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ATOMIC ABSORPTION AS AN INDEX OF THE SILVER CONCENTRATION IN PRECIPITATION

Silver Iodide Plume Studies, Part 1

by

Joel E. Fletcher and H. C. Millar

Wasatch Weather Modification Project
Under Contract No. 14-06-D-6003
U. S. Department of the Interior
U. S. Bureau of Reclamation

Utah Water Research Laboratory
College of Engineering
Utah State University
Logan, Utah

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PR-WG30-4

Preface

The mention of a trade name in this report does not constitute an endorsement either by the Bureau of Reclamation or by Utah State University.

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Abstract

The Perkin Elmer Model 303, equipped with the DCR-1, digital concentration readout, was evaluated as to its ability to provide an index of silver concentration in water solutions, without concentrating in any manner. The procedures, principal settings, and adjustments which must be observed are described.

This instrument can detect the difference between concentrations of 10^{-15} and 10^{-12} gm/ml. However, as the concentration of silver decreases the experimental error increases to a point at which the error becomes greater than the differences in readout due to differences in silver concentration.

Introduction

As plans developed for studying the Atmospheric Water Resources of the Wasatch Mountains of Utah, the need for some method to trace the silver iodide plume from the cloud seeding became apparent. Furthermore, if the method for tracing the plume was sufficiently fast and reliable to show the location of the plume during each seeding period, the whole experiment could be executed on a more controlled basis.

Investigations into methods for tracing this plume were to be multibranched and cover such directions as nuclei sampling, both on the ground and in the air and chemical analyses of the precipitation. The chemical approaches were to be further divided into subbranches to investigate analyses for both silver and iodide.

Isono, Komabayasi, Ono, and Ikebe (1966) using randomized seeding experiments, found that in the area where the effect of seeding was highly significant, the concentration of seeded silver iodide and precipitation collected in the target area was high in areas where precipitation amount was large. Secondly, the area of maximum silver iodide concentration and precipitation appeared in areas at some distance from the seeding site, indicating that the silver iodide concentration was not the result of capture of silver iodide particles by falling drops. Last, the information obtained suggested that a continued supply of ice nuclei is necessary for inducing a significant precipitation increase.

Studies in Australia by Warburton (1963, 1965) and Warburton and Maher (1965) showed that concentrations of silver in precipitation were likely to be smaller than 10^{-11} gram of silver per milliliter of precipitation but could be as high as 10^{-8} gram of silver per milliliter under some conditions. Lack of methods for measuring the smaller concentrations found in samples of precipitation from unseeded conditions leaves these levels unknown. Furthermore, it was observed by Warburton and Maher (1965) that losses to container walls could be as high as 35% in 7 days from solutions with silver concentrations in the 10^{-11} gm/ml range.

The present series of studies was directed toward obtaining a rapid, sensitive method for measuring silver which could be used either with or without enhancement of the concentrations before analysis. Even though the investigators felt that such enhancement was necessary, they felt the advantages of a direct method justified some attention. Such reports as Palacios (1963), Koenig (1959), and McHugh and Sheffield (1965) suggested leads for a multipronged investigation of the direct methods. These investigations should lead to a series of reports in general areas as follows: atomic absorption for silver; adsorption of silver on container walls; a filter paper test for silver; colorimetric measurement of silver; measurement of iodides; and others. This paper is the first in the series, and deals with the measurement of silver in water solutions using the Perkin-Elmer Model 303 Atomic Absorption Spectrometer, equipped with the DCR-1, Digital Concentration Readout.

Instrumentation

Belcher, Dagnall, and West (1964) Huffman, Mensik, and Roder (1966); Kahn and Slavin (1963); and Keats (1965) describe the theory and use of atomic absorption instruments for analyses of metal ions and they include the use of a digital concentration readout.

The particular model of Perkin-Elmer Model 303 Atomic Absorption Spectrometer used in this investigation is equipped with a "meter response switch" in place of the older phase control switch (see Fig. 2). A block diagram of the system is given in Fig. 1, and the two control panels are shown in Figs. 2 and 3.

For maximum sensitivity the dials in Fig. 2 are set as follows:

Source - 12 ma but should be checked with each hollow cathode tube for maximum sensitivity

