

Correction for Instrumental Drift in Flame Photometry

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The application of the principles of experimental design to correct for drift in instrumental measurements, specifically in flame photometry, is described. Based on the procedure proposed by Youden, samples and reference standards may be measured in combinations of pairs in a manner such that errors caused by drift can be minimized and the actual amount of drift can be determined. Where the drift is dependent on the magnitude of the quantity measured, grouping by magnitude prior to final measurement is necessary. Application of the procedure to flame photometric determination of alkali elements, under conditions of severe drift, resulted in improving coefficients of variation from an original range of 2.0 to 3.5 to a range of 0.6 to 1.2.

1. Introduction

In any series of measurements, drift in the response of the measuring instrument may introduce appreciable errors. Although the errors may be reduced by improved adjustment or design of the instrument, some drift may be inevitable.

An unusual example of drift was encountered in measurements with a flame photometer. Replacement of the detector, a photomultiplier tube, was later found to overcome most of the drift; however, the possibility of compensating for drift by appropriate design of the experiment in this and similar cases was explored.

Youden¹ proposed a design and statistical treatment of data using a method of incomplete blocks to minimize errors caused by instrumental drift, and at the same time, to measure the magnitude of this effect. The applicability of his procedure to this drift problem was examined.

2. Experimental Procedures

During the development of a method for determining the alkali metals with a Beckman model DU² flame photometer with photomultiplier attachment, it was noted that the readings of the instrument were shifting with time. The determinations were being made on a long series of solutions, so that a shift in readings would seriously affect the results.

In Youden's method to compensate for drift,¹ the objects to be measured (here the sample and standard solutions) are arranged in an appropriate sequence. Specifically, the objects are grouped in pairs, so that each object appears in a pair with every other object. For example, 5 objects are grouped in 10 pairs, as shown in table 1, the sequence of the pairs being immaterial. The objects are then measured on the instrument in a manner such that the time between measurements on the objects in a pair is small in comparison to the time between pairs.

The rigorous method of Youden for computing the drift involves long arithmetic calculations. A simplified, yet accurate, alternate method, suggested later by Youden, will be described here. No difference was found in the values computed by the

TABLE 1. *Design of experiment*

Pair.....	1	2	3	4	5
Object.....	AB	DE	BC	EA	CD
Pair.....	6	7	8	9	10
Object.....	EB	AC	BD	CE	DA

two methods, within the accuracy of the data. The method involves, first, the determination of calculated, or corrected, values for the measurements on the objects, A, B, C, etc., and second, the computation of drift using the observed values and calculated values of the objects.

A calculated value for each object is determined as is shown by the steps in table 2. In the table, A_1 represents the measured value of object A in pair 1, C_7 the measured value of object C in pair 7, etc. The differences between A and the object with which it appears are summed, $+A$ and $-A$ are added to the left side of the equation, the equation is divided by five, and everything but A is transposed to the right side. Since the expression $(A+B_1+C_7+D_{10}+E_4)/5$ will be approximately equal to the average of the 20 measurements, (that is, four each on A, B, C, D, and E, divided by 20), the last equation is obtained. A similar computation is performed to obtain the calculated values for the other objects, B, C, D, and E.

In addition to correction for drift, the method also provides a measure of the drift. Table 3 shows the method of computing the average drift for each pair. The differences between the observed values and the calculated values of the two objects in the pair are averaged, and the result represents the average drift for the pair. The drift for the pairs is then plotted as the deviation from the mean drift. It should be noted that the validity of the statistical method rests on the assumptions that the objects do not change in the course of the measurements and that the drift is independent of the magnitude of the measurements made.

TABLE 2. *Calculated value for object A*

$$\begin{aligned} A_1 - B_1 &= X_1 \\ A_7 - C_7 &= X_2 \\ A_{10} - D_{10} &= X_3 \\ A_4 - E_4 &= X_4 \end{aligned}$$

$$4A - (B_1 + C_7 + D_{10} + E_4) = \sum_1^4 X_i$$

$$A = \text{Average of all measurements} + \frac{\sum_1^4 X_i}{5}$$

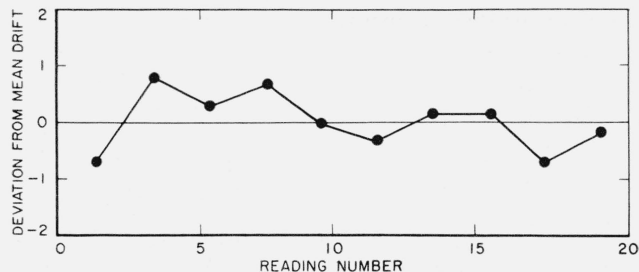
¹ W. J. Youden, *Science* **120**, No. 3121, 627 (1954).

² H. H. Carey and A. O. Beckman, *J. Opt. Soc. Am.* **31**, 682 (1941).

