 2 and 4 are the same as our previous example.

From the data in Table 4, we calculated the sum of squares and the mean sum of squares, which are displayed in table 5. It says that the sum of squares by PWMA is 100, and the mean sum of squares is 8.33, so the rank of the mean sum of squares is labeled with * as it is the smallest. If we don't count the PWMA in comparison, algorithm 3 is the best. It has the smallest mean sum of squares, 9.09; thus algorithm 3 suggested by Limbeck is the best for the tube PPM401 for element Fe. The number of acceptable data points for each algorithm is given in the row labeled N; if the test plan was followed exactly, and the algorithm performed satisfactorily for the calibration samples, N would equal 12 for each case. If the algorithm performed totally unsatisfactorily, its N value is 0 and its mean sum of squares was set equal to 888 (see algorithm 5 in Table 5).

The sum of squares, the mean sum of squares, and the rank of the algorithm for tube 401 for 9 elements are summarized in Table 6.

Table 6 shows the best algorithm for each element. Algorithm 3 is the best algorithm for element Fe. Algorithm 1 has the smallest mean sum of squares for Ag, and so on. As can be seen, the

best algorithm differs according to the element. For tube 401, no single algorithm is the best for all the elements.

Table 4. Estimated Concentration by 6 Algorithms

Standard	Algorithm					
	PWMA	1	2	3	4	5
10.00	9.00	8.87	9.31	13.44	39.75	.00
40.00	44.00	44.79	44.00	45.66	36.57	.00
70.00	70.00	70.23	67.04	67.96	67.18	.00
10.00	13.00	13.21	13.57	17.64	29.09	.00
40.00	42.00	42.32	41.36	43.08	32.93	.00
70.00	70.00	70.23	67.04	67.96	67.18	.00
10.00	8.00	8.00	8.34	17.04	53.22	.00
40.00	43.00	43.05	42.64	60.82	36.86	.00
70.00	74.00	75.32	74.43	88.77	83.90	.00
10.00	6.00	6.07	6.39	13.58	66.29	.00
40.00	36.00	35.69	35.19	52.89	26.16	.00
70.00	73.00	73.52	72.64	87.41	81.58	.00

Table 5. Algorithm Comparison for Fe

	Algorithm					
	PWMA	1	2	3	4	5
SS (Fe)	100.00	128.08	121.12	109.09	3119.08	.00
N	12.00	12.00	12.00	12.00	12.00	.00
MSS	8.33	10.67	10.09	9.09	259.92	888.00
RANK	*	3	2	1	4	5

In Chapter 2 we mentioned that Langley used 6 tubes, Myrtle Beach used 5 tubes, Pensacola used 11 tubes, and Elmendorf used 6 tubes. Due to missing data, we excluded several tubes in our analyses. For example, tube PPM406 doesn't have verification sample 70 data. For similar reasons we discard 1 tube from Langley, 1 tube from Myrtle Beach, 2 tubes from Pensacola, leaving 24 tubes in all. The summary of 24 tubes for each element is shown in Table 7 through Table 15. We may say

Table 6. Summary of the Ranks for Table 401

	Algorithm					
	PWMA	1	2	3	4	5
SS (Fe)	100.00	128.03	121.08	109.09	3119.08	.00
n	12.00	12.00	12.00	12.00	12.00	.00
MSS	8.33	10.67	10.09	9.09	259.92	888.00
RANK	*	3	2	1	4	5
SS (Ag)	2.00	.85	1.70	1.48	12.34	.67
n	12.00	12.00	12.00	12.00	12.00	6.00
MSS	.17	.07	.14	.12	1.03	.11
RANK		1	4	3	5	2
SS (Al)	268.00	317.88	300.21	297.57	429.29	.00
n	12.00	12.00	12.00	12.00	12.00	.00
MSS	22.33	26.49	25.02	24.80	35.77	888.00
RANK	*	3	2	1	4	5
SS (Cr)	16.00	17.29	17.16	17.10	39.32	.00
n	12.00	12.00	12.00	12.00	12.00	.00
MSS	1.33	1.44	1.43	1.42	3.28	888.00
RANK	*	3	2	1	4	5
SS (Cu)	106.00	102.05	100.06	99.74	100.09	107.97
n	12.00	12.00	12.00	12.00	12.00	12.00
MSS	8.83	8.50	8.34	8.31	8.34	9.00
RANK		4	2	1	3	5
SS (Mg)	91.00	170.50	156.21	148.12	179.10	.00
n	12.00	12.00	12.00	12.00	12.00	.00
MSS	7.58	14.21	13.02	12.34	14.92	888.00
RANK	*	3	2	1	4	5
SS (Ni)	38.00	34.87	26.02	31.70	192.41	.00
n	12.00	12.00	12.00	12.00	12.00	.00
MSS	3.17	2.91	2.17	2.64	16.03	888.00
RANK		3	1	2	4	5
SS (Si)	162.00	149.09	141.29	166.29	171.89	103.04
n	12.00	12.00	12.00	12.00	12.00	6.00
MSS	13.50	12.42	11.77	13.86	14.32	17.17
RANK		2	1	3	4	5
SS (Ti)	135.00	142.77	364.12	141.42	134.41	141.47
n	12.00	12.00	12.00	12.00	12.00	12.00
MSS	11.25	11.90	30.34	11.79	11.20	11.79
RANK		4	5	2	1	3