Scale - 10

Meter Response - 4

Zero Control - to "Null Meter" 0

Gain - adjust to Energy Meter reading 6.2 to 6.4*

Filter Switch - out

Power Switch - on

Slit - 4

Wave Length - 3281 **

Absorption - 00.0

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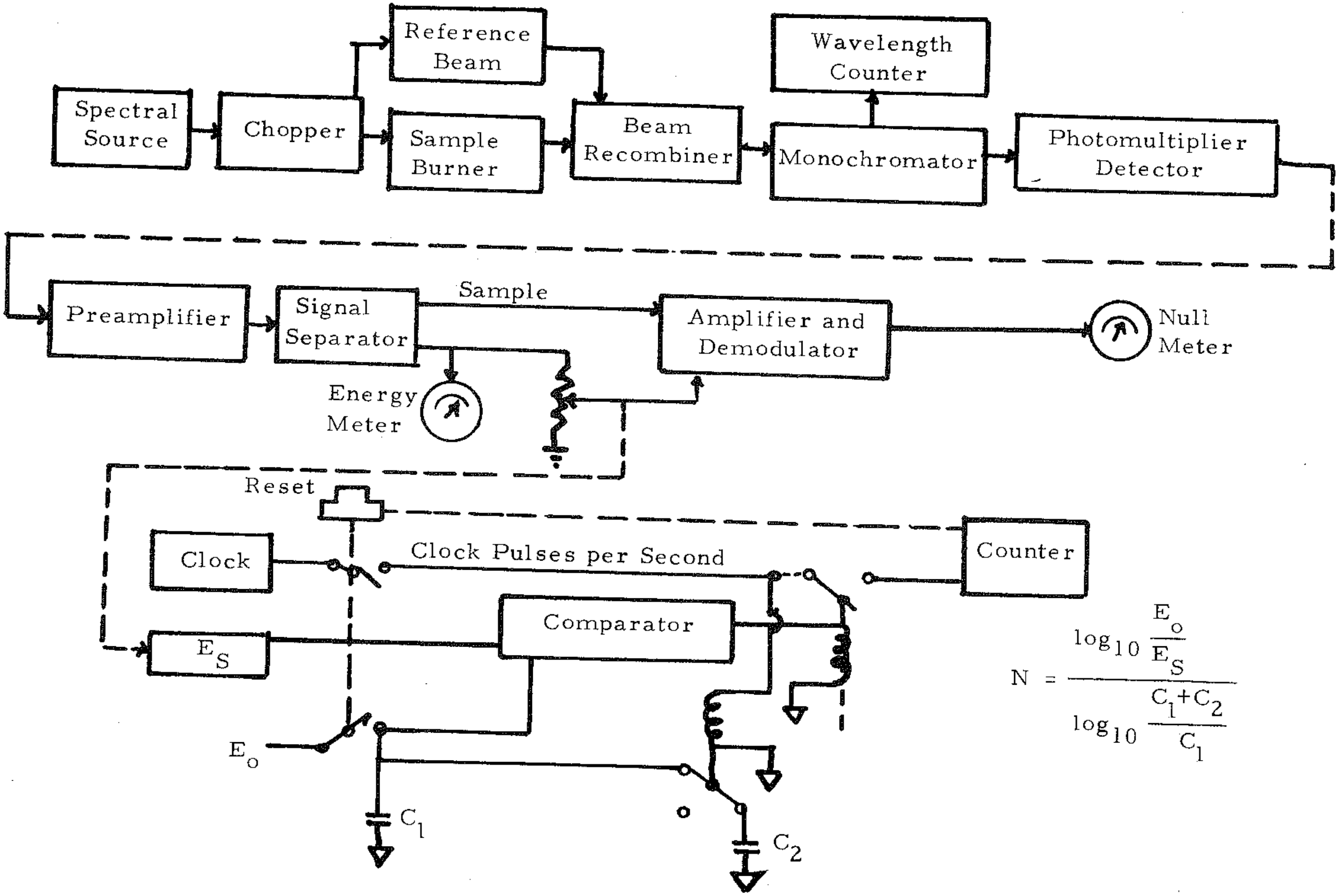
*The more precisely the energy can be maintained at a single value, the more precise the readings are at low silver levels.

**Set wavelength precisely by adjusting to maximum deflection to the right on Energy Meter.



$$N = \frac{\log_{10} \frac{E_o}{E_S}}{\log_{10} \frac{C_1+C_2}{C_1}}$$

Fig. 1. Block Diagram of Atomic Absorption Instrument, Perkin-Elmer 303 and Digital Readout DCR-1.

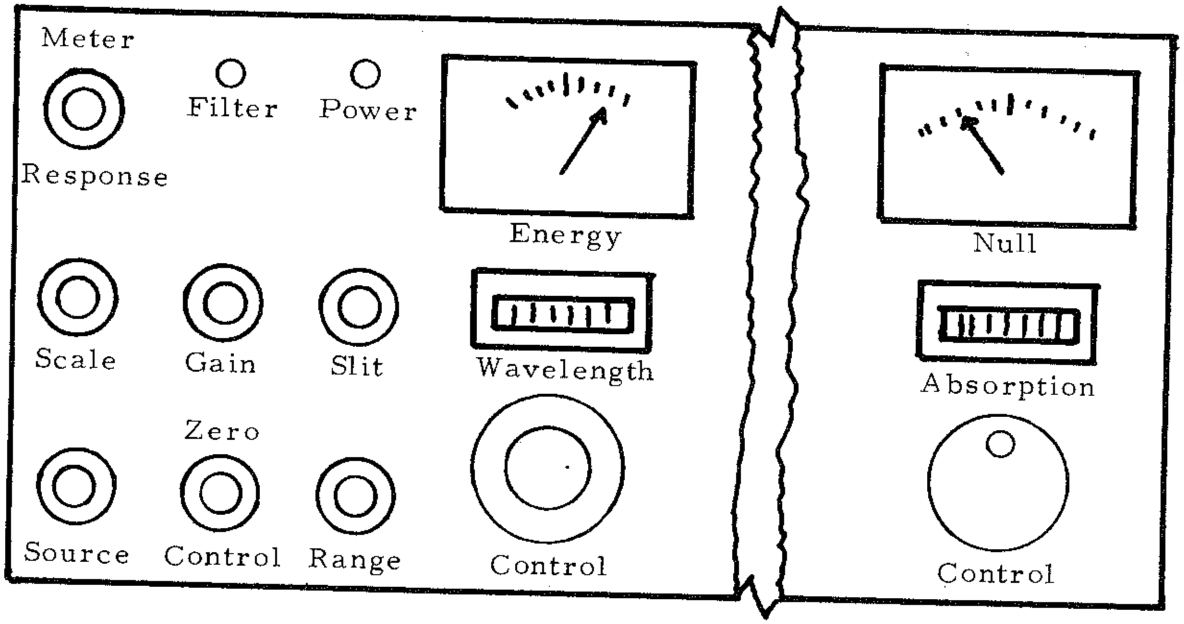


Fig. 2. Control panel of Atomic Absorption Spectrometer, Perkin-Elmer Model 303.