TABLE 3. *Computation of drift in pair 1*

Value observed	Value calculated	Difference
A ₁ B ₁	A B	X Y
Average drift = $\frac{X+Y}{2}$		

Figure 1 shows an instrumental-drift curve obtained by this method for a series of readings on sodium. This is a normal type of curve with narrow limits. The abscissa is the number rather than the time of the reading, since the only time requirement is that the 2 objects in any 1 pair are immediately consecutive. Thus, for example, the third point on the graph is plotted midway between readings 5 and 6, since these 2 readings were used to compute the point. The ordinate is the deviation from mean drift in terms of instrument readings and in this particular case one instrument unit represents approximately 2 percent of the amount of sodium present.

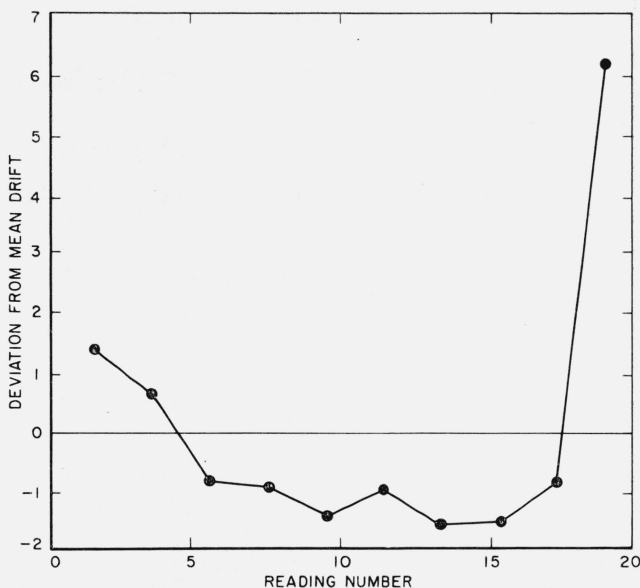
FIGURE 1. *Instrument drift during a series of measurements on sodium.*

One ordinate unit equals approximately 2 percent of the amount of sodium present.

The value of this method became immediately evident upon examination of the curve shown in figure 2. This represents a series of readings on potassium in which, unexpectedly, the range of the instrument had to be changed from low to high during the measurement of the series. The instrument response was evidently slow.

The original method employed in these determinations consisted of making measurements on a series of unknown solutions with standard solutions measured periodically during the series. A large change in readings on an object during any series of readings with other objects is, of course, evident to the observer. Instead of having to discard data and begin over, as was done in the original method, the information obtained when using a drift correction is perfectly valid. Similarly, any small instrumental drift, unnoticed by the observer, is corrected for in the calculations. Another advantage of the method is that the experimenter may interrupt a series of readings at any point between pairs, and upon return may resume at the point of interruption, rather than start over again.

The coefficients of variation obtained when using

FIGURE 2. *Instrument drift during a series of measurements on potassium.*

The range of the instrument was changed between readings 18 and 19.

this refinement show a marked improvement over those obtained with the previously mentioned original method, in which no instrumental drift correction was applied. Coefficients (obtained from 10 determinations on each of 2 samples of lithium solutions and 2 of potassium) which were in the range of 2.0 to 3.5 were improved to fall in a range of 0.6 to 1.2 by the new method.

In an effort to determine the nature and cause of the drift, the statistical method of incomplete blocks was again employed. A sodium determination was made on 10 solutions of widely different concentrations under standard-operating conditions in a statistically designed sequence during a 2¼ hr time interval. From the observed readings, the drift was computed and was plotted as a function of time. The curve obtained (fig. 3) indicated an initially rapid but continually decreasing drift with an irregular drift superimposed on it. Because the "reality" of the superimposed drift was doubted, additional measurements were made on a solution containing 3 ppm of lithium and on a solution containing 20 ppm of potassium. Experiment had shown that determinations of these elements are less subject to random fluctuations than those for sodium and they are less liable to error because of contamination by contact with dust in the air. The runs in each case were made on a single solution and the drift was computed as the deviation of the observed readings from their mean. With both the potassium and the lithium solutions only the initially rapid but continually decreasing drift was obtained, and none of the superimposed, irregular drift was present. This would indicate that the drift may be dependent on the magnitude of the measurement being made, contrary to one of the assumptions of the statistical method.