Table 7. Ranks of 24 Tubes for Fe

Algo.	rank					
	*	1	2	3	4	5
PWMA	10					
1		7	1	11	5	0
2		7	8	3	0	5
3		5	12	6	1	0
4		1	0	0	12	11
5		4	3	3	6	8

Table 8. Ranks of 24 Tubes for Ag

Algo.	rank					
	*	1	2	3	4	5
PWMA	6					
1		7	3	4	8	2
2		7	8	5	2	2
3		0	7	11	6	0
4		1	3	1	5	13
5		9	3	3	3	6

Table 9. Ranks of 24 Tubes for Al

Algo.	rank					
	*	1	2	3	4	5
PWMA	12					
1		2	8	6	4	4
2		10	4	7	3	0
3		6	8	9	1	0
4		3	1	1	10	9
5		3	3	1	6	11

Table 10. Ranks of 24 Tubes for Cr

Algo.	rank					
	*	1	2	3	4	5
PWMA	9					
1		9	2	7	5	1
2		4	6	10	2	2
3		3	15	4	2	0
4		0	0	2	11	11
5		8	1	0	4	10

Table 11. Ranks of 24 Tubes for Cu

Algo.	rank					
	*	1	2	3	4	5
PWMA	15					
1		12	1	1	9	1
2		4	8	5	6	1
3		1	7	9	0	2
4		2	2	3	4	13
5		5	6	1	5	7

Table 12. Ranks of 24 Tubes for Mg

Algo.	rank					
	*	1	2	3	4	5
PWMA	12					
1		12	5	6	0	1
2		4	7	11	2	0
3		6	9	4	5	0
4		0	2	3	14	5
5		2	1	0	3	18

Table 13. Ranks of 24 Tubes for Ni

Algo.	rank					
	*	1	2	3	4	5
PWMA	7					
1		13	2	8	1	0
2		4	2	2	5	11
3		4	18	2	0	0
4		1	1	3	16	3
5		2	1	9	2	10

Table 14. Ranks of 24 Tubes for Si

Algo.	rank					
	*	1	2	3	4	5
PWMA	11					
1		3	7	8	3	2
2		8	7	2	3	4
3		7	2	3	11	1
4		1	7	3	4	3
5		4	1	2	3	13

Table 15. Ranks of 24 Tubes for Ti

Algo.	rank					
	*	1	2	3	4	5
PWMA	11					
1		5	9	3	5	2
2		7	3	2	8	4
3		4	1	6	7	6
4		5	5	11	2	1
5		3	5	3	2	11

Table 16. The Best Algorithm for Each Element

	Element								
	Fe	Ag	Al	Cr	Cu	Mg	Ni	Si	Ti
First	1	2	2	1	1	1	1	2	2
Second	3	1	3	3	2	3	3	3	1,4

that algorithms which have the most rank 1 or rank 2 scores but the least rank 4 or rank 5 scores are good ones, and algorithms which have the least rank 1 or rank 2 scores but the most rank 4 or rank 5 scores are not good ones. The entries in these tables are the counts of the ranks. For example, in table 7 algorithm 1 for Fe has 7 rank 1's, 1 rank 2, 11 rank 3's, 5 rank 4's, and 0 rank 5 out of 24. For Fe, the PWMA internal algorithm, with rounded concentrations, had the smallest mean sum of squares 10 time out of 24. In Table 7, we conclude that algorithm 1 is better than algorithms 2, 3, 4, and 5. Algorithm 2 has 7 rank 1's but also 5 rank 5's. Therefore, algorithm 2 is not as good as algorithm 1. If algorithm 2 did not have those undesirable cases with denominator zero, then it would be the best. Also algorithm 4 has 11 rank 5's because it has a lot of deviations for two extreme cases as we saw in the previous Chapter. Algorithm 5 is almost the same as algorithm 4. Algorithm 3, with 5 rank 1's and 12 rank 2's, is acceptable but not as good as algorithm 1. We conclude that algorithm 1 is the best for element Fe.

For element Ag, even though algorithm 5 has 9 rank 1's, it also has 6 rank 5's. Therefore, we can not select algorithm 5 as the best one. Algorithm 2, or 1 are acceptable for element Ag.

For Al, algorithm 2 dominates the other algorithms, since it has 10 rank 1's. Algorithm 3 is the second algorithm. Algorithm 3 could be use able even though it has fewer rank 1 scores.

For Cr, algorithm 4 is not acceptable, for it has 22 tubes rank 4's or 5's. Algorithm 1 is the best for element Cr.

For Cu, Mg, and Ni, algorithm 1 dominates the others. For Si, algorithm 2 or 3 are the best. For Ti, algorithm 2 is good. Algorithm 1 and 4 are acceptable too.

Table 16 summarizes the results of the previous table by listing the best and alternate algorithm for each element. We can say that algorithm 1 provides the best fir for elements Fe, Cr, Cu, Mg, and Ni, and algorithm 2 provides the best fit for elements Ag, Al, Si, and Ti.

5. Conclusions and Recommendations

There is no single best algorithm for all nine elements, since the degree of curvature is different

according to the element. The PWMA didn't consider different algorithms for different elements. The computation in the PWMA used only by one algorithm for all nine elements. If we employ different algorithms for different elements in an analyzer, it will be better because each element has different characteristics. We recommend that one may use algorithm 1 for elements Fe, Cr, Cu, Mg, and Ni and algorithm 2 for elements Ag, Al, Si, and Ti to obtain better estimation in computing concentration. The microprocessor can easily check for the existence of an asymptote. If one occurs, use algorithm 1.

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