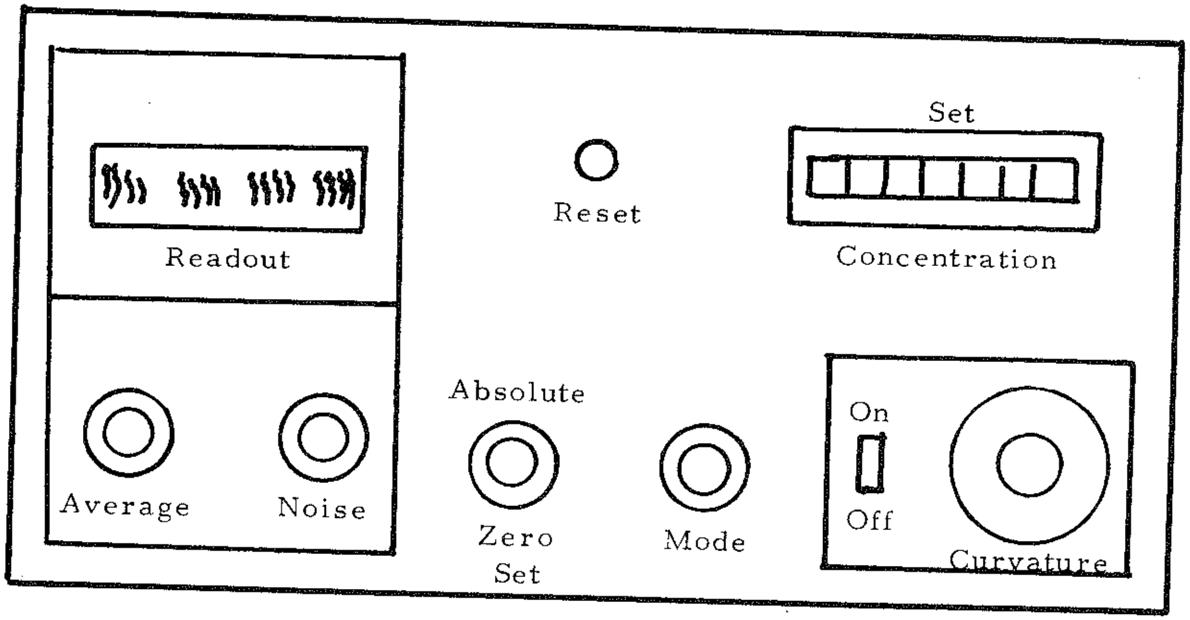


Fig. 3. Panel of Digital Concentration Readout, DCR-1.

The dials of the panel in Fig. 3 are also set as follows:

Average - 8X

Noise - 2

Absolute Zero - set for solvent to read approximately 40

Mode - concentration

Curvature Switch - off

Curvature Dial - 0

Set Concentration - 9999.

Silver Standards

The standard silver stock solutions were made by dissolving either of two different silver salts in distilled water. The first solution was made by dissolving 1.5766 grams of silver nitrate in distilled water and diluting to one liter to give a silver concentration of 10^{-3} gram of silver per milliliter of solution. The second solution was made by dissolving 1.4511 grams of 99.6% silver sulfate in distilled water and diluting to one liter for a concentration of 10^{-3} gram of silver per milliliter of solution. Silver sulfate is easier to weigh since it is generally in the form of a powder but the sulfate is very slow to go into solution.

All other solution concentrations were made by dilution of one of these two solutions. Each solution was made up to a volume of one liter in a 32 ounce brown polyethylene bottle. Atomic absorption was measured on fresh solutions* except for a cross-reference sample which was 10-months old and had attained stability with respect to the adsorption of silver on its container.

Calibration of the Instrument

Fresh samples of each of the above standard silver solutions were aspirated into the flame of Perkin-Elmer 303 Atomic Absorption Spectrometer and concentration readings were taken on the DCR-1, Digital Concentration Readout. Whenever the "Average Switch" is set on 8X, the DCR-1 computes the average of eight different readings of atomic absorption before showing a fixed number on the display. In making the calibration a minimum of 10 such displays were read and recorded. It is important that at least one full cycle in the DCR-1 readings be taken in a group. A cycle is not always the same number of readings but is the readings between the first readings and the place where they again repeat. (Note the irregular cycles in Figs. A1 and A2.)

The DCR-1 is incapable of handling negative readings. Therefore the solvent (water) atomic absorption must be set on a positive value, usually above 4.0. The solvent readings are taken between each series of sample readings and the mean solvent reading is subtracted from the mean sample reading to obtain the corrected reading for that particular

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*Always less than 8-hours old.

sample. Furthermore, the readings on the upper end of the scale were adjusted or standardized with a 10-month old silver solution in a concentration of either 10^{-3} or 10^{-6} gram per milliliter (gm/ml) of solution, depending on the range of concentrations of the samples to be analyzed. (See Appendix.) In other words, for samples in the concentration range between 10^{-3} and 10^{-6} gm/ml, the DCR-1 was set with the 10^{-3} gm/ml solution. For samples with concentrations lower than 10^{-6} gm/ml, the 10^{-6} gm/ml solution was used to set the DCR-1.