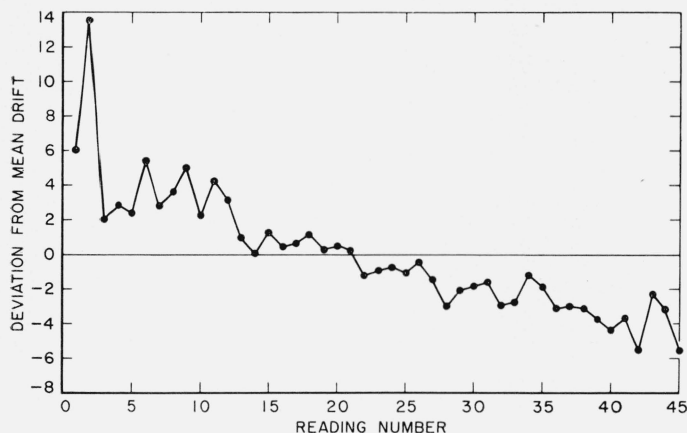


FIGURE 3. Instrument drift obtained when measuring a series of 10 sodium solutions having widely different concentrations.

To test the effect of a wide range of concentrations on the drift, runs were made on 2 lithium solutions, 1 twice the concentration of the other. The drift in each case was computed as the difference between the observed readings and their mean and was plotted as a function of time as shown in figure 4. The ordinates of the two curves are in a constant ratio at all points along the abscissa, within the accuracy of the readings, showing the drift is dependent upon the intensity of the light being measured.

The variation of the drift with the incident light intensity explains the irregular character of the drift obtained previously (fig. 3) on the group of sodium solutions having different sodium concentrations. The larger deviations were caused by the large drift of the readings for the highly concentrated solutions and the points closer to the average drift curve by the small drift for the less concentrated solutions. The particular sequence of solutions of high and low concentrations resulted in the irregular drift.

The cause of the drift was finally ascertained to be due to fatigue of the photomultiplier tube, a phenomenon usually associated with these tubes³ but only at much higher phototube current levels than those encountered here. This effect may be in either a positive or negative direction, although it is most commonly negative.

The phenomenon of fatigue is not a strictly reversible process, that is, the recovery curve is much less steep than the fatigue curve. However, the statistical method described here is based in part on the assumption that the drift is independent of the measurements made; accordingly, a modification was made in the procedure to ensure accurate results. When a particular element in a group of unknown solutions is to be determined, a quick initial run is made without the use of any statistical sequence or repetition of readings. This gives a good approximation of the concentrations of all the unknown solutions. The solutions are then grouped according to these preliminary results so that the concen-

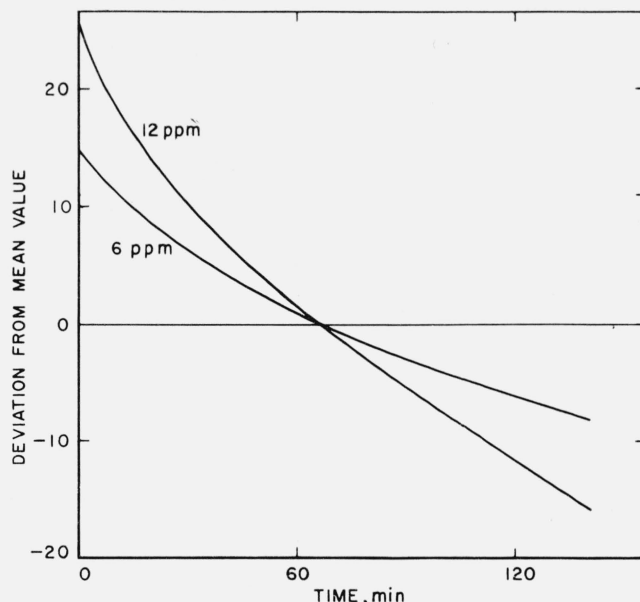


FIGURE 4. Instrumental-drift curves of 6 ppm and 12 ppm lithium solutions.

Instrument sensitivity is approximately 0.04 ppm per unit.

trations of all the solutions within one group are very near one another. Standard solutions for each group are selected to approximate the concentrations of the group. The group of samples and standard solutions is then measured using the method of incomplete blocks, the normal drift curves are computed, and the results are corrected for drift. There is no irregular trend of the curves, since all the readings in a group are close together. This grouping is also advantageous from the standpoint that smaller errors in interpolation are introduced when readings on standards and unknowns are close together.

3. Conclusion

This paper has discussed a problem of instrumental drift in the laboratory to which a statistical solution involving incomplete blocks has been applied. While the magnitude of the drift encountered was not characteristic of the instrument, it served as a good example of a complicated drift problem. The statistical method improved the precision and provided a measure of the drift, except when quantities of widely different magnitudes were intercompared. Investigation showed that the drift resulted from fatigue of the photoelectric tube involved in the measurement, and that the drift was dependent upon the intensity of the light to which the tube was exposed. When drift is dependent on the magnitude of the measurement, it appears necessary to group the quantities according to order of magnitude before final measurements are made and the drift correction is applied.

Suggestions received from W. J. Youden during the course of this work are gratefully acknowledged.

WASHINGTON, August 15, 1958.

³ R. W. Engstrom, J. Opt. Soc. Am. **37**, 420 (1947).