The silver solutions used for reference settings were aged for 10 months to reduce the changes in their concentration with time due to adsorption on the container walls. The two reference readings--distilled water and the 10-month old standard (computed to a reading of 100.0 on the DCR-1 (see Appendix))--serve as standards or reference points at each end of the concentration scale. It is not necessary to know the actual concentration of these references but only that they remain constant.

Reference readings are a means of correcting for any drift error which may occur in the instrument from a variety of causes. For example, at time (a), distilled water is aspirated into the burner, and the "Zero Set" is adjusted to read 4.0 on the DCR-1. An aged silver solution at a concentration of 10^{-6} gm/ml is then aspirated into the burner and read on the DCR-1. Whatever this reading, it is used as a reference reading of 100.0. If at time (b), some period of time after time (a), distilled water and the same silver solution can again be aspirated into the burner, most often the readings on the DCR-1 will not be the same as they were at time (a). Thus, the readings at times (a) and (b) are not comparable except through the reference reading. The procedure is to subtract the water reading, divide by the reference standard reading and multiply by 100. For example suppose at time (a) the mean water reading is 6.0, the 10^{-6} gm/ml reference reading is 154.6 and the sample mean is 100.0. The procedure would be

$$\frac{(100.0 - 6.0)\,100.0}{(154.6 - 6.0)} = \frac{100.0\,(94.0)}{148.6} = 63.2$$

If the reading on water at time (b) is 10.0, on the reference is 148.4, and on the sample is 100.4 then

$$\frac{(97.5 - 10.0)\,100.0}{(148.4 - 10.0)} = 63.2$$

The value of 60.8 at time (a) is directly comparable to 60.9 at time (b) without knowing the actual concentration of the reference solution.

Fig. 4 shows the curve obtained when the mean of more than ten 8X readings adjusted for a reference solution and distilled water are plotted on a log scale against the known concentration of the solution on an arithmetic scale. The curve for the relation between silver concentration and adjusted DCR-1 readings is linear at concentrations greater than 10^{-7} gm/ml and seems to vary with silver concentration throughout its length.

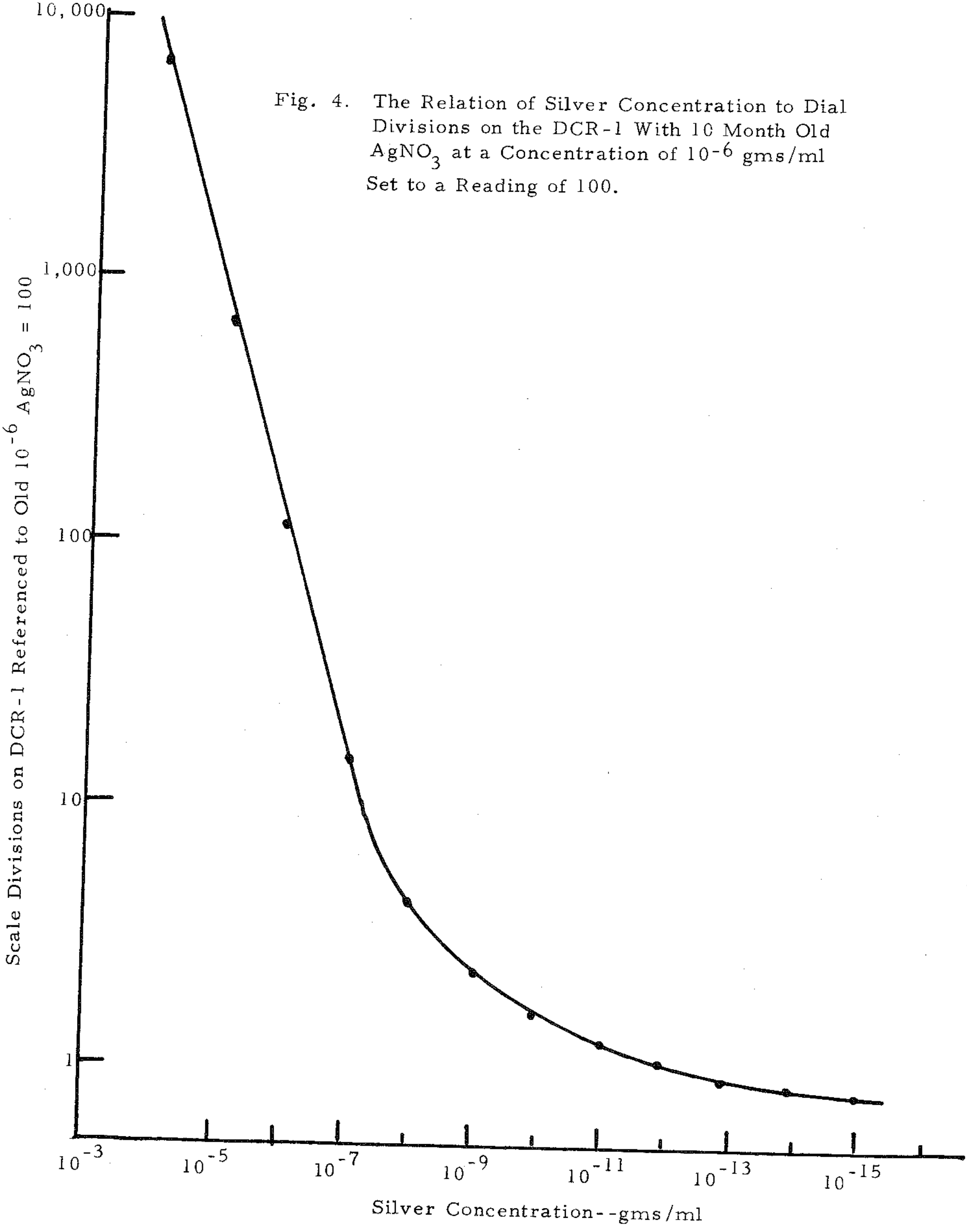

Fig. 4. The Relation of Silver Concentration to Dial Divisions on the DCR-1 With 10 Month Old $AgNO_3$ at a Concentration of 10^{-6} gms/ml Set to a Reading of 100.

The relative reproducibility of these means can be shown by their coefficients of variation or

$$CV = \frac{s_x}{\overline{x}}$$

wherein

s_x = standard deviation = $\left(\frac{\Sigma(x - \overline{x})}{n-1}\right)^{1/2}$

$\overline{x}$ = mean

n = number of observations

CV = coefficient of variation

Values of CV for a variety of solutions whose silver contents were known are tabulated in Table 1. The CV is referenced to the corrected mean reading on the DCR-1.

The differences between the observed corrected means of the measurements on concentrations of 10^{-12} and 10^{-15} gm/ml and between distilled water and a concentration of 10^{-15} gm/ml are statistically significant as shown by Student's (Spiegel, 1961) t test.

10^{-12} vs 10^{-15} $t = 2.15$ (2% probability level)

10^{-15} vs distilled water $t = 3.99$ (near 0.1% probability level)

Observations and Precautions

The Perkin-Elmer 303 Atomic Absorption Spectrometer, equipped with the DCR-1 Digital Concentration Readout appears to have the capability for measuring silver to lower concentrations than the 10^{-8} gm/ml

Table 1. Coefficient of variation of DCR-1 readings on a variety of solutions using Perkin-Elmer 303 Atomic Absorption Spectrometer. Coefficients based on corrected means rather than mean reading directly.

Silver Concentration gm/ml	Coefficient of Variation (fraction)
10^{-5}	0.0065
10^{-6}	0.023
10^{-7}	0.105
10^{-8}	0.31
10^{-9}	0.74
10^{-10}	1.15
10^{-11}	1.32
10^{-12}	1.09
10^{-13}	.94
10^{-14}	1.49
10^{-15}	0.92
Water	0.34

claimed by the manufacturer. If concentrations as small as the lower concentrations found in precipitation under seeded conditions are to be measured, certain precautions must be rigidly adhered to. These precautions are as follows:

1. Extra care must be exercised in peaking the wavelength on top of the cathode transmission (adjust to peak on energy meter).

2. The Energy Meter Reading must be maintained at a constant value by adjusting the gain throughout any series of measurements.

3. A voltage regulator (200 VA) or a constant voltage source must be used ahead of the instrument (not a square wave type) in areas of unsteady voltage.

4. When the DCR-1 is operating at maximum sensitivity, standards or solvent blanks must be used both immediately ahead of and behind each set of samples. For high precision, at least 10 separate readings at 8X or 16X on the DCR-1 must be made to get the kind of differences shown on the calibration curve. Furthermore, it is advisable to insert "standard" readings between the readings on the sample when making large numbers of replicates. (See Figs. A1 and 2 for DCR-1 readings vs time.)

5. Solvent blanks must be set sufficiently high that no negative or zero readings appear in the segments of readings going into the machine averages.

6. All of the alignments of burner, phasing, hum, etc. must be carefully checked in at the location and the position the instrument is

to be used.

7. Sample temperatures must be maintained constant within ±1°C.

8. Whenever the burner is cleaned, it should be operated on a known sample or water until the readings of the DCR-1 are repeating as in Fig. A1 (Appendix).

The writers strongly recommend that further work be done to reduce the technical problems involved in using this technique and equipment in its present state of development and reduce the time lapse between readings--about 1/2-minute.

The writers believe the Perkin-Elmer 303, equipped with the high sensitivity burner and the DCR-1, can be used with reasonable confidence for measuring silver in samples of precipitation in which the silver has not been artificially concentrated. Conversely, the writers believe that the method should not be attempted by operators who are not specifically trained or until the technique has been improved to eliminate some of the problems.

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Appendix

Method for computing corrected means.

DCR-1 Readings Sample A	Water with A		10-Month Old Reference	Water with Reference	
4.3	4.4	Before A	154.6	4.4	before ref
3.4	4.1		155.3	4.2	
3.1	3.8		153.2	4.3	
2.1	4.6		154.5	4.5	
3.1	4.0		153.2	4.3	
3.5	1.6		155.1	4.0	after ref
3.6	2.5	After A	156.3	3.6	
4.8	1.7		154.5	3.8	
4.0	1.3		153.4	3.9	
5.1	2.2		153.5	3.5	
5.3	4.6		Σ = 1543.6	Σ = 40.5	
4.4	2.3		$\overline{X}$ = 154.36	$\overline{X}$ = 4.05	
4.1	3.7				
3.4	Σ = 40.8				
3.5	$\overline{X}$ = 3.14				
4.6					
4.7					
3.9					
4.4					
3.3					
4.1					
4.2					
Σ = 86.9					
$\overline{X}$ = 3.95					

$$\text{Corrected Mean} = \frac{[\text{Sample Mean - Water Mean}]\ 100}{\text{Reference Mean - Water Mean (ref)}}$$

$$0.54 = \frac{[3.95 - 3.14]\ 100}{154.36 - 4.05}$$

Method for computing coefficient of variation, CV

Reading on DCR-1 (X)
4.7
5.5
5.4
1.6
4.2
3.3
4.1
3.6
3.2
2.1
2.8
4.3
4.5
3.3
3.9
2.5
3.4
3.2
6.9
3.9
3.5
3.9
2.4
1.4
$\Sigma = 87.6$
$\overline{X} = 3.65$

Water mean = 2.07

Reference mean (corrected) = 188.07

$$CV = \frac{s_x}{\overline{x}} = \frac{\sqrt{\frac{\Sigma X^2 - (\Sigma X)^2/n}{n-1}}}{\Sigma(X)/n}$$

$$1.49 = \frac{\sqrt{\frac{355.74 - 319.74}{23}}}{\frac{100[3.65 - 2.07]}{188.07}} = \frac{1.25}{.84}$$

Method for determining minimum sample numbers

Following burner cleaning, a water sample maintained at 67°C was aspirated into the burner. Readings were taken on the DCR-1 against time. These readings and corresponding times are plotted in Fig. A1.

The data were smoothed by multiple point means. The first smoothing was by 10-point means and is shown in Fig. A2. There is some cycling even on the 10-point mean curve suggesting that the water standards should be taken such that both sample and standard represent each part of a cycle.

Raw data obtained on standards

The raw data readings on the DCR-1 and each water mean and corrected reference mean are given in Table A1.

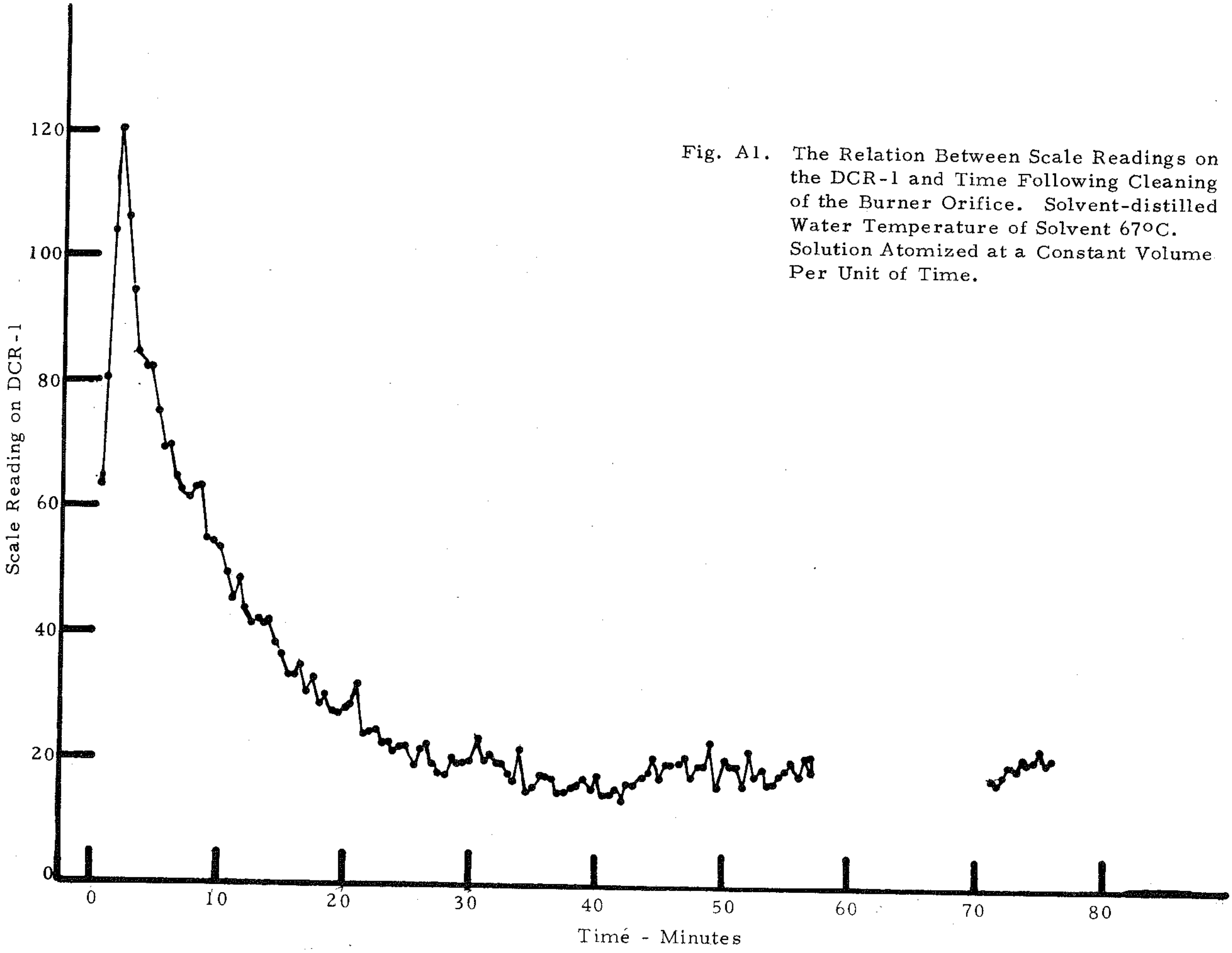

Fig. A1. The Relation Between Scale Readings on the DCR-1 and Time Following Cleaning of the Burner Orifice. Solvent-distilled Water Temperature of Solvent 67°C. Solution Atomized at a Constant Volume Per Unit of Time.

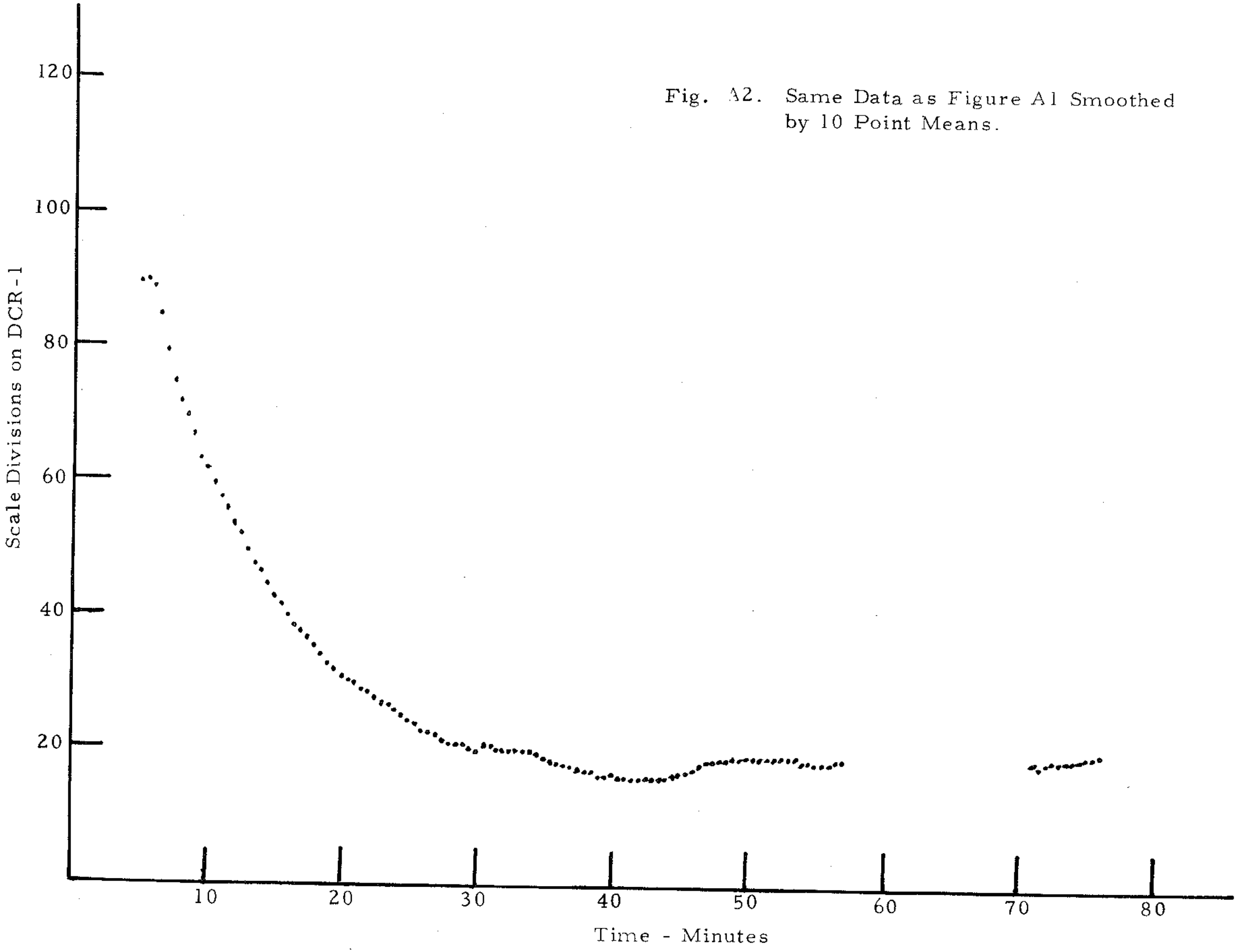

Fig. A2. Same Data as Figure A1 Smoothed by 10 Point Means.

Table A1. Readings on the DCR-1 with samples whose concentrations are known.

	Silver Concentration gm/ml					
	10^{-15}	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}
	4.3	4.7	3.3	17.5	8.1	12.2
	3.4	5.5	4.2	18.0	5.4	14.2
	3.1	5.4	2.5	18.0	6.8	12.4
	2.1	1.6	2.7	16.4	7.1	10.1
	3.1	4.2	2.1	17.5	7.6	9.2
	3.5	3.3	2.2	17.6	7.9	8.5
	3.6	4.1	2.2	17.2	9.8	11.4
	4.8	3.1	2.9	16.0	8.4	9.4
	4.0	3.2	1.4	15.4	10.4	9.1
	5.1	2.1	2.1	15.6	10.8	10.7
	5.3	2.8	2.7	17.4	7.8	
	4.4	4.3	1.2	16.5		
	4.1	4.5	2.0	16.1		
	3.4	3.3	1.1	18.6		
	3.5	3.9		15.2		
	4.6	2.5		17.6		
	4.7	3.4		16.2		
	3.9	3.2		19.7		
	4.4	6.9		16.7		
	3.3	3.9		18.2		
	4.2	3.5		17.4		
	4.1	3.9		16.6		
		2.4		18.3		
		1.4		17.5		
Water Mean	2.43	2.07	0.64	14.55	6.97	9.12
Reference Mean (Corrected)	188.07	188.07	188.07	258.70	101.10	101.10

Table A1. (Continued)

	Silver Concentration gm/ml				
	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}
	8.4	10.6	23.0	135.1	1061.3
	5.7	9.7	23.1	135.7	1057.9
	6.8	7.3	21.1	138.8	1067.8
	4.7	9.0	24.2	140.6	1051.8
	6.4	11.6	22.2	138.6	1063.0
	7.3	8.5	21.4	140.7	1063.9
	8.7	8.0	20.8	139.8	1069.2
	10.8	8.9	23.0	141.4	1063.4
	6.8	8.0	23.9	140.6	1072.3
	6.2	9.6	19.1	141.8	1066.7
				144.3	
Water Mean	4.80	4.92	7.02	10.12	18.10
Reference Mean (Corrected)	101.10	100.00	101.10	112.73	121.58

Method for making the t-test using the corrected means

The t-test was conducted as follows:

1. Compute the sample mean, the water mean for the sample, the reference mean, and the reference water mean.

2. Compute the corrected sample means as

$$\frac{100\,(\bar{x}_1 - \bar{w}_1)}{\bar{x}\text{ ref} - \bar{w}\text{ ref}} = \bar{x}_1 \quad \text{and} \quad \frac{100\,(\bar{x}_2 - \bar{w}_2)}{\bar{x}\text{ ref} - \bar{w}\text{ ref}} = \bar{x}_2 \quad \text{in Eq. (1)}$$

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\dfrac{N_1 s_{x_1}{}^2 + N_2 s_{x_2}{}^2}{N_1 + N_2 - 2}} \sqrt{\dfrac{1}{N_1} + \dfrac{1}{N_2}}} \quad \dots\dots \quad (1)$$

wherein

N_1 = number of readings on solution A

N_2 = number of readings on solution B

$s_{x_1}{}^2$ = standard deviation squared on solution A

$s_{x_2}{}^2$ = standard deviation squared on solution B

3. Compute $s_{x_1}{}^2$ and $s_{x_2}{}^2$ from $s_{x_1}{}^2 = \dfrac{\Sigma(A_1 \dots A_{22})}{N_1 - 1}$ and

$$s_{x_2}{}^2 = \frac{\Sigma(B_1 \dots B_{24})}{N_2 - 1}$$

4. Compute t from Eq. (1)

Example of computation of t

Readings on DCR-1 for solutions A and B and water before and after each

Solution A	Water (solution A)	Solution B	Water (solution B)
4.3	4.4	4.7	1.6
3.4	4.1	5.5	2.5
3.1	3.8	5.4	1.7
2.1	4.6	1.6	1.3
3.1	4.0	4.2	2.2
3.5	1.6	3.3	4.6
3.6	2.5	4.1	2.3
4.8	1.7	3.6	3.7
4.0	1.3	3.2	2.5
5.1	2.2	2.1	1.4
5.3	4.6	2.8	2.5
4.4	2.3	4.3	3.4
4.1	3.7	4.5	4.4
3.4		3.3	2.2
3.5	$\Sigma w_1 = 40.8$	3.4	2.9
	$\bar{w}_1 = 3.14$		
4.6	reference mean = 103.14	2.5	1.9
4.7		3.4	$\Sigma w_2 = 41.1$
3.9		3.2	$\bar{w}_2 = 2.57$
4.4		6.9	reference mean = 102.57
3.3		3.9	
4.1		3.5	
4.2		3.9	
		2.4	
		1.4	

$\Sigma A = 86.9$

$\bar{x}_1 = 3.95$

$\Sigma B = 87.6$

$\bar{x}_2 = 3.65$

$$\bar{x}_1 = \frac{100\,(3.95 - 3.14)}{(103.14 - 3.14)} = 0.81 \qquad \bar{x}_2 = \frac{100\,(3.65 - 2.57)}{(102.57 - 2.57)} = 1.08$$

$\Sigma(A_1^2 + A_2^2 \ . \ . \ . \ A_{22}^2) = 355.17$

$(\Sigma A)^2/N_1 = 343.25$

difference $= 11.92$

$\text{diff}/N_1 - 1 = s_{x_1}^2 = 0.5676$

$\Sigma(B_1^2 + B_2^2 \ . \ . \ . \ B_{24}^2) = 355.74$

$(\Sigma B)^2/N_2 = 319.74$

$= 36.00$

$\text{diff}/N_2 - 1 = s_{x_2}^2 = 1.5652$

$$t = \frac{(1.08 - .81)}{\sqrt{\frac{21(.5676) + 24(1.5652)}{21 + 24 - 2}} \cdot \sqrt{\frac{1}{21} + \frac{1}{24}}} = \frac{0.27}{1.07\,(.298)} = 0.84